CHARACTERIZATION OF BIODIESEL **OXIDATION AND OXIDATION PRODUCTS**

CRC Project No. AVFL-2b

Task 2 Results

Experimental Investigation of Biodiesel Oxidation and Deposition Tendency

SwRI[®] Project No. 08.10721

Prepared for The Coordinating Research Council 3650 Mansell Road, Suite 140 Alpharetta, GA 30022

National Renewable Energy Laboratory **U.S. Department of Energy 1617 Cole Boulevard Golden, CO 80401**

> **August 2007 Final Report**



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> August 2007 Final Report

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EXECUTIVE SUMMARY

In August 2005, a literature survey was reported in accordance with Task 1 of this project. That literature survey covered work previously done concerning the oxidation stability of biodiesel and the fatty oils from which they are derived. The report identified two areas in which there was a deficiency of technical understanding:

- 1. The relationship between a biodiesel's tendency to form insolubles and other stability indicators.
- 2. The relationship between a biodiesel's instability and its tendency to form deposits on hot metal surfaces such as engine parts.

Based on this finding, a Task 2 experimental program was designed to address these two areas of deficiency. This experimental program involved obtaining three B100's and evaluating them by the stability indicator test methods identified in the Task 1 report. These stability indicator test methods included Rancimat, modified D2274, total acid number (TAN), peroxide value, polymer content, anisidine value, and conjugated diene content. In addition, the three B100's were evaluated for their ability to form deposits on a hot steel surface by using the Jet Fuel Thermal Oxidation Tester (JFTOT). JFTOT testing was done at 260°C and 300°C and used steel heater tubes. Deposit volume was measured using ellipsometry.

After initial results were obtained and evaluated, two of the three B100's were selected for further testing. These two B100's were both soy-based, one having a typical stability as measured by Rancimat induction period (IP), and the other having unusually high stability. These two B100's were aged by two different methods. One method, referred to as quiescent aging, involved storing the fuels with sealed and limited atmospheric headspace for six weeks at 50°C. The other method, referred to as agitated aging, consisted of stressing the fuel under ASTM D2274 conditions (95°C, constant oxygen bubbling through the sample, 16 hours duration). After aging, the two B100's were evaluated again by the stability indicator tests and the results were compared against each other and against the "before aging" results. Also, each of the two B100's was blended with an ASTM D975-compliant ultra-low sulfur diesel fuel (ULSD) to provide two B20's. These two B20's were initially evaluated and then stressed by the quiescent and agitated aging procedures. Stability indicator test results for the two B20's, before and after aging, were evaluated and compared against each other and against the corresponding B100 results.

Test results indicated that the original three B100's varied widely in their stability. There was a corresponding variation in the JFTOT deposit volume formed. For the two B100's that were further evaluated, data spanning the fuels before aging, after quiescent aging, and after agitated aging showed that a somewhat rough correlation did exist between Rancimat IP and D2274 total insolubles. This correlation had features that were similar to an exponential decay function. Specifically, B100's with zero Rancimat IP had very high D2274 total insolubles. As the Rancimat IP increased, the D2274 total insolubles dropped and approached a very low value. Several other stability indicators including TAN, TAN increase after D2274 (delta TAN), polymer content, polymer content increase after D2274 (delta polymer), and peroxide value also showed similar features of exponential decay when plotted as a function of Rancimat IP. The most striking correlation involved an extremely well-defined linear relationship between polymer

content and TAN. This correlation combined with the behavior of other stability indicators as a function of Rancimat IP suggested that either delta TAN or delta polymer might be a very good indicator of overall B100 stability when used with Rancimat IP.

The data indicated that the stability-related differentiation observed between the two B100's was eliminated or minimized for the B20's in all but the most severe oxidative stressing.

JFTOT deposit volume did vary for the initial B100's and B20's, indicating that relative stability can have an effect on the tendency of a biodiesel-containing fuel to form deposits on hot steel surfaces. For the initial, non-aged B100's, the very stable B100 showed a deposit volume vs. temperature slope that was radically different from the lower, more typical stability B100. At 260°C, the higher stability B100 gave significantly less deposit volume compared to the other B100. However, at 300°C, the two B100's formed essentially equivalent JFTOT deposit volumes. The effect of aging the B100's was to make their JFTOT deposit volumes more similar as the severity of the aging process increased. Also, the repeatability of the JFTOT deposit volumes became much poorer as both B100's were progressively stressed by the aging processes. Similar behavior was observed for the B20's. The overall JFTOT deposit volume data suggested that as the biodiesel fuels were made unstable by aging, deposit volumes were reaching maximum values as the JFTOT tube surface became saturated. Reducing the test fuel volume from the customary 600 ml to a much lower volume may reduce the overall deposit volumes.

The poor JFTOT deposit repeatability for the aged fuels made it difficult to identify any clear correlation between stability indicators and deposition tendency. However, there was some indication that D2274 iso-octane insolubles and polymer content may be involved in JFTOT deposit formation.

The effect of the stressing imparted to the B100 or B20 by the JFTOT was minimal. Peroxide values typically were reduced and anisidine values were correspondingly increased, but this effect was only significant for the less stable B100 or for the more stable B100 after it had been significantly reduced in stability by aging.

The results of this project demonstrate that a relationship between a biodiesel fuel's stability and its tendency to form deposits on hot steel surfaces does exist. The results at 260°C suggest that the tendency to form deposits on a metal tube surface is related to both the extent of prior oxidation and the oxidation stability of both B100 and B20 samples. The data seem to indicate that for the least stable samples and for all tests conducted at 300°C, the metal tubes became saturated with deposit making discrimination between samples impossible. Saturation occurred for both B20 blends and B100 samples. The JFTOT appears to hold promise as a method to help define that relationship. Additional tests at a shorter residence time and perhaps lower temperature should be attempted. Optimization of the JFTOT procedure for biodiesel fuels may provide a new useful tool to help define the relationship between biodiesel stability and its long-term impact on user equipment.

This report is presented as a main body text that provides a discussion of the most important results along with the indicated conclusions and recommendations for further work. More detailed discussions of each of the major sections of work are provided in a series of appendices.

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1.0 INTRODUCTION AND OBJECTIVE

Naturally occurring fats and oils are used in nearly every part of modern life in every part of the world. Because these materials are so widely used, much work has been done to better understand the chemical reactions (primarily oxidation) to which they are subject. As such, the oxidation reactions of these lipids are well understood.

Biodiesel, the methyl esters of selected fatty acids, is already in widespread use in Western Europe as a fuel for compression-ignition engines. The use of biodiesel is also growing rapidly in the United States. However, probably the single largest problem associated with the use of biodiesel is the susceptibility of the fuel to oxidation and other chemical reactions. The by-products of these reactions can lead to engine deposits, water-separation problems, potentially accelerated microbial growth, filter plugging, and corrosion of fuel-system components.

The reactions that occur in biodiesel are similar, if not the same, as those that occur in fats and oils. However, the environment in which these reactions occur is often quite different. Some of the differences include:

- Mixture of the biodiesel with petroleum diesel to make biodiesel blends.
- Storage of the biodiesel in storage tanks and fuel tanks containing water, various metals, microbial growth, varying amounts of heat, and varying amounts of oxygen.
- Thermal cycling either in storage or in the vehicle fuel system.
- Exposure of the biodiesel to fuel-system components and conditions including heat, metal, oxygen, elastomers, and other fuel deposits.

For these reasons, the chemistry of lipid oxidation cannot be directly applied to biodiesel in order to measure or predict the stability of biodiesel in storage and use. Any attempt to understand the stability of biodiesel must include consideration of the differences listed above, as well as the effects that unstable biodiesel might have on the fuel, fuel system, and engine.

As with instability chemistry of petroleum diesel fuel, the chemical reactions of a very small fraction of the fuel can result in significant instability-related problems.

The objective of this project was to gain a quantitative understanding of the effects of the above environmental factors on the oxidation and resulting quality of biodiesel. In this study, emphasis was placed on the biodiesel feed stocks commonly used in the United States, i.e., soy oil and waste cooking oil.

In order to accomplish this objective, the project was divided into two tasks. Task 1 was a literature survey designed to understand and document the state of technical understanding on oxidation chemistry as it applies to biodiesel fuel. This Task was completed and the report was issued in August 2005. Two of the primary deficiencies identified in the Task 1 report involved the lack of technical understanding concerning:

- 1. The relationship between a biodiesel's tendency to form insolubles and other stability indicators that were identified in the Task 1 report.
- 2. The relationship between a biodiesel's instability and its tendency to form deposits on hot metal surfaces such as engine parts.

Accordingly, Task 2 of this project was designed as an experimental program to understand better these two areas. The remainder of this report documents the experimental program, results and discussion, conclusions, and recommendations of Task 2.

2.0 EXPERIMENTAL

2.1 Experimental Project Plan

The final project plan for Task 2 is given below:

- 1. Obtain three B100 fuels with no added antioxidants.
 - a. Two soy-based, one drum each
 - b. One used cooking oil-based (yellow grease), one drum
 - c. B100 drums will be stored at 4°C (40°F) with N₂ purging; samples of the B100's will be taken from drums only as needed for the experimental program as described below.
- 2. Obtain one ultra-low sulfur No. 2 diesel fuel, one drum.
 - a. Fuel will be stored at 4°C (40°F) with N₂ purging; samples of the fuel will be taken from drums only as needed for the experimental program as described below.
- 3. Characterize the new fuels against the appropriate specifications to insure compliance; run oxidation reaction product (ORP) tests as appropriate to each new fuel.
- 4. Run soy B100's on Jet Fuel Thermal Oxidation Tester (JFTOT) at 260°C and 300°C.
 a. Run in triplicate; tubes evaluated visually and by ellipsometer.
 b. The ORP tests will be run on the fuel after one of the triplicate JFTOT runs for 4a.
- 5. Run yellow grease B100 on JFTOT using the same procedure as with the soy B100 (see steps 4a–b).
- 6. Based on test results obtained thus far, choose two of the three B100's as the designated fuel for further testing. Also choose one test temperature for all subsequent JFTOT tests (if data justifies such a choice).
- 7. Run quiescent aged designated fuels, AL-27102-F and AL-27144-F, (see step six) on JFTOT using same procedure as with the soy B100 (see steps 4a–4b).
 - a. Quiescent aging to be done by storage at 50°C for 6 weeks with no agitation and sealed limited atmospheric headspace with no replenishment of oxygen.

- 8. Run agitated aged designated fuels, AL-27102-F and AL-27144-F, (see step six) on JFTOT using same procedure as with soy B100 (see steps 4a–4b).
 - a. Agitated aging to be done under ASTM D2274 conditions of 95°C, with constant O_2 bubbling, 16 hours duration.
- 9. Prepare B20 blends using designated B100's AL-27102-F and AL-27144-F (see step six). Then run initial evaluations of the B20's according to step 3. Then run the B20's on JFTOT using same procedure as with soy B100 (see steps 4a–4b).
- 10. Run quiescent aged B20 blends using designated B100's AL-27102-F and AL-27144-F (see step six) on JFTOT using same procedure as with soy B100 (see steps 4a–4b). See step 7a for quiescent aging details.
- 11. Run agitated aged B20 blends using designated B100's AL-27102-F and AL-27144-F (see step six) on JFTOT using same procedure as with soy B100 (see steps 4a–4b). See step 8a for agitated aging details.

Further details of this project plan as it relates to the test fuels, aging procedures, and the test methods are provided in the subsequent sections 2.2–2.5.

2.2 Test Fuels

In the original project plan, two B100's, one soy-based and one yellow grease, were to be selected for evaluation. Those two fuels were AL-27102-F and AL-27097-F, respectively. Both fuels were shown to comply with ASTM D6751 (the current B100 specification), as outlined in step 3 of the above experimental project plan. Subsequently, both B100's were evaluated according to steps 1–5 of the experimental project plan. However, the usually stable nature of the soy-based B100 and the rather unstable nature of the yellow grease made it desirable to find a third B100. After discussions with the AVFL-2b Committee, it was decided to obtain and evaluate another soy-based B100 with a more typical stability as measured by Rancimat induction period (3–5 hours). Several soy-based B100's were obtained, but all had one or more problems that made them unsuitable for use. Finally, an acceptable soy-based B100, AL-27144-F, was obtained. This fuel was evaluated according to steps 1–4 of the experimental project plan.

Initial D6751 test data for the three B100's are given in Table 1. The only property that exceeded the specification requirement was the D1160 distillation value. However, this test when run in our laboratory has been shown to have a systematic error that gives results that are excessively high. Taking into account this error, the three B100's were considered as acceptable.

An additive-free ultra-low sulfur No. 2 diesel fuel (ULSD), AL-27242-F, was obtained from ConocoPhillips and evaluated according to step 2 of the experimental project plan. Initial ASTM D975 test data is provided in Table 2. The fuel complied with the specification requirements except for the distillation requirement. Because of the problems associated with this test and the fact that ConocoPhillips had certified this sample as on specification, the fuel was considered acceptable.

Property	Test Method	D6751 Limit	Measured Value				
Type of Biodiesel			Soy	Yellow Grease	Soy		
Sample Identification			AL-27102-F	AL-27097-F	AL-27144-F		
Flash Point, °C	D93	130, min	169	176	162		
Water and Sediment, %(vol)	D2709	0.050, max	0.01	0.01	<0.005		
Kinematic Viscosity @ 40°C , mm ² /sec	D445	1.9 - 6.0	4.09	4.68	4.11		
Sulfated Ash, %(mass)	D874	0.020, max	< 0.001	< 0.001	<0.001		
Sulfur, %(mass)/ppm(wt)	D5453	0.05/500	0.00008/0.8	0.00063/6.3	0.00006/0.6		
Copper Strip Corrosion, 3 hr at 50°C	D130	No. 3, max	1B	1B	1B		
Cetane Number	D613	47, min	51.4	63.9			
Cloud Point, °C	D2500	report value	0	5	0		
Carbon Residue, %(mass)	D4530	0.050, max	0.0293	0.0099	0.0097		
Total Acid Number, mg KOH/g	D664	0.80, max	0.38	0.69			
Free Glycerin, %(mass)	D6584	0.020, max	< 0.001	0.004	0004		
Total Glycerin, %(mass)	D6584	0.240, max	0.137	0.126	0.221		
Phosphorus Content, ppm	D4951	0.001, max	<5	<5			
Distillation, Atmospheric Equivalent, °C	D1160						
90% recovered		360, max	368	370	361		
Peroxide Value, meq O ₂ /kg	D3703		<1	245	73		
Oxidation Stability Index @ 110°C, hr.	ISO 6886		9.11	1.03	5.04		

Table 1. Initial Biodiesel Test Data

Note: off specification values or extremely atypical values are in red.

Property	Test Method	D975 Limit	Measured Value
Flash Point, ^o C	D93	52, min	61.1
Water and Sediment, %(vol)	D2709	0.05, max	0.01
Kinematic Viscosity @ 40°C, mm ² /sec	D445	1.9 - 4.1	2.52
Ash, %(mass)	D482	0.01, max	<0.001
Sulfur, ppm(wt)	D2622	15, max	4.8
Copper Strip Corrosion, 3 hr at 50°C	D130	No. 3, max	1A
Cetane Index	D976	40, min	45.7
Ramsbottom Carbon on 10% res., %(mass)	D524	0.35, max	0.07
Total Acid Number, mg KOH/g			
Distillation, °C	D86		
Initial boiling point			159.6
5% recovered			196
10% recovered			204.5
50% recovered			256.4
90% recovered		282, max	314.6
total recovery, %			98.1
HFRR @ 60 C, ave. wear scar diameter, mm	D6079		576
Total Acid Number, mg KOH/g	D664		0.00
Peroxide Value, meq O ₂ /kg	D3703		0
Oxidation Stability, mg/100 ml	D2274		
adherent insolubles			0.1
filterable insolubles			0.1
total insolubles			0.2
Total Acid Number after D2274	D664		0.00

Table 2.	Initial Ultra-Low	Sulfur No. 2 Diese	el Fuel (AL-27242-F	[:]) Test Data
				-

After further discussion with the AVFL-2b Committee, the decision was made to expand the project plan scope to include two B100's for evaluation in the remaining experimental plan steps 7–11. The reasons for this decision are discussed in section 3.2. The two B100's chosen were the two soy-based fuels, AL-27102-F (high stability) and AL-27144-F (typical stability).

By the time Task 2 experimental work began, significant problems had been experienced with B100's stored at 4°C. Frequently, such B100's experienced considerable drop-out. Sometimes, the dropped-out material did not re-dissolve with subsequent heating and stirring. Accordingly, the drums of B100 were purged with N_2 , sealed, and stored in a covered area at outside ambient temperature.

2.3 Aging Procedures

After initial evaluation, each of the two B100's was stressed by two procedures: quiescent aging and agitated aging. Quiescent aging was accomplished by placing 3,000 ml of B100 in a one-gallon glass jug, tightly capping it so as to preserve the natural headspace of air without any replenishment, and storing the glass jug at 50°C for six weeks. After the six week aging, the fuel was evaluated according to the experimental test plan. Agitated aging was accomplished by stressing each B100 according to D2274. For each B100, eight D2274 tubes were filled with 400 ml. After the 16-hour stressing, the contents of the eight tubes were consolidated into a one-gallon glass jug and thoroughly mixed. The mixed fuel was then evaluated according to the experimental test plan.

2.4 Stability Test Methods

The B100's and corresponding B20's selected for the experimental test plan were evaluated by a set of test methods identified during the preparation of the Task 1 literature survey report. That set of test methods provided stability indicators for the B100's and B20's. They were named the Oxidation Reaction Product (ORP) tests, a term first used in the original project proposal, SwRI[®] Proposal 08-39316, submitted on January 23, 2004. The original ORP test methods included the following:

Stability Performance Bench Tests

- 1. Rancimat Induction Period (IP) @ 110°C, ISO 6886
- 2. Modified ASTM D2274

Physical Properties

- 1. Kinematic Viscosity at 40°C, ASTM D445
- 2. Refractive Index

Primary Oxidation Products

- 1. Peroxide Value (PV), ASTM D3703
- 2. Conjugated dienes by UV adsorption at 232 nm, ISO 3656

Secondary/Tertiary Oxidation Products

- 1. Anisidine Value, a measure of aldehydes (AV), EN ISO 6885
- 2. Polymer Content, BS EN ISO 16931
- 3. Total Acid Number, ASTM D664
- 4. Total Base Number, ASTM D2896

Compositional Properties of the Biodiesel Fuel

- 1. % Ester Content, Pr EN 14103
- 2. % Oleic, % linoleic, % linolenic content of the methyl ester biodiesel, Pr EN 14103
- 3. OX (Oxidizability) = (0.02*(% oleic) + (% linoleic) + 2*(% linolenic))/100
- 4. TOTOX = 2*PV + AV
- 5. Allylic Position Equivalent (APE), a measure of the allylic carbons
- 6. Bis-Allylic Equivalent (BAPE), a measure of the doubly allylic

The Rancimat test, also known as Oxidation Stability Index (OSI) was originally run in triplicate, but as more data became available the excellent repeatability allowed duplicate determinations to be performed.

ASTM D2274 is a well-established method to determine the oxidation stability of petroleum diesel fuels. The procedure involves heating a glass tube containing 350 ml of a pre-filtered fuel in a hot oil bath at 95°C for 16 hours while bubbling oxygen through though it. At the conclusion of the test, the fuel is cooled and filtered to determine the filterable insolubles generated during the test. The amount of adherent insolubles left on the glass tube is also determined. The sum of the filterable and adherent insolubles is considered the total insolubles content of the stressed fuel.

The modified ASTM D2274 procedure used in this project is currently being considered by ASTM as a method for evaluation of biodiesel stability. The primary procedural modification is the measurement of iso-octane insolubles after the 16-hour D2274 oxidative stress. This is accomplished by adding 100 ml of the filtered post-stress B100 to 400 ml of pre-filtered iso-octane, allowing the thoroughly mixed blend to set for at least one hour, then filtering it to determine the insolubles. The result is considered a potential measure of oxidative insoluble precursors that remain soluble in the very polar B100, but are insoluble in a very non-polar material such as iso-octane. All modified D2274 determinations were performed in duplicate on the initial B100, as outlined in steps 1–5 of the experimental project plan. In the subsequent steps 7–11, all modified D2274 determinations were single run evaluations, due to limitations of test fuel volume and the excellent repeatability that had been thus far observed in the results of that test. For B20 blends, the iso-octane portion of the modified D2274 method was not run, since this parameter is only applicable to B100's.

During the initial modified D2274 evaluations of the first two B100's (AL-27102-F and AL27097-F), the iso-octane insolubles were evaluated using the "stacked blank filter" procedure outlined in D2274. It was determined that this procedure produces very high blank filter weight

gains that obscure the actual iso-octane insolubles levels. Therefore, starting with the initial evaluation of the third B100 (AL-27144-F), each fuel sample was filtered with just one filter instead of the two filters stacked upon each other. A separate blank determination using just one filter was performed for every set of modified D2274 determinations. This method proved to correct the previous blank problem.

All D2274-stressed B100's were evaluated for total acid number and polymer content. All D2274-stressed B20's were evaluated for total acid number.

Polymer content was determined by BS EN ISO 16931, a method using HPLC size exclusion chromatography. It was determined that this method failed when used on biodiesel blends containing petroleum diesel fuel. The chromatography column was unable to cleanly resolve the ester and hydrocarbon components. Accordingly, polymer content was only run on B100's.

Anisidine value is a method to determine the level of aldehydes, one of the classes of compounds known to form when hydroperoxides decompose. Conjugated dienes are determined by UV adsorption at 232 cm⁻¹ and 268 cm⁻¹, although the former value appears to be the more important one based on the results of the Task 1 literature survey. Consequently, although both conjugated diene measurements were performed and tabulated, only the 232 cm⁻¹ values were graphically displayed.

For the initial B100's, the fatty acid methyl ester profile (FAME analysis) was determined by the gas chromatographic method Pr EN14103. Three parameters calculated entirely from the FAME analysis results, OX, APE, and BAPE, were identified as useful from the Task 1 literature survey report. OX (Oxidizability) represents an average susceptibility to oxidation based on the relative oxidation kinetics for oleic, linoleic, and linolenic fatty acid chains. APE (Allylic Position Equivalent) represents the relative concentration of allylic carbons present in a fatty oil or ester; BAPE (Bis-Allylic Position Equivalent) represents the relative concentration of bis-allylic carbons similarly present.

TOTOX, another parameter identified from the Task 1 literature survey report, is an attempt to add the effects of peroxide value (primary oxidation products) with anisidine value (secondary oxidation products).

Kinematic Viscosity, Refractive Index, and Total Base Number were test methods that had been identified as potentially useful in the Task 1 literature survey report. The initial evaluation results of steps 1–5 indicated that these methods were not providing revealing information. Accordingly, they were discontinued for the remainder of the experimental project plan. The significance of the other test methods and their results are provided in the following section 3 covering results and discussion.

2.5 Method to Measure Tendency to Form Deposits on Hot Metal Surface

Originally, the project proposal specified that a single tube heat exchanger (STHE) apparatus would be developed. This apparatus would have an extended length of steel tube immersed in a hot oil or sand bath. The B100 would be cycled through the steel tube at a temperature

sufficiently high to provide necessary thermal stressing. After each test, the tube would be cut into small sections, and the deposits formed within each segment would be determined by carbon burnoff. However, several attempts failed to achieve temperatures high enough to provide significant thermal stressing to a B100.

After discussions with the AVFL-2b Committee, it was decided to use the Jet Fuel Thermal Oxidation Tester (JFTOT). The JFTOT is used to measure deposit-forming tendency for petroleum jet fuels in several methods as described in ASTM D3241.

In the JFTOT, 450 ml fuel is passed over an annular metal heater tube at a flow rate of 3 ml/minute. The JFTOT heater tube has an outer diameter of 0.125; the operating portion of the heater tube is 60 mm long. The tube surface temperature can be adjusted depending on the needs of the test. For the purposes of this project, tests were run at 260°C and 300°C using steel heater tubes. These temperatures are within a reasonable range of what diesel fuels experience as they pass through the hot injector tip within the diesel engine combustion chamber. Also, these two JFTOT test temperatures were selected only after discussion with and approval by the AVFL-2b Committee. After each test, the heater tube deposits were measured volumetrically using an ellipsometer. The heater tube pre-filter was removed so as to not eliminate solids formed by oxidative stressing from contact with the hot steel surface. The post-heater tube filter is a more integral part of the JFTOT and was not removed. All fuels evaluated in the JFTOT, both non-aged and aged, were run without any pre-filtering.

3.0 RESULTS AND DISCUSSION

3.1 Initial Evaluation of Test Fuels

As already mentioned, the original experimental test plan specified that two B100 samples, a soy-based product and yellow grease, were to be selected and used. Those two products, AL-27102-F and AL-27097-F respectively, were initially evaluated. Results of that evaluation were complete by August 2005. The third B100, a soy-based B100 with more typical stability (as determined by Rancimat induction period) was obtained and initially evaluated by April 2006. The ULSD fuel was obtained and evaluated by November 2006. A complete discussion of those results is provided in Appendix A. The most important initial evaluation results are summarily discussed below. Note that all figures displaying these initial evaluation results are labeled as "original results" so as to distinguish them from the re-evaluation results that will be discussed in section 3.2.

3.1.1 Initial Biodiesel Stability

The soy B100 AL-27102-F was much more stable than the yellow grease B100 AL-27097-F, based on both the initial values of Rancimat induction period (IP) and ASTM D2274 total insolubles. The second soy B100 AL-27144-F was of intermediate stability based on both Rancimat IP and D2274 total insolubles (Table 3). The 9.11-hour Rancimat IP for AL-27102-F is extremely unusual, based on all reported Rancimat IP results for non-additized soy-based B100's. Indeed, as already mentioned, one of the reasons the AVFL-2b Committee requested that another soy B100 be obtained was the recognition that AL-27102-F was extremely unusual

based on all available B100 initial stability survey data. As documented in the Task 1 literature report, naturally occurring antioxidants do not provide that level of stability, and additional amounts of naturally occurring antioxidants such as Tocopherols do not provide significant further improvements when added to B100's or fatty oils that have not previously had their natural antioxidants removed. Based on the literature covered in the Task 1 report, the only demonstrated method to increase Rancimat IP to the level observed in AL-27102-F is the addition of an effective synthetic antioxidant.

B100 Tested		Soy	Yellow Grease	Soy
Sample Identification		AL-27102-F	AL-27097-F	AL-27144-F
Property	Method	Initial Value	Initial Value	Initial Value
Oil Stability Index @ 110°C, hr.	ISO 6886	9.11	1.03	5.04
Oxidation Stability, mg/100 ml	Modified ASTM D2274			
adherent insolubles, average		0.5	0.7	1.0
filterable insolubles, average		0.0	5.3	0.1
total insolubles, average		0.5	6.0	1.1
iso-octane insolubles, average		0.0	0.0	2.5
modified total insolubles, average		0.5	6.0	3.6
polymer content after D2274, average	BS EN ISO 16931	0.99	6.29	2.62
Total Acid Number after D2274, average	D664	0.49	2.02	1.13
Total Acid Number, initial	D664	0.38	0.69	0.38
Polymer Content, initial	BS EN ISO 16931	0.64	1.08	1.33

Table 3. Initial Oxidation Stability of the B100 Fuels

The increase in TAN and polymer content caused by D2274 stressing appeared to roughly correlate with the initial fuel stability as measured by Rancimat IP. Specifically, stressing by D2274 only slightly increased TAN and polymer content for the most stable soy B100 AL-27102-F compared to the initial unstressed fuel (Table 3); D2274 stressing did significantly increase TAN and polymer content for the more typical (lower) stability soy B100 AL-27144-F and the yellow grease B100 compared to the initial unstressed fuel (Table 3; Figures 1–2).



Figure 1. Effect of D2274 on Total Acid Number: Original Results



Figure 2. Effect of D2274 on Polymer Content: Original Results

The more stable soy B100 AL-27102-F appeared to have less initial oxidative degradation than the yellow grease B100, based on the initial values of peroxide value (PV), conjugated dienes (adsorption at 232 cm⁻¹), anisidine value, TOTOX, polymer content, and total acid number (TAN) (Table 4). The lower stability soy B100 AL-27144-F appeared to have an intermediate level of oxidative degradation relative to the other two B100's based on the same test methods. These results directionally agree with the initial Rancimat and D2274 stability results (Table 3).

B100 Tested		Soy	Yellow Grease	Soy
Sample Identification		AL-27102-F	AL-27097-F	AL-27144-F
Property	Method	Initial Value	Initial Value	Initial Value
Peroxide Value, meq O ₂ /kg	D3703	<1	245	73
Conjugated Dienes	ISO 3656			
E ^{1%} _{1cm} (232)		1.86	13.30	4.10
E ^{1%} _{1cm} (268)		0.20	2.58	1.59
Anisidine Value	EN ISO 6885	1.5	33.8	4.4
тотох		<3.5	523.8	150.4
Polymer Content, %(mass)	BS EN ISO 16931	0.64	1.08	1.33
Ester Content, %(mass)	BS EN ISO 16931	99.36	98.92	98.67
TAN, mg KOH/g	D664	0.38	0.69	0.38
TBN, mg KOH/g	D2896	0.13	0.14	ND

 Table 4. Primary and Secondary Oxidation Analysis of the B100 Fuels

Both soy B100's appeared to be more susceptible to oxidation than the yellow grease B100 based on the initial FAME analysis and the calculated parameters of OX, APE, and BAPE (Table 5).

B100 Tested			Soy Yellow Grease			e	Soy			
Sample Identification			AL-27102-F			AL-27097-F			AL-27144-F	
Property	Method	Initial Value	Final 260°C	Final 300°C	Initial Value	Final 260°C	Final 300°C	Initial Value	Final 260°C	Final 300°C
FAME Analysis	Pr EN 14103									
Ester Content, %		104.92	105.19	104.44	102.57	102.13	101.59	105.33	ND	ND
Methyl Palmitate (16:0), %		10.39	10.41	10.50	13.29	13.45	13.40	11.54	ND	ND
Methyl Stearate (18:0), %		4.30	4.30	4.28	8.64	8.61	8.41	4.44	ND	ND
Methyl Oleate (18:1), %		23.10	23.13	23.09	45.76	45.61	45.95	24.23	ND	ND
Methyl Linoleate (18:2), %		51.70	51.70	51.67	22.69	22.65	22.54	51.31	ND	ND
Methyl Linolenate (18:3), %		7.78	7.79	7.78	1.71	1.70	1.71	6.51	ND	ND
OX (Oxidizability)		0.68	0.68	0.68	0.27	0.27	0.27	0.65	ND	ND
Allylic Position Equivalent (APE)	Calculated from FAME	165.16	165.24	165.08	140.32	139.92	140.40	164.10	ND	ND
Bis-Allylic Position Equivalent (BAPE)	Calculated from FAME	67.26	67.28	67.23	26.11	26.05	25.96	64.33	ND	ND

Table 5. Initial Compositional Analysis of the Biodiesel Fuels Relating to Oxidation Susceptibility

The disagreement between the susceptibility to oxidation as indicated by initial bulk fatty acid composition parameters (Table 5) and the actual stability-related results (Tables 3 - 4) suggests that the soy B100 AL-27102-F may contain a significant level of synthetic antioxidant despite our request for an additive free product. However, the provider insisted that such was not the case. We have learned that both soy B100's were not distilled. If the feed soybean oil for AL-27102-F had been additized prior to its delivery to the biodiesel plant, this antioxidant would carry over into the B100 with little or no effect. There is no way to verify this. However, additional results reported later in this report continue to be consistent with the presence of a synthetic antioxidant in AL-27102-F.

3.1.2 JFTOT Deposition Tendency

For both test temperatures, the JFTOT deposit volumes gave reasonably good repeatability for both fuels (Figures 3–4). Deposit volume appeared to be a better parameter for JFTOT deposit formation compared to deposit thickness. In all subsequent JFTOT test results, only deposit volumes are reported.

The average JFTOT deposit volumes for all three B100's at both test temperatures are shown in Figure 5. The less stable soy B100 AL27144-F gave more JFTOT deposit volume than the yellow grease AL-27097-F at both 260°C and 300°C. This ranking is consistent with their predicted stability as determined by their susceptibility to oxidation as indicated by their fatty acid composition (Table 5). However, it is opposite the ranking as predicted by their initial Rancimat and D2274 results (Table 3). Also, the deposit volume vs. temperature slope was similar for AL-27144-F and AL-27097-F.



Figure 3. Repeatability of JFTOT Deposit Volume, 260°C: Original Results



Figure 4. Repeatability of JFTOT Deposit Volume, 300°C: Original Results



Figure 5. Effect of Temperature on JFTOT Deposit Volume: Original Results

The JFTOT data for the more stable soy B100 AL-27102-F was decidedly different from the other two B100's. At 260°C it gave the least deposit volume of all three B100's, and at 300°C it gave the most deposit volume of all three B100's. The deposit volume vs. temperature slope was radically different for AL-27102-F compared to the other two B100's. This data indicates that something is very different about the more stable soy B100 AL-27102-F compared to the less stable soy B100 AL-27144-F and the yellow grease AL-27097-F. While such a difference may be expected for AL-27102-F (a soy B100) compared to AL-27097-F (a yellow grease), it is very noteworthy that AL-27102-F would have such a different JFTOT deposit vs. temperature profile compared to AL-27144-F (another soy B100). Both soy B100's had essentially the same predicted oxidation susceptibility based on their fatty acid composition. However, AL-27144-F showed more initial oxidative degradation compared to AL-27102-F. The fact that AL-27144-F showed significantly less increase in JFTOT deposits when the temperature was increased to 300°C is not consistent with these facts. A hindered phenol antioxidant, if present in AL-27102-F, could account for its unusually high Rancimat IP, low D2274 insolubles level, and increased JFTOT deposit level at 300°C. Since hindered phenols are well known to rapidly decrease in antioxidant performance and even promote oxidation at high temperatures, the 300°C JFTOT tube temperature could possibly result in dramatic reduction in stability.

It should be mentioned that thus far no data has been found that measures the effect of an antioxidant on the tendency of biodiesel fuels to form deposits on hot metal surfaces. Therefore, it has not yet been established if antioxidants reduce the tendency of B100's to form deposits on hot metal surfaces. If an effective antioxidant did reduce the deposit-forming tendency of a B100, then the data given in Figure 5 could be explained. However, since the manufacturer states that they did not add an antioxidant, and since it is not possible to determine if an antioxidant was added before the soybean oil was transesterified, the unusual behavior of AL-27102-F cannot be explained with certainty. Note that in Figure 5 the repeatability of the average deposit volumes is not displayed since the size of the gap between the highest and lowest value for all B100's is less than the size of the symbol used to plot the point.

The deposit volume formed by both biodiesels was large compared to typical deposit volumes observed by Jet A fuels that give No. 1 visual ratings. However, jet fuels are tested using aluminum heater tubes while the biodiesel work done herein uses steel tubes. Since the deposit forming tendencies are significantly affected by the heater tube metallurgy, precise comparisons between previously evaluated hydrocarbon fuels and biodiesel fuels are not yet possible. It should be noted that every JFTOT test involving a B100 or B20 in this project gave a visual heater tube rating of greater than 4, with both an abnormal and peacock pattern.

3.1.3 Effect of JFTOT Stressing on Biodiesel Stability

JFTOT stressing caused, for the most part, minor or no changes in the stability characteristics of the three biodiesels as measured by Rancimat and D2274 (Figures 6–7). There was a minor but progressive decrease in Rancimat IP in the most stable of the three B100's, the soy-based AL-27102-F. The notable exception involved the yellow grease B100 that had been stressed in the JFTOT at 300°C. This stressed fuel gave significantly increased D2274 total insolubles compared to the initial yellow grease B100 that had not yet been stressed in the JFTOT.



Figure 6. Effect of JFTOT on Rancimat Induction Period: Original Results



Figure 7. Effect of JFTOT on ASTM D2274 Total Insolubles: Original Results

JFTOT stressing had no significant effect on TAN (Figure 8) for the three B100's. A minor progressive increase in polymer content was observed for only the yellow grease AL-27097-F (Figure 9). However, JFTOT stressing caused a significant increase in post-D2274 polymer content for the yellow grease compared to the same fuel before being JFTOT-stressed (Figure 10). This indicates that if the initial fuel stability is low enough (Rancimat IP = 1.0 hr.)

brief contact with a sufficiently hot metal surface can cause some increase in polymer content. If this JFTOT-stressed B100 is then further stressed by D2274 (as provided in steps 4 and 5 of the experimental project plan of section 2.1), significant further deterioration can result in significant increases in polymer content relative to the same B100 stressed only by D2274.



Figure 8. Effect of JFTOT on Total Acid Number: Original Results



Figure 9. Effect of JFTOT on Polymer Content: Original Results



Figure 10. Effect of JFTOT on Post-D2274 Polymer Content: Original Results

Peroxide value was very low for the most stable B100, the soy-based AL-27102-F, and JFTOT stressing did not cause a significant change (Figure 11). The effect was minimal for the less stable soy B100 AL-27144-F, with only a minor decrease in peroxide value as JFTOT stressing increased from 260°C to 300°C. The yellow grease gave a similar result when the JFTOT was run at 260°C. However, when stressed at 300°C, the yellow grease B100 peroxide value dropped from 245 meq O_2/kg to 1.07 meq O_2/Kg . This is most likely caused by the thermal decomposition of hydroperoxides at the higher temperature. The likely reasons why the yellow grease gave such a dramatic decrease in peroxide value with the 300°C JFTOT stressing are due to its very poor stability and its very high initial level of hydroperoxides. It is also possible that hydroperoxides formed in yellow greases are less thermally stable than those formed in soy B100's.

JFTOT stressing at either temperature had no effect on overall bulk biodiesel composition as measured FAME analysis (Table 5). Likewise, JFTOT stressing had no effect on the FAME-calculated parameters OX, APE, or BAPE. Accordingly, subsequent B100's were not evaluated by these methods. This confirms what was noted earlier, namely that the manifestation of fuel chemical instability is the result of chemical changes derived from small fractions of the bulk composition.



Figure 11. Effect of JFTOT on Peroxide Value: Original Results

3.2 Re-evaluation of Test Fuels

The initial evaluation of soy B100 AL-27102-F and yellow grease AL-27097-F was completed by August 2005. Initial evaluation of the third B100, soy-based AL-27144-F, was completed in April 2006. As previously mentioned, the AVFL-2b Committee decided to expand the remaining experimental project plan steps 7–11 to include evaluation of two B100's instead of the originally planned one B100. The two B100's selected for the remainder of the project work were the two soy-based B100's, AL-27102-F and AL-27144-F. The two reasons for this selection were:

- 1. The yellow grease sample was very low in stability (Rancimat IP = 1.0 hr.) and may not be representative of yellow greases;
- 2. The two soy B100's taken together would represent a wide range of initial stability with AL-27102-F representing unusually high stability (Rancimat IP = 9.1 hr.), and AL-27144-F representing typical stability (Rancimat IP = 5.0).

By the time this decision was made, significant time had elapsed since both soy-based B100's had been initially evaluated. Accordingly, both of the soy B100's were re-evaluated during November 2006. Prior to this re-evaluation, the two B100's had been purged with N_2 , sealed, and stored in their original 55-gallon drums under outside ambient temperature. Therefore, the re-evaluation represented a 14-month ambient temperature aging for AL-27102-F and a 6-month ambient aging for AL-27144-F. The re-evaluation data for the two soy B100's are referred to as "before aging" since the primary reason for the re-evaluation was to provide more accurate baseline data for comparison to the agitated and quiescent aging data that would be generated in

the remaining experimental project plan steps. Also, comparing the initial evaluation data with the re-evaluation data provides useful information on the effect of months of ambient aging on stability and JFTOT deposition tendency.

Most of the observations pertaining to the original evaluation data that were documented in the previous section 3.1 remained valid in the re-evaluation data. However, some noteworthy changes were observed. A more complete discussion of this data is provided in Appendix B. The most important points are summarily discussed below.

3.2.1 Initial Biodiesel Stability

Comparing the initial evaluation data to the re-evaluation data, both B100's experienced some minor reduction in stability as measured by Rancimat induction period (Figure 12). The less stable B100 AL-27144-F experienced a small increase in D2274 total insolubles while AL-27102-F did not significantly change (Figure 13).

Comparing the initial evaluation data to the re-evaluation data, the less stable B100 AL-27144-F significantly increased in the D2274 iso-octane insolubles (Figure 14). Since the initial evaluation of D2274 iso-octane insolubles for AL-27102-F was not considered reliable, no meaningful comparison can be made for that property.

Comparing the initial evaluation data to the re-evaluation data, Post-D2274 TAN, post-D2274 polymer content, and initial peroxide value all experienced significant increases for the less stable AL-27144-F (Figures 15, 16, and 17, respectively). No significant change in these properties was observed for the more stable AL-27102-F.







Figure 13. ASTM D2274 Total Insolubles for B100's: Original Results vs. Results Before Aging



Figure 14. ASTM D2274 Iso-Octane Insolubles for B100's: Original Results vs. Results Before Aging







Figure 16. Initial and Post-D2274 Polymer Content for B100's: Original Results vs. Results Before Aging



Figure 17. Peroxide Value for B100's: Original Results vs. Results Before Aging

3.2.2 JFTOT Deposition Tendency

JFTOT deposit volume repeatability in the re-evaluation results continued to be good at both test temperatures (Figures 18–19). However, there was a somewhat larger repeatability gap between 300°C deposit volume values for the less stable AL-27144-F, compared to the earlier repeatability for that B100.

Comparing the initial evaluation data to the re-evaluation data, the JFTOT deposit volume of both B100's increased significantly at 260°C (Figure 20). However, the less stable AL-27144-F increased more than the more stable AL-27102-F. The JFTOT deposit volume of the less stable AL-27144-F also increased significantly at 300°C. The JFTOT deposit volume at 300°C for the more stable AL-27102-F did not significantly change. It should be mentioned that although the 260°C JFTOT deposit volumes for both B100's experienced an overall significant increase during the time between the original and current tests, the slopes of the two B100 lines relative to each other did not significantly change. Note that in graphs of JFTOT deposit volumes such as Figures 5 and 20, some individual data points representing average deposit volumes are bracketed so as to display their highest and lowest replicate values. This is done to provide a visual indication of repeatability and is done only for those data points where repeatability is of sufficient magnitude to make such a display meaningful. This convention will be used in the remaining figures where trends in deposit volumes are graphically compared.



Figure 18. Repeatability of JFTOT Deposit Volume, 260°C: B100's Before Aging



Figure 19. Repeatability of JFTOT Deposit Volume, 300°C: B100's Before Aging



Figure 20. Effect of Temperature on JFTOT Deposit Volume for B100's: Original Results vs. Results Before Aging

As already noted in the previous section 3.2.1, only minor changes in Rancimat IP and D2274 total insolubles were experienced by the two soy B100's during their storage between the original evaluation and re-evaluation. The significant increase in JFTOT deposit volume experienced by both B100's during that period may indicate that subtle decreases in B100 stability data may result in significant increases in the tendency to form deposits on hot metal surfaces under conditions similar to those experienced in the JFTOT. Although the less stable AL-27144-F did experience substantial increases in post-D2274 TAN, post-D2274 polymer content, and initial peroxide value, the more stable AL-27102-F did not. Therefore, any attempt to link the increase in JFTOT deposits for AL-27144-F to those test parameter increases is not consistent with the observed behavior of AL-27102-F.

3.2.3 Effect of JFTOT Stressing on Biodiesel Stability

Re-evaluation data shows no significant effect of JFTOT at either stress temperature on D2274 total insolubles for AL-27102-F. For the less stable AL-27144-F, JFTOT stressing at 260°C and 300°C caused a progressive decrease in D2274 total insolubles (Figure 21). Similarly, with respect to the effect of JFTOT stressing at 260°C and 300°C on D2274 iso-octane insolubles, the re-evaluation data show no significant effect for the more stable AL-27102-F. For the less stable AL-27144-F, JFTOT stressing at 260°C and 300°C caused a substantial decrease in iso-octane insolubles (Figure 22). This may indicate that as a B100's stability decreases, short term, high temperature stressing from a hot metal surface may remove insolubles and insoluble precursors. This may correspond to insolubles and insoluble precursors being a source of JFTOT deposits.



Figure 21. Effect of JFTOT on ASTM D2274 Total Insolubles: B100's Before Aging



Figure 22. Effect of JFTOT on ASTM D2274 lso-Octane Insolubles: B100's Before Aging

With respect to the effect of JFTOT stressing at 260°C and 300°C on peroxide value, the reevaluation data (Figure 23) showed a progressive decrease for the less stable AL-27144-F, most likely due to a thermal decomposition similar to what was observed for the yellow grease AL-27097-F. For the more stable AL-27102-F, the peroxide value was initially low and JFTOT stressing produced no significant effect.



Figure 23. Effect of JFTOT on Peroxide Value: B100's Before Aging

3.3 Initial Evaluation of B20 Blends

Each of two soy B100's was blended with the ULSD to obtain B20 blends. The two B20 blends were given the sample designations CL06-0663 (containing AL-27102-F) and CL06-0664 (containing AL-27144-F). Those B20 blends were initially evaluated to provide baseline data for the aging steps that would subsequently be performed on them. A more complete discussion of these initial evaluation results is provided in Appendix C. The most important points are summarily discussed below.

3.3.1 Initial Blend Stability

Initial stability evaluation results are provided in Table 6. The more stable B100 AL-27102-F provided the more stable B20, relative to the B20 made from the less stable B100 AL-27144-F. This superior B20 stability was evidenced in the initial values of Rancimat induction period, peroxide value, and anisidine value.

ASTM D2274 total insolubles for the two B20's were leveled to essentially the same low value of about 0.4-mg/100 ml despite the fact that the corresponding B100's were significantly different.

Both B20's had comparable initial TAN values (Figure 24). This is similar to what was observed for the two B100's. Both B20's also had comparable TAN values after D2274 stressing. This is in contrast to the B100 data where the less stable AL-27144-F had a much higher post-D2274 TAN compared to AL-27102-F (Figure 15).

Sample Identification		CL06-0663	CL06-0664
B100 Used		AL-27102-F	AL-27144-F
Property	Method	Initial Value	Initial Value
Oxidation Stability Index (OSI) @ 110°C, hr.	ISO 6886		
average value		13.07	7.74
Oxidation Stability, mg/100 ml	Modified ASTM D2274		
adherent insolubles, average		0.3	0.0
filterable insolubles, average		0.2	0.4
total insolubles, average		0.5	0.4
Total Acid Number after D2274, average	D664	0.12	0.11
Peroxide Value, meq O ₂ /kg	D3703	3.60	18.40
Conjugated Dienes	ISO 3656		
E ^{1%} _{1cm} (232)		19.91	23.09
E ^{1%} _{1cm} (268)		7.68	8.51
Anisidine Value	EN ISO 6885	0.6	1.5
тотох		7.8	38.3
TAN, mg KOH/g	D664	0.10	0.09

Table 6.	Evaluation	of the	B20 Fuels	Before	Aging
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Figure 24. Effect of D2274 on Total Acid Number: B20's Before Aging

Overall, the stability of the two initial B20's appeared closer to each other than did the stability of the corresponding initial B100's. This is likely due to the diluting effect of the non-polar ULSD. Also, this partial leveling effect suggests that at least for these two B100's there was no interactive effect between ULSD and B100 that magnified the resulting blend instability. Since neither B100 used to make the B20's was highly unstable, it cannot be determined from this data if a B100 and ULSD will always blend non-interactively with respect to instability-related properties.

3.3.2 JFTOT Deposition Tendency

As with the B100 JFTOT results, repeatability for the deposit volume was good (Figures 25–26).



Figure 25. Repeatability of JFTOT Deposit Volume, 260°C: B20's Before Aging



Figure 26. Repeatability of JFTOT Deposit Volume, 300°C: B20's Before Aging
The relative trend in JFTOT deposit volume for the two B20's (Figure 27) was identical to the trend previously observed for the corresponding B100's (Figure 20). At least for the two B100's of this project, the relative deposit-forming tendencies of B20 blends appeared to be determined by the relative deposit-forming tendencies of the B100's from which they were made.

The overall magnitude of JFTOT deposit volume for the initial B20's was similar to the JFTOT deposit volume for the corresponding B100's before aging. This will be discussed further in the section 3.5.2 on the JFTOT deposition tendency of aged B20's.

3.3.3 Effect of JFTOT Stressing on Blend Stability

For both B20's, JFTOT stressing at 260°C and 300°C had little or no significant effect on Rancimat IP (Figure 28), D2274 total insolubles (Figure 29), TAN (Figure 30), and peroxide value (Figure 31). For the less stable CL06-0664, the peroxide values of the initial B20 and the B20 after JFTOT stressing were much less than what was observed for the corresponding B100 AL-27144-F (Figure 23).

3.4 Evaluation of B100's After Aging

As indicated in the experimental project plan provided in section 2.1, each of the two B100's was stressed by two procedures: quiescent aging and agitated aging. The stressed fuels were then evaluated by the ORP tests as described in section 2.4 of this report. A more complete discussion of these evaluation results is provided in Appendix D. The most important points with representative data are summarily discussed below.



Figure 27. Effect of Temperature on JFTOT Deposit Volume: B20's Before Aging



Figure 28. Effect of JFTOT on Rancimat Induction Period: B20's Before Aging



Figure 29. Effect of JFTOT on ASTM D2274 Total Insolubles: B20's Before Aging



Figure 30. Effect of JFTOT on Total Acid Number: B20's Before Aging



Figure 31. Effect of JFTOT on Peroxide Value: B20's Before Aging

3.4.1 Aged B100 Stability

Agitated aging was much more oxidatively severe than quiescent aging. For both B100's, there was a progressive deterioration from the "before aging" to the "after quiescent aging" to the "after agitated aging" test results for Rancimat IP, D2274 total insolubles, D2274 iso-octane insolubles, TAN, TAN after D2274, initial polymer content, polymer content after D2274, peroxide value, anisidine value, and conjugated dienes. This data also consistently confirms the fact that AL-27144-F is much less stable than AL-27102-F. Data for the Rancimat IP behavior is shown below in Figure 32.



Figure 32. Effect of Aging on B100 Rancimat Induction Period

For agitated aged AL-27102-F, Rancimat IP dropped to 1.44 hours, compared to 7.94 hours before aging. The agitated aged AL-27144-F Rancimat IP dropped to 0 hours compared to 4.43 hours before aging.

For both B100's, the pattern of increase for D2274 total insolubles after quiescent and agitated aging (Figure 33) is similar to the pattern of increase for D2274 iso-octane insolubles (Figure 34). Both B100's showed a dramatic increase in D2274 total and iso-octane insolubles after agitated aging. However, for the less stable AL-27144-F, D2274 total insolubles actually decreased in the quiescent aged fuel compared to the B100 before aging. The reason for this cannot be determined with certainty, but may be due in part to the fact that stressed fuels were pre-filtered before being evaluated by D2274.



Figure 33. Effect of Aging on B100 D2274 Total Insolubles



Figure 34. Effect of Aging on B100 D2274 Iso-Octane Insolubles

For both B100's, the pattern of increase for TAN in the quiescent and agitated aged samples (Figure 35) was identical to the pattern of increase experienced in the polymer content (Figure 36). Similarly, the pattern of increase for post-D2274 TAN in the quiescent and agitated aged samples (Figure 37) was essentially identical to the pattern of increase experienced in the post-D2274 polymer content (Figure 38). This similarity between trends in TAN and polymer content was observed in the non-aged B100's. A more complete discussion of this is provided in section 3.6 on global trends.



Figure 35. Effect of Aging on B100 Initial Total Acid Number



Figure 36. Effect of Aging on B100 Initial Polymer Content



Figure 37. Effect of Aging on B100 Post-D2274 Total Acid Number



Figure 38. Effect of Aging on B100 Post-D2274 Polymer Content

3.4.2 JFTOT Deposition Tendency

JFTOT deposit volumes with repeatability intervals are shown for the aged B100's in Figures 39–40. Repeatability for the deposit volume of the aged B100's was not as good as the B100's before aging or B20's before aging. The repeatability of the JFTOT deposit volume appeared to be slightly worse for the more severely agitated B100's compared to the quiescent aged samples.

Also, the repeatability of the JFTOT deposit volume was generally worse for tests run at 260°C compared to 300°C. The reason for the erratic nature of the deposit data cannot be determined, but may be partially due to the increased level of oxidative deterioration of the stressed B100's. This will be further discussed in the subsequent section 3.6 on global trends. The somewhat inconsistent JFTOT deposit data makes further observations concerning relative performance between B100's uncertain.



Figure 39. Effect of Aging on JFTOT Deposit Volume for AL-27102-F



Figure 40. Effect of Aging on JFTOT Deposit Volume for AL-27144-F

3.4.3 Effect of JFTOT Stressing on Aged B100 Stability

JFTOT stressing had no significant effect on the Rancimat IP of any of the quiescent and aged B100's (Figure 41–42).



Figure 41. Effect of JFTOT on Rancimat Induction Period of Quiescent Aged B100's



Figure 42. Effect of JFTOT on Rancimat Induction Period of Agitated Aged B100's

JFTOT stressing had no significant effect on the D2274 total insolubles of the quiescent or agitated aged AL-27102-F (Figures 43–44). For the quiescent aged AL-27144-F, D2274 total insolubles increased significantly after JFTOT stressing at 300°C. For the agitated aged AL-27144-F, a small but progressive decrease in D2274 total insolubles was observed after JFTOT stressing at 260°C and 300°C. Note that only AL-27144-F after agitated aging has no oxidative reserve left, as evidenced by its essentially zero Rancimat IP. Under those conditions, the effect of JFTOT stressing on subsequent D2274 total insolubles may simply reflect a balance of insolubles formation and insolubles deposition that favored deposition.



Figure 43. Effect of JFTOT on D2274 Total Insolubles of Quiescent Aged B100's





JFTOT stressing had no significant effect on the D2274 iso-octane insolubles of either of the quiescent aged B100's (Figure 45). However, for the agitated aged AL-27144-F there was a very significant progressive decrease in D2274 iso-octane insolubles after JFTOT stressing at 260°C and 300°C (Figure 46). This trend is similar, but of a much larger magnitude, to the previously noted trend for D2274 total insolubles for the same B100 after agitated aging. It is also similar to the trend observed for the iso-octane insolubles of the same B100 before aging. Since the agitated aged AL-27144-F had a Rancimat IP of essentially zero, it would be expected to be sensitive to the short term, high temperature stress of the JFTOT. The dramatic decrease in D2274 iso-octane insolubles may reflect an insolubles precursor formation rate that is less than the rate by which those precursors are either deposited in the JFTOT tube or converted to insolubles that are deposited.

JFTOT stressing at 260°C and 300°C caused a progressive decrease in peroxide value for all the quiescent and agitated aged B100's (Figure 47–48). This is very similar to the trends seen before for the less stable B100 AL-27144-F before aging (Figure 23), and is likely due to thermal decomposition of hydroperoxides by the hot steel surface of the JFTOT heater tube.



Figure 45. Effect of JFTOT on D2274 Iso-Octane Insolubles of Quiescent Aged B100's



Figure 46. Effect of JFTOT on D2274 Iso-Octane Insolubles of Agitated Aged B100's



Figure 47. Effect of JFTOT on Peroxide Value of Quiescent Aged B100's



Figure 48. Effect of JFTOT on Peroxide Value of Agitated Aged B100's

JFTOT stressing had no significant effect on the initial iso-octane insolubles (iso-octane insolubles before D2274 stressing) for the agitated aged AL-27102-F (Figure 49). For agitated aged AL-27144-F, JFTOT stressing at 260°C more than doubled the initial iso-octane insolubles. When JFTOT stressing was at 300°C, initial iso-octane insolubles decreased to an intermediate level. This behavior may represent the balance between the formation and decomposition of iso-octane insolubles in the agitated aged AL-27144-F during the JFTOT stressing at 260°C and 300°C. The relationship between the initial iso-octane insolubles, D2274 iso-octane insolubles, and D2274 total insolubles is obviously complex and insufficient data is available to define it. Measurement of initial iso-octane insolubles was not possible for the quiescent aged B100 samples before JFTOT stressing due to insufficient sample quantity. Accordingly, trends for these fuels could not be plotted. However, the available data suggests that initial iso-octane insolubles were low and insensitive to JFTOT stressing.



Figure 49. Effect of JFTOT on Initial Iso-Octane Insolubles of Agitated Aged B100's

3.5 Evaluation of B20 Blends After Aging

Each of the two B20 blends discussed in section 3.3 was stressed by the quiescent aging and agitated aging procedures. The stressed fuels were then evaluated by the ORP tests as described in section 2.4 of this report. A more complete discussion of these evaluation results is provided in Appendix E. The most important points with representative data are summarily discussed below.

3.5.1 Aged B20 Blend Stability

Overall, the effects of quiescent and agitated aging appear to be less for the B20 blends compared to what was observed for the corresponding B100's.

The progressive deterioration of stability-related test results observed for quiescent and agitated aged B100's was not as consistently observed for the aged B20's. This can be seen by comparing the aged B20 results for total insolubles (Figure 50), initial TAN (Figure 51), and TAN after D2274 (Figure 52) with the results for the aged B100's (Figures 33, 35, and 37, respectively).



Figure 50. Effect of Aging on B20 D2274 Total Insolubles







Figure 52. Effect of Aging on B20 Post-D2274 Total Acid Number

For both B20's, quiescent and agitated aging did not produce any significant change in total insolubles or initial TAN when compared to the non-aged B20's. This is in contrast to the corresponding data for the aged B100's which showed significant increases in both those properties (Figures 33, 35), especially for the less stable AL-27144-F. TAN after D2274 did sharply increase for only the agitated aged CL06-0664 compared the non-aged value.

For both B20's, quiescent and agitated aging did produce a moderate and progressive reduction in Rancimat IP relative to the non-aged blends (Figure 53). However, the amount of reduction in Rancimat IP going from the non-aged to the agitated aged B20's is not as large as what was observed for the corresponding B100's (Figure 32).



Figure 53. Effect of Aging on B20 Rancimat Induction Period

3.5.2 JFTOT Deposition Tendency

JFTOT deposit volumes with repeatability intervals are shown for the aged B20's in Figures 54– 55. Repeatability for the deposit volume of the aged B20's was roughly comparable to that of the aged B100's. It was not as good as the B100's before aging or B20's before aging. Like the aged B100's, the repeatability of the JFTOT deposit volume appeared to be somewhat worse for the more severely agitated B20's compared to the quiescent aged samples. As already mentioned in the case of the B100's after aging, the reason for the erratic nature of the deposit data cannot be determined, but may be partially due to the increased level of oxidative deterioration of the stressed B20's. This will be further discussed in the subsequent section 3.6 on global trends. The inconsistent JFTOT deposit data makes further observations concerning relative performance between B20's uncertain.



Figure 54. Effect of Aging on JFTOT Deposit Volume for CL06-0663



Figure 55. Effect of Aging on JFTOT Deposit Volume for CL06-0664

Despite the poor repeatability of the data, the overall JFTOT deposit volumes for the aged B20's appear to be of similar magnitude to the JFTOT deposit volumes of the corresponding aged B100's. This is exactly what was previously observed when comparing the JFTOT deposit volumes for the non-aged B100's with the non-aged B20's. This is noteworthy, since the B20's have only 20% the amount of oxidatively unstable material. Since the JFTOT deposit tendency of the ULSD was not determined, the exact cause cannot be determined. However, additional comments will be provided in section 3.6 on Global Trends.

3.5.3 Effect of JFTOT Stressing on Aged B20 Blend Stability

JFTOT stressing at both temperatures had the same effect on the Rancimat IP of the quiescent and aged B20's: JFTOT stressing at 260°C caused a small reduction in Rancimat IP compared to the initial aged B20; JFTOT stressing at 300°C caused the Rancimat IP to either remain unchanged or slightly increase compared to the initial aged B20 (Figures 56–57). This pattern was not observed for the non-aged B20's (Figure 21). There is not enough information to determine the cause of this minor but apparently real effect.

JFTOT stressing had no significant effect on the D2274 total insolubles of the quiescent aged B20's (Figure 58). Likewise, for the agitated aged CL06-0663, there was not significant effect on D2274 total insolubles. However, there was a significant increase in D2274 total insolubles for the 260°C stressed sample (Figure 59).



Figure 56. Effect of JFTOT on Rancimat Induction Period of Quiescent Aged B20's



Figure 57. Effect of JFTOT on Rancimat Induction Period of Agitated Aged B20's



Figure 58. Effect of JFTOT on D2274 Total Insolubles of Quiescent Aged B20's



Figure 59. Effect of JFTOT on D2274 Total Insolubles of Agitated Aged B20's

JFTOT stressing at 300°C caused a decrease in peroxide value for all the quiescent and agitated aged B20's compared to the initial aged B20's (Figures 60–61). JFTOT stressing at 260°C caused a small increase in peroxide value for all aged fuels except for the agitated aged CL06-0664, where a decrease was observed. Apparently, for the 300°C JFTOT stressing, the overall effect on the aged B20's is to provide a net decomposition of hydroperoxides, just as was observed for the aged B100's (Figures 47–48). At the lower 260°C JFTOT stressing, the amount of hydroperoxides formed in most cases was greater than the amount that was decomposed, resulting in a net increase. The difference in this pattern cannot be determined with certainty, but may be partially due to the effect of the JFTOT stressing on the ULSD component.



Figure 60. Effect of JFTOT on Peroxide Value of Quiescent Aged B20's



Figure 61. Effect of JFTOT on Peroxide Value of Agitated Aged B20's

3.6 Global Trends

Further analysis of the previously discussed results provides insight into trends that span all or significant parts of the data. Accordingly, these trends shed light on the chemistry of biodiesel oxidation as it applies to the relationships between various stability indicators (ORP test results) and deposition tendency (JFTOT results). To accomplish this, ORP test data spanning the initial, before aging, quiescent aged, and agitated aged B100 test results were evaluated together. Additionally, overall trends found in the JFTOT deposition tendency of the B100's and B20's were examined. A more complete discussion of these evaluation results is provided in Appendix F. The most important points with representative data are summarily discussed below.

3.6.1 Trends Concerning Stability-Related Test Results for B100

A general relationship was observed between the Rancimat IP and D2274 total insolubles for B100's, as indicated in Figure 62. For both B100's, whether evaluated initially, just prior to aging, or after the two aging processes, a relationship somewhat similar to an exponential decay pattern is observed in the data. For B100's with Rancimat IP values less than 2 hours, D2274 total insolubles are very high. As the Rancimat IP increases, the D2274 total insoluble level rapidly decreases. When the Rancimat IP approaches 6 hours, the D2274 total insoluble level has essentially reached its low asymptotic value. Although a simple exponential function as available by Excel software only provides an R^2 value of 0.6707, a more involved exponential equation would certainly yield a better fit. A simple quadratic fit of the Figure 62 data provides an excellent R^2 value of 0.9439. However, this is an intrinsically flawed approach, since the resulting curve increases parabolically just at the high end of the plotted Rancimat values, a trend that should not happen in real B100 samples. It is interesting to note that the data from the both B100's appear to mesh together to form one unified trend despite the fact that the initial

stabilities of these fuels were quite different from each other. Also, as already discussed, the more stable AL-27102-F shows consistent signs of a significant dose of a synthetic antioxidant, while the less stable AL-27144-F does not. If this is indeed the case, then the way that the data from these two B100's fit together is even more remarkable. If AL-27102-F does not contain an antioxidant, but instead has extremely atypical initial stability for some unknown reason not suggested by the overall data and the prior stability literature, then the result is still the same: the apparent unifying trend in Figure 62 is noteworthy. However, this trend spans only two fuels. It remains to be seen whether a much larger group of B100's similarly evaluated would have conformed to the plot provided in Figure 62.



Figure 62. Correlation of B100 D2274 Total Insolubles vs. Rancimat IP

The general features of the exponential decay curve observed in Figure 62 were repeated when other stability indicators were plotted as a function of Rancimat IP. These include TAN, TAN increase after D2274—hereafter referred to as delta TAN—, initial polymer content, increase in polymer content after D2274—hereafter referred to as delta polymer—, peroxide value, anisidine value, TOTOX, and conjugated diene content. Representative graphs or TAN, delta TAN, polymer content and delta polymer are provided in Figures 63–66, respectively.

The rate of decrease with increasing Rancimat IP varied depending on which stability indicator was plotted. For instance, TAN and initial polymer content dropped very rapidly and leveled off quickly as Rancimat IP increased from zero. However, delta TAN and delta polymer dropped off much more gradually (nearly linearly) before leveling off. These figures show that as the oxidation stability reserve as indicated by Rancimat IP decreases, other stability indicators tend to increase. The point at which a given stability indicator will increase and the rate by which that increase occurs will depend on which stability indicator is considered.



Figure 63. Correlation of B100 Initial Total Acid Number vs. Rancimat IP



Figure 64. Correlation of Increase in Post-D2274 Total Acid Number vs. Rancimat IP



Figure 65. Correlation of B100 Initial Polymer Content vs. Rancimat IP



Figure 66. Correlation of B100 Increase in Post-D2274 Polymer Content vs. Rancimat IP

Delta TAN and delta polymer appear to be an advanced indicator of the onset of gross instability. Delta TAN began to increase when Rancimat IP was reduced to about 6 hours; delta polymer showed exactly the same behavior. In contrast, other stability indicators such as TAN, polymer content, initial peroxide value, anisidine value, and conjugated dienes did not begin to increase until Rancimat IP dropped to about 2 hours. D2274 total insolubles began to increase as

Rancimat IP decreased from 6 hours to 4 hours. This behavior is consistent with the previously observed effect of agitated aging (D2274 stressing) on Rancimat IP for the two B100's: for the more stable AL-27102-F, Rancimat IP dropped by more than 6 hours; for the less stable B100 AL-27144-F, Rancimat IP dropped by more than 4 hours, resulting in a final Rancimat IP of zero. Therefore, the effect of agitated aging (D2274 stressing) was to dramatically reduce the oxidative stability reserve. This was reflected in greatly increased TAN and polymer content compared to the same B100 before the D2274 stressing.

The most striking correlation of stability indicator data is the relationship between polymer content and TAN (Figure 67). This linear plot provides an R² value of 0.9500. This is consistent with what has been reported in previous work, as documented in the Task 1 literature survey. The linear relationship between polymer content and TAN shows that the polymeric materials formed as B100 oxidizes are either the primary source of TAN increase, or else the acidic materials are tightly linked byproducts of the same process that forms the polymeric material. This result, combined with the information outlined in the previous item 3, suggest that initial TAN combined with delta TAN may be an excellent indicator of B100 stability, perhaps more reliable than D2274 total insolubles. Certainly, TAN and delta TAN are much easier to obtain since all filtrations and gravimetry are avoided. Unfortunately, previously reported work where D2274 testing was done has almost always not included TAN after D2274, despite the extreme ease by which this additional determination could be obtained.



Figure 67. Correlation of B100 Total Acid Number vs. Polymer Content

The relationship between iso-octane insolubles content and TAN is given in Figure 68. Both initial iso-octane insolubles data and D2274 iso-octane insolubles data are plotted against their corresponding TAN values for all B100's for which that data is available. This figure is the exact analog to Figure 67. As can be seen, the linear correlation for TAN vs. iso-octane insolubles (R^2 = 0.7734) is significantly less defined than that previously noted for TAN vs. polymer content $(R^2 = 0.9500)$. This difference points to a very significant fact. Iso-octane insolubles, either in the initial B100 or in the D2274-stressed B100, are an indicator of total insoluble precursors. That is, higher molecular weight materials, although still soluble in the B100, may precipitate out when the B100 is blended with a non-polar fluid such as an ULSD. The polymer content is a measure of the actual compounds that have a molecular size (and molecular weight) much greater than the fatty acid methyl esters. Actual polymer test results show what appear to be dimers and trimers of the methyl esters. Because of the nature of the chromatographic polymer test procedure (see section 2.4), all polymeric material will be indicated in the test result. However, it is routinely observed that when B100 samples with high iso-octane insolubles are diluted with the iso-octane, and when the resulting turbid solution is filtered, the turbidity of the filtrate is never significantly reduced. This implies that much of the precipitated material formed during the iso-octane insolubles test is not caught by the 0.8-micron filter used in the test. It has already been observed that TAN is a reliable indicator of the formation of polymeric material during B100 oxidation. Therefore, Figures 67 and 68 show that TAN and delta TAN (or polymer content and delta polymer content) may be potentially superior stability indicators compared to initial iso-octane insolubles and D2274 iso-octane insolubles.



Figure 68. Correlation of B100 Total Acid Number vs. Iso-Octane Insolubles

3.6.2 Trends Concerning Stability-Related Test Results for B20 Blends

The general relationship observed between the Rancimat IP and D2274 total insolubles for B100's was not observed for the B20's (Figure 69). All values except one had D2274 total insolubles of 0.5 mg/100 ml or less regardless of observed Rancimat IP range of 13.07 hours to 3.75 hours. This is the direct consequence of the previously discussed leveling effect observed in the B20 blends relative to the corresponding B100's. Similarly, TAN values only varied from 0.09 to 0.14 mg KOH/g regardless of Rancimat IP (Figure 70).



Figure 69. Correlation of B20 D2274 Total Insolubles vs. Rancimat IP



Figure 70. Correlation of B20 Initial Total Acid Number vs. Rancimat IP

The delta TAN vs. Rancimat IP plot (Figure 71) was the only B20 relationship between stability indicators that showed a exponential curve similar to what was observed for most of the B100 data. However, only the three points with Rancimat IP values below 5 hours had dramatically increasing delta TAN values. These three data points represent the CL06-0664 (made from the less stable AL-27144-F) after agitated aging, i.e., the least stable B20 blend after the most severe oxidative stress.

The plot of peroxide value vs. Rancimat IP was roughly linear with an R2 value of 0.7556 (Figure 72).



Figure 71. Correlation of B20 Increase in TAN after D2274 vs. Rancimat IP



Figure 72. Correlation of B20 Initial Peroxide Value vs. Rancimat IP

3.6.3 Trends Concerning JFTOT Deposition Tendency

The overall repeatability of the JFTOT deposit data for both B100's became worse as the fuels were more progressively aged as shown in Figures 73–74. Also, repeatability was worse for the quiescent aged B100's compared to the agitated aged B100's. Comparing the two B100's with each other, neither appeared to be clearly superior to the other in terms of deposit volume repeatability.



Figure 73. Effect of Progressive Aging on JFTOT Deposit Volume: AL-27102-F



Figure 74. Effect of Progressive Aging on JFTOT Deposit Volume: AL-27144-F

Deposit volumes for both fuels as they were aged appear to top out at about $30 \times 10^{-5} \text{ cm}^3$. As previously mentioned, this amount of deposit is very large compared to what is typically observed when testing jet fuels (using aluminum instead of steel JFTOT heater tubes).

As can be seen, the deposit volumes of the two B100's appear to converge as they are more severely stressed. Also, the deposit volumes of the two B100's are more similar to each other when tested at 300°C compared to 260°C.

These observations are consistent with the idea that biodiesel deposit formation can reach a maximum level beyond which discrimination between fuels of significantly differing stability is lost. This loss of discrimination apparently occurs when the B100's are increasingly aged with concomitant reduction in stability. For sufficiently unstable B100's, discrimination can also be lost or reduced when the JFTOT stressing occurs at 300°C compared to 260°C. Mechanistically, this loss of discrimination may be due to the heater tube metal surface being so deeply covered (saturated) that deposit precursors within the adjacent fuel layer are unable to be affected by the metal surface. Also, a thermal insulating effect may reduce further deposits after a certain deposit thickness is achieved. In retrospect, running the JFTOT test with a smaller sample volume might have reduced the overall deposit volumes and increased discrimination between fuels of differing stability.

Additionally, it is useful to analyze the JFTOT deposit volume results with various measures of the extent of oxidation and oxidation stability. For the B100's, these comparisons are given in Figures 75–84. As noted earlier, the deposit volumes at 300°C were all roughly equivalent (~30 x 10^{-5} cm³) and therefore provide little useful information. However, at 260°C there is some discrimination between samples.

The data show that there is a general correlation between JFTOT deposit volume, at 260°C, and almost any of the measures of extent of oxidation prior to JFTOT testing. For example, the following figures show JFTOT deposit volume as a function of peroxide value (PV), total acid number (TAN), polymer content, and TOTOX (an index based on both PV and anisidine value). TOTOX and PV seem to be the best predictors, suggesting that the deposits on the tube form, as would be expected, from peroxides and carbonyl compounds. However, conjugated dienes (which are formed from the initially present allylic double bond configuration upon initial radical formation) also correlate with JFTOT deposit volume as well as these other parameters (not shown). In all four cases, the most oxidized sample is off the right-hand side of the chart, but still has only 30×10^{-5} cm³ of deposit volume.



Figure 75. JFTOT Deposit Volume vs. Initial Peroxide Value (B100)



Figure 76. JFTOT Deposit Volume vs. Total Acid Number (B100)



Figure 77. JFTOT Deposit Volume vs. Initial Polymer Content (B100)



Figure 78. JFTOT Deposit Volume vs. TOTOX (B100)

Some measures of oxidation stability are also somewhat predictive of JFTOT deposit volume. The following charts for Oxidation Stability Index (OSI), D2274 insolubles, D2274 TAN and delta TAN, D2274 polymer, and D2274 delta polymer indicate that only D2274 total insolubles has no relationship to deposit volume. Other parameters are at least somewhat predictive.



Figure 79. JFTOT Deposit Volume vs. Oxidation Stability Index (B100)



Figure 80. JFTOT Deposit Volume vs. D 2274 Total Insoluble (B100)



Figure 81. JFTOT Deposit Volume vs. D 2274 TAN (B100)



Figure 82. JFTOT Deposit Volume vs. D 2274 Delta TAN (B100)



Figure 83. JFTOT Deposit Volume vs. D 2274 Polymer Content (B100)


Figure 84. JFTOT Deposit Volume vs. Delta Polymer (B100)

These results tend to confirm that the JFTOT tube surface becomes saturated when testing at the highest temperature and for the unstable or highly oxidized samples. The results do not point to one type of chemical species or the results of one analysis as being related to deposit formation on hot metal surface, but rather to the extent of oxidation and potential to form additional oxidation products.

The corresponding data for the B20's are given in Figures 85–86. The overall repeatability of the JFTOT deposit data for both B20's is similar to that of the B100's in that repeatability became worse as the fuels were aged. However, unlike the B100's, overall deposit volume repeatability for the B20's did not appear to differ greatly when comparing results measured at 260°C and 300°C.



Figure 85. Effect of Progressive Aging on JFTOT Deposit Volume: CL06-0663



Figure 86. Effect of Progressive Aging on JFTOT Deposit Volume: CL06-0664

As previously discussed, the JFTOT deposit volumes for the B20's (non-aged and aged) were of a similar magnitude to the JFTOT deposit volumes for the B100's (non-aged and aged). This behavior is consistent with the idea that deposit formation is topping out due to the extremely unstable nature of biodiesel fuel relative to conventional fuels that are evaluated on the JFTOT (e.g., jet fuels).

Plots for JFTOT deposit volume as a function of PV, TAN, and TOTOX are shown below (Figures 87–89). As with the B100 samples, the results at 300°C are not informative, presumably because of saturation of the tubes surface with deposit. It is also interesting to note that the saturation deposit level is the same for B20 blends, i.e. fuels containing only 20% biodiesel are producing the same level of deposit. This indicates that the B100 deposit tendency is more than 5 times larger than the B20 deposit tendency, or is a manifestation of the negative synergy observed in previous studies where blends can produce higher deposits on the D2274 test than the parent B100—as long as the B100 was unstable (OSI of less than 1 hour). For the 260°C data, all three parameters tend to be predictive of deposit formation on the tube surface.



Figure 87. JFTOT Deposit Volume vs. Initial Peroxide Value (B20)



Figure 88. JFTOT Deposit Volume vs. Total Acid Number (B20)



Figure 89. JFTOT Deposit Volume vs. TOTOX (B20)

Based on the following plots (Figures 90–93), OSI is reasonably predictive of deposit forming tendency at 260°C, with longer induction time samples clearly showing lower deposits. We might expect higher JFTOT deposits for samples with higher D2274 deposits, but this expectation is not confirmed by the data. TAN after D2274 and delta-TAN are both also reasonable predictors of deposit formation.



Figure 90. JFTOT Deposit Volume vs. Oxidation Stability Index (B20)



Figure 91. JFTOT Deposit Volume vs. D 2274 Total Insoluble (B20)



Figure 92. JFTOT Deposit Volume vs. D 2274 TAN (B20)



The results at 260°C suggest that the tendency to form deposits on a metal tube surface is related to both the extent of prior oxidation and the oxidation stability of both B100 and B20 samples. An interesting observation is that JFTOT deposit formation is not related to D2274 insoluble formation but is related to the formation of acids on this test. The data seem to indicate that for the least stable samples and for all tests conducted at 300°C, the metal tubes became saturated with deposit making discrimination between samples impossible. Saturation occurred for both B20 blends and B100 samples. Additional tests at shorter residence time and perhaps lower temperature should be attempted.

Since the effect of the ULSD on JFTOT deposit volume was not determined, it is difficult to completely interpret the B20 deposit data in relation to the corresponding B100 data. However, any improvements to the JFTOT test procedure that increase the discriminating power for B100's will likely also be beneficial to biodiesel blends.

[One additional comment regarding JFTOT deposit volume measurements is appropriate at this time. As discussed, the tube deposit data showed a maximum value of approximately 30×10^{-5} cm^3 . Another possible explanation for this observation is that the ellipsometric device, which uses a laser to measure thickness, may not be able to measure deposits beyond this thickness. (A detailed analysis of the ability of the ellipsometer to measure biodiesel deposits has not been conducted.) If such is the case, the deposits may actually be thicker than the measured value. This possibility also points to the need for further work to evaluate the JFTOT as a tool to measure deposit tendencies of biodiesel and biodiesel blends.]

4.0 CONCLUSIONS

The results discussed in this report support the following conclusions:

- 1. Total acid number and polymer content, determined both initially and after D2274 stressing, are very tightly correlated to each other. Either of these test parameters may hold significant promise as a more meaningful stability indicator for B100 qualification, especially when used along with Rancimat IP.
- 2. When B20's are made from differing B100's, the differences in most of the stability indicators observed in the parent B100's may be reduced in the B20's, assuming that all the blends use the same ULSD. However, wide differences in the B100 Rancimat IP values will continue to be observed in the corresponding B20's.
- 3. When a B100 or B20 is continuously flowing over a hot metal surface, the effect on the fuel will be minimal as measured by changes in the fuel's stability indicators. Exceptions to this can include peroxide value and anisidine value, which can decrease and increase, respectively. However, other stability indicators such as Rancimat IP, D2274 total insolubles, iso-octane insolubles, and polymer content can also significantly change as the fuel's initial stability has experienced a sufficient decrease. This is especially true as the hot metal surface temperature increases.
- 4. Using the JFTOT, biodiesel-containing fuels can be evaluated for their tendency to produce deposits on hot metal surfaces. Some discrimination between fuels of differing initial stability can be obtained. However, the standard JFTOT method used for petroleum jet fuels does not appear to provide satisfactory discrimination over the range of stability observed in differing B100's and B20's when aged under widely differing conditions. This is apparently due to a maximum deposit level being achieved as B100 or B20 stability decreases. A modified method that does not alter the surface chemistry during JFTOT stressing but reduces the overall deposit volume may provide the desired discrimination. The most obvious way to achieve this would be to reduce the test fuel volume from 600 ml to a much lower value, perhaps as low as 100 ml or 200 ml.
- 5. With an optimized JFTOT test method, it is likely that the relationship between stability indicators and deposition tendency can be determined if sufficient research is performed.
- 6. Despite claims to the contrary, the biodiesel fuel AL-27102-F behaved in a manner entirely consistent with the presence of a significant dose of an effective synthetic antioxidant such as BHT or pyrogallol. If AL-27102-F does not contain a synthetic antioxidant, there is no other explanation consistent with the literature survey of Task 1 that will explain *all* the data.

5.0 RECOMMENDATIONS

Based on the conclusions provided above, the following recommendations for potential future work are given:

- 1. Additional work should be done to modify and optimize the JFTOT by using two B100's of widely differing stability, as based on Rancimat IP and modified D2274. The two B100's should ideally contain no added synthetic antioxidants. The effect of fuel volume should be determined to optimize the repeatability and discrimination. Tests should continue to be run at both 260°C and 300°C unless data clearly show otherwise. It may also be useful to determine if deposit volumes are affected by whether or not the test fuel is pre-filtered before evaluation in the JFTOT.
- 2. If the JFTOT procedure can be satisfactorily optimized using the two B100's as recommended above, the resulting test procedure should be evaluated with different lots of steel heater tubes to verify that minor differences in heater tube surface metallurgy do not affect results.
- 3. If JFTOT test results continue to look promising, a larger set of B100's should be evaluated for their deposition tendencies. The results should be correlated with appropriate stability indicators.
- 4. If JFTOT results continue to look promising, the effect of one or more antioxidants should be determined. If this work is correctly designed, it may help to explain some of the results provided in this report.
- 5. If JFTOT results continue to provide useful data for B100's, then research should be expanded to include B20's with the objective being to link B100 stability and deposition tendency to the deposition tendency of the corresponding biodiesel blend. It will probably be necessary to determine the role of the ULSD.
- 6. If the optimized JFTOT procedure continues to provide repeatable discrimination among biodiesel fuels of widely and moderately differing stability, then follow up testing should be done using actual engine components. Such testing could include engine fuel delivery systems, as well as full engine testing. Results of such tests should be compared to the JFTOT and stability indicator test results for the B100 and/or biodiesel blends used.

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APPENDIX A INITIAL EVALUATION OF TEST FUELS

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Overview

The original experimental test plan specified that two B100 samples, a soy-based product and yellow grease, were to be selected and used. Those two products, AL-27102-F and AL-27097-F respectively, were initially evaluated. Results of that evaluation were complete by August 2005. The third B100, a soy-based B100 with more typical stability (as determined by Rancimat induction period) was obtained and initially evaluated by April 2006. The ULSD fuel was obtained and evaluated by November 2006. Results of those initial evaluations are provided at the end of this appendix in Tables A1–A6 and Figures A1–A13, and are therein referred to as "original results". This is done to distinguish them from the re-evaluation results (discussed in Appendix B) that were determined before the aging. Initial evaluation results are discussed in the following three sections.

Initial Biodiesel Stability

The soy B100 AL-27102-F was much more stable than the yellow grease B100 AL-27097-F, based on both the initial values of Rancimat induction period (IP) and ASTM D2274 total insolubles. The second soy B100 AL-27144-F was of intermediate stability based on both Rancimat IP and D2274 total insolubles (Table A3). The 9.11-hour Rancimat IP for AL-27102-F is extremely unusual, based on all reported Rancimat IP results for non-additized soy-based B100's. Indeed, as already mentioned, one of the reasons the AVFL-2b Committee requested that another soy B100 be obtained was the recognition that AL-27102-F was extremely unusual based on all available B100 initial stability survey data. As documented in the Task 1 literature report, naturally occurring antioxidants do not provide that level of stability, and additional amounts of naturally occurring antioxidants such as tocopherols do not provide significant further improvements when added to B100's or fatty oils that have not previously had their natural antioxidants removed. Based on the literature covered in the Task 1 report, the only demonstrated method to increase Rancimat IP to the level observed in AL-27102-F is the addition of an effective synthetic antioxidant.

The increase in TAN and polymer content caused by D2274 stressing appeared to roughly correlate with the initial fuel stability as measured by Rancimat IP. Specifically, stressing by D2274 only slightly increased TAN and polymer content for the most stable soy B100 AL-27102-F compared to the initial unstressed fuel (Table A3); D2274 stressing did significantly increase TAN and polymer content for the more typical (lower) stability soy B100 AL-27144-F and the yellow grease B100 compared to the initial unstressed fuel (Table A3; Figures A1–A2).

For the soy B100 AL-27102-F and the yellow grease AL-27097-F, no significant D2274 isooctane insolubles were measured using the modified D2274 procedure (Table A4). As already mentioned, the cause of this apparent inaccuracy appeared to be due to the stacked blank filter method used. By the time the soy B100 AL-27144-F was obtained, a separate blank was run for each set of modified D2274 filtrations. This improved technique gave a D2274 iso-octane insoluble level of 2.45-mg/100 ml for AL-27144-F.

The more stable soy B100 AL-27102-F appeared to have less initial oxidative degradation than the yellow grease B100, based on the initial values of peroxide value (PV), conjugated dienes

(adsorption at 232 cm⁻¹), anisidine value, TOTOX, polymer content, and total acid number (TAN) (Table A5). The lower stability soy B100 AL-27144-F appeared to have an intermediate level of oxidative degradation relative to the other two B100's based on the same test methods. These results directionally agree with the initial Rancimat and D2274 stability results (Table A4).

Both soy B100's appeared to be more susceptible to oxidation than the yellow grease B100 based on the initial FAME analysis and the calculated parameters of OX, APE, and BAPE (Table A6).

The disagreement between the susceptibility to oxidation as indicated by initial bulk fatty acid composition parameters (Table 6A) and the actual stability-related results (Tables A4–A5) suggests that the soy B100 AL-27102-F may contain a significant level of synthetic antioxidant despite our request for an additive free product. However, the provider insisted that such was not the case. We have learned that both soy B100's were not distilled. If the feed soybean oil for AL-27102-F had been additized prior to its delivery to the biodiesel plant, this antioxidant would carry over into the B100 with little or no effect. There is no way to verify this. However, additional results reported later in this report continue to be consistent with the presence of a synthetic antioxidant in AL-27102-F.

JFTOT Deposition Tendency

For both test temperatures, the JFTOT deposit volumes gave reasonably good repeatability for both fuels (Table A3; Figures A3–A4).

The average JFTOT deposit volumes for all three B100's at both test temperatures are shown in Figure A5. The less stable soy B100 AL27144-F gave more JFTOT deposit volume than the yellow grease AL-27097-F at both 260°C and 300°C. This ranking is consistent with their predicted stability determined by their susceptibility to oxidation as indicated by their fatty acid composition (Table A6). However, it is opposite the ranking predicted by their initial Rancimat and D2274 results (Table A4). Also, the deposit volume vs. temperature slope was similar for AL-27144-F and AL-27097-F.

The JFTOT data for the more stable soy B100 AL-27102-F was decidedly different from the other two B100's. At 260°C it gave the least deposit volume of all three B100's, and at 300°C it gave the most deposit volume of all three B100's. The deposit volume vs. temperature slope was radically different for AL-27102-F compared to the other two B100's. This data indicates that something is very different about the more stable soy B100 AL-27102-F compared to the less stable soy B100 AL-27144-F and the yellow grease AL-27097-F. While such a difference may be expected for AL-27102-F (a soy B100) compared to AL-27097-F (a yellow grease), it is very noteworthy that AL-27102-F would have such a different JFTOT deposit vs. temperature profile compared to AL-27144-F (another soy B100). Both soy B100's had essentially the same predicted oxidation susceptibility based on their fatty acid composition. However, AL-27144-F showed significantly less increase in JFTOT deposits when the temperature was increased to 300°C is not consistent with these facts. A hindered phenol antioxidant, if present in AL-27102-F, could account for its unusually high Rancimat IP, low D2274 insolubles level, and increased JFTOT deposit level at 300°C. Since hindered phenols are well known to rapidly decrease in antioxidant performance and even

promote oxidation at high temperatures, the 300°C JFTOT tube temperature could possibly result in dramatic reduction in stability.

It should be mentioned that thus far no data has been found that measures the effect of an antioxidant on the tendency of biodiesel fuels to form deposits on hot metal surfaces. Therefore, it has not yet been established if antioxidants reduce the tendency of B100's to form deposits on hot metal surfaces. If an effective antioxidant did reduce the deposit-forming tendency of a B100, then the data given in Figure A5 could be explained. However, since the manufacturer states that they did not add an antioxidant, and since it is not possible to determine if an antioxidant was added before the soybean oil was transesterified, the unusual behavior of AL-27102-F cannot be explained with certainty. Note that in Figure A5 the repeatability of the average deposit volumes is not displayed since the size of the gap between the highest and lowest value for all B100's is less than the size of the symbol used to plot the point.

Although both mean deposit thickness and deposit volume gave good discrimination, deposit volume appeared to be the better parameter for distinguishing JFTOT deposit tendencies for the two biodiesel fuels (Table A3). In all subsequent JFTOT test results, only deposit volumes are reported.

The deposit volume formed by both biodiesels was large compared to typical deposit volumes observed by Jet A fuels that give No. 1 visual ratings. However, jet fuels are tested using aluminum heater tubes while the biodiesel work done herein uses steel tubes. Since the deposit forming tendencies are significantly affected by the heater tube metallurgy, precise comparisons between previously evaluated hydrocarbon fuels and biodiesel fuels are not yet possible. It should be noted that every JFTOT test involving a B100 or B20 in this project gave a visual heater tube rating of greater than 4, with both an abnormal and peacock pattern.

Effect of JFTOT Stressing on Biodiesel Stability

For the most part, JFTOT stressing caused only minor or no change in the stability characteristics of the three biodiesels as measured by Rancimat and D2274 (Figures A6–A7). There was a minor but progressive decrease in Rancimat IP in the most stable of the three B100's, the soybased AL-27102-F. The notable exception involved the yellow grease B100 that had been stressed in the JFTOT at 300°C. This stressed fuel gave significantly increased D2274 total insolubles compared to the initial yellow grease B100 that had not yet been stressed in the JFTOT.

JFTOT stressing had no significant effect on TAN (Figure A8) for the three B100's. A minor progressive increase in polymer content was observed for only the yellow grease AL-27097-F (Figure A9). However, JFTOT stressing caused a significant increase in post-D2274 polymer content for the yellow grease compared to the same fuel before being JFTOT-stressed (Figure A10). This indicates that if the initial fuel stability is low enough (Rancimat IP = 1.0 hr.) brief contact with a sufficiently hot metal surface can cause some increase in polymer content. If this JFTOT-stressed B100 is then further stressed by D2274 (as provided in steps 4 and 5 of the experimental project plan of section 2.1), significant further deterioration can result in significant increases in polymer content relative to the same B100 stressed only by D2274.

Peroxide value was very low for the most stable B100, the soy-based AL-27102-F, and JFTOT stressing did not cause a significant change (Figure A11). The effect was minimal for the less stable soy B100 AL-27144-F, with only a minor decrease in peroxide value as JFTOT stressing increased from 260°C to 300°C. The yellow grease gave a similar result when the JFTOT was run at 260°C. However, when stressed at 300°C, the yellow grease B100 peroxide value dropped from 245 meq O_2/kg to 1.07 meq O_2/Kg . This is most likely caused by the thermal decomposition of hydroperoxides at the higher temperature. The reason why the yellow grease gave such a dramatic decrease in peroxide value with the 300°C JFTOT stressing is likely due to its very poor stability and its very high initial level of hydroperoxides. It is also possible that hydroperoxides formed in yellow greases are less thermally stable than those formed in soy B100's.

Anisidine value generally increased for both biodiesel fuels when they were stressed in the JFTOT (Figure A12). Conjugated dienes levels (adsorption at 232 cm⁻¹) did not exhibit any clear trend when the three B100's were stressed in the JFTOT (Figure A13).

JFTOT stressing at either temperature had no effect on overall bulk biodiesel composition as measured FAME analysis (Table A6). Likewise, JFTOT stressing had no effect on the FAME-calculated parameters OX, APE, or BAPE. Accordingly, subsequent B100's were not evaluated by these methods. This confirms what was noted earlier, namely that the manifestation of fuel chemical instability is the result of chemical changes derived from small fractions of the bulk composition.

In summary, the effect of passing a biodiesel fuel over a hot metal surface appears to have minimal effect on fuel properties. Only certain trace compositional properties are affected. The fuel stability properties as measured by either induction period tests such as Rancimat or insolubles formation tests such as D2274 do not appear to be radically affected by such short duration high temperature stressing.

Property	Test Method	D6751 Limit		Measured Value	
Type of Biodiesel			Soy	Yellow Grease	Soy
Sample Identification			AL-27102-F	AL-27097-F	AL-27144-F
Flash Point, °C	D93	130, min	169	176	162
Water and Sediment, %(vol)	D2709	0.050, max	0.01	0.01	<0.005
Kinematic Viscosity @ 40°C , mm²/sec	D445	1.9 - 6.0	4.09	4.68	4.11
Sulfated Ash, %(mass)	D874	0.020, max	<0.001	<0.001	<0.001
Sulfur, %(mass)/ppm(wt)	D5453	0.05/500	0.00008/0.8	0.00063/6.3	0.00006/0.6
Copper Strip Corrosion, 3 hr at 50°C	D130	No. 3, max	1B	1B	1B
Cetane Number	D613	47, min	51.4	63.9	
Cloud Point, °C	D2500	report value	0	5	0
Carbon Residue, %(mass)	D4530	0.050, max	0.0293	0.0099	0.0097
Total Acid Number, mg KOH/g	D664	0.80, max	0.38	0.69	
Free Glycerin, %(mass)	D6584	0.020, max	<0.001	0.004	0004
Total Glycerin, %(mass)	D6584	0.240, max	0.137	0.126	0.221
Phosphorus Content, ppm	D4951	0.001, max	<5	<5	
Distillation, Atmospheric Equivalent, °C	D1160				
90% recovered		360, max	368	370	361
Peroxide Value, meq O ₂ /kg	D3703		<1	245	73
Oxidation Stability Index @ 110°C, hr.	ISO 6886		9.11	1.03	5.04

Table A1. Initial Biodiesel Test Data

Note: off specification values or extremely atypical values are in red.

Property	Test Method	D975 Limit	Measured Value
Flash Point, °C	D93	52, min	61.1
Water and Sediment, %(vol)	D2709	0.05, max	0.01
Kinematic Viscosity @ 40°C, mm²/sec	D445	1.9 - 4.1	2.52
Ash, %(mass)	D482	0.01, max	<0.001
Sulfur, ppm(wt)	D2622	15, max	4.8
Copper Strip Corrosion, 3 hr at 50°C	D130	No. 3, max	1A
Cetane Index	D976	40, min	45.7
Ramsbottom Carbon on 10% res., %(mass)	D524	0.35, max	0.07
Total Acid Number, mg KOH/g			
Distillation, °C	D86		
Initial boiling point	1		159.6
5% recovered	1		196
10% recovered	1		204.5
50% recovered			256.4
90% recovered		282, max	314.6
total recovery, %			98.1
HFRR @ 60 C, ave. wear scar diameter, mm	D6079		576
Total Acid Number, mg KOH/g	D664		0.00
Peroxide Value, meq O ₂ /kg	D3703		0
Oxidation Stability, mg/100 ml	D2274		
adherent insolubles			0.1
filterable insolubles			0.1
total insolubles			0.2
Total Acid Number after D2274	D664		0.00

Table A2. Initial Ultra-Low Sulfur No. 2 Diesel Fuel (AL-27242-F) Test Data

B100 Tested			Soy		7	ellow Grease			Soy	
Sample Identification		AL-27102-F	CL05-0372	CL05-0378	AL-27097-F	CL05-0373	CL05-0379	AL-27144-F	CL06-0147	CL06-0150
Property	Method	Initial Value	Final 260°C	Final 300°C	Initial Value	Final 260°C	Final 300°C	Initial Value	Final 260°C	Final 300°C
Oxidation Stability Index (OSI) @ 110°C, hr.	ISO 6886									
replicate 1		0.6	8.0	7.2	1.1	1.2	1.1	2.0	4.7	4.8
replicate 2		6'8	6.7	7.4	1.0	1.3	1.1	2.1	4.6	4.8
replicate 3		9.5						5.0	4.5	4.8
number of replicates		3.0	2.0	2.0	2.0	2.0	2.0	3.0	3.0	3.0
average value		9.11	7.98	7.30	1.03	1.25	1.09	5.04	4.57	4.77
Oxidation Stability, mg/100 ml	Modified ASTM D2274									
adherent insolubles, replicate 1		0.4	0.5	0.1	0.0	0.5	0.8	1.0	1.0	0.0
filterable insolubles, replicate 1		0.0	0.1	0.0	8.4	4.1	0.0	0.1	0.2	0.3
total insolubles, replicate 1		0.4	0.0	0.1	9.4	4.6	0.8	1.1	1.2	1.2
iso-octane insolubles, replicate 1		0.0	0.0	0.0	0.0	0.0	0.0	2.5	0.3	0.8
modified total insolubles, replicate 1		0.4	0.6	0.2	9.4	4.6	0.8	3.6	1.5	2.0
polymer content after D2274, replicate 1	BS EN ISO 16931	1.00	1.04	1.03	8.28	4.19	11.50	2.74	3.22	3.12
Total Acid Number after D2274, replicate 1	D664	0.50	0.50	ND	1.87	2.52	ND	1.21	1.22	1.46
adherent insolubles, replicate 2		0.49	0.49	0.09	0.49	0.63	0.71	0.04	1.43	0.80
filterable insolubles, replicate 2		90'0	0.03	00.0	2.14	6.71	17.71	07.0	0.23	0.17
total insolubles, replicate 2		0.55	0.52	0.09	2.63	7.34	18.42	1.14	1.66	0.97
iso-octane insolubles, replicate 2		00'0	00'0	00.0	00.0	0.05	0.14	2.40	1.10	1.20
modified total insolubles, replicate 2		0.55	0.52	0.09	2.63	7.39	18.56	3.54	2.76	2.17
polymer content after D2274, replicate 2	BS EN ISO 16931	0.98	1.06	1.05	4.29	6.70	10.29	2.50	3.70	2.97
Total Acid Number after D2274, replicate 2	D664	0.47	0.51	ND	2.16	2.82	ND	1.05	1.46	1.22
adherent insolubles, average		0.46	0.52	0.12	0.72	0.57	0.74	66'0	1.22	0.85
filterable insolubles, average		0.03	0.05	00.00	5.29	5.41	8.86	0.15	0.20	0.24
total insolubles, average		0.49	0.56	0.12	6.00	5.98	9.60	1.13	1.42	1.09
iso-octane insolubles, average		00'0	00'0	0.02	00.0	0.03	0.07	27.45	02.0	1.00
modified total insolubles, average		0.49	0.56	0.13	6.00	6.01	9.67	33.58	2.12	2.09
polymer content after D2274, average	BS EN ISO 16931	0.99	1.05	1.04	6.29	5.45	10.90	2.62	3.46	3.05
Total Acid Number after D2274, average	D664	0.49	0.51	ND	2.02	2.67	ΠN	1.13	1.34	1.34
Kinematic Viscosity @ 40°C, mm ² /sec	D445	4.09	4.04	4.01	4.68	4.59	4.65	4.11	ND	ND
Refractive Index		1.4568	1.4560	ND	1.4525	1.4519	ND	ΠN	ΠN	ND
Peroxide Value, meq O ₂ /kg	D3703	0.5	3	9	245	207	1.07	22	51	32
Conjugated Dienes	ISO 3656									
E ^{1%} _{1cm} (232)		1.86	5.72	2.13	13.30	13.71	12.89	4.10	4.08	4.11
E ^{1%} _{1cm} (268)		0.20	1.20	0.37	2.58	2.95	3.18	1.59	1.75	1.90
Anisidine Value	EN ISO 6885	1.5	4.7	4.5	33.8	53.6	93.6	7'7	14.7	25.7
τοτοχ		<3.5	10.7	16.5	523.8	467.6	95.74	150.4	116.7	89.7

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B100 Tested			Sov		7	ellow Grease			Sov	
Sample Identification		AL-27102-F	CL05-0372	CL05-0378	AL-27097-F	CL05-0373	CL05-0379	AL-27144-F	CL06-0147	CL06-0150
Property	Method	Initial Value	Final 260°C	Final 300°C	Initial Value	Final 260°C	Final 300°C	Initial Value	Final 260°C	Final 300°C
Polymer Content, %(mass)	BS EN ISO 16931	0.64	0.59	0.68	1.08	1.28	1.34	1.33	1.21	1.29
Ester Content, %(mass)	BS EN ISO 16931	99.36	99.41	99.32	98.92	98.72	98.66	98.67	98.79	98.71
TAN, mg KOH/g	D664	0.38	0.35	0.45	0.69	0.66	0.66	0.38	0.39	0.40
TBN, mg KOH/g	D2896	0.13	0.11	0.14	0.14	0.12	0.13	DN	ΠN	ΠN
Free Glycerin	D6584	<0.001	<0.001	<0.001	0.004	0.003	0.002	004	ΠN	DN
Total Glycerin	D6584	0.137	0.140	0.139	0.126	0.106	0.128	0.221	ND	ND
FAME Analysis	Pr EN 14103									
Ester Content, %		104.92	105.19	104.44	102.57	102.13	101.59	105.33	ND	ND
Methyl Palmitate (16:0), %		10.39	10.41	10.50	13.29	13.45	13.40	11.54	ΠN	DN
Methyl Stearate (18:0), %		4.30	4.30	4.28	8.64	8.61	8.41	4.44	ΠN	ND
Methyl Oleate (18:1), %		23.10	23.13	23.09	45.76	45.61	45.95	24.23	ΠN	DN
Methyl Linoleate (18:2), %		51.70	51.70	51.67	22.69	22.65	22.54	51.31	ΠN	DN
Methyl Linolenate (18:3), %		7.78	7.79	7.78	1.71	1.70	1.71	6.51	QN	DN
OX (Oxidizability)		0.68	0.68	0.68	0.27	0.27	0.27	0.65	ΠN	ND
Allylic Position Equivalent (APE)	Calculated from FAME	165.16	165.24	165.08	140.32	139.92	140.40	164.10	ΠN	QN
Bis-Allylic Position Equivalent (BAPE)	Calculated from FAME	67.26	67.28	67.23	26.11	26.05	25.96	64.33	ΠN	DN
JFTOT Results										
Run Number 1										
Run Temperature			260	300		260	300		260	300
Deposit Thickness, minimum, nm			2.90	10.70		4.22	5.02		ΠN	DN
Deposit Thickness, maximum, nm			105.53	704.13		255.41	541.37		ΠN	ΠN
Deposit Thickness, mean, nm			49.46	413.10		114.37	182.95		ΠN	DN
Deposit Volume x 10 ⁻⁵ , cm ³			2.75	28.8		6.36	10.2		60.6	14.99
Run Number 2										
Run Temperature			260	300		260	300		260	300
Deposit Thickness, minimum, nm			1.46	5.30		6.17	5.32		ΠN	QN
Deposit Thickness, maximum, nm			247.97	704.89		228.41	510.35		ΠN	DN
Deposit Thickness, mean, nm			55.60	409.45		111.70	172.99		ND	DN
Deposit Volume x 10 ⁻⁵ , cm ³			3.09	28.4		6.22	9.63		9.25	14.60
Run Number 3										
Run Temperature			260	300		260	300		260	300
Deposit Thickness, minimum, nm			2.14	1.65		0.07	4.49		ND	ND
Deposit Thickness, maximum, nm			98.25	705.19		699.83	386.62		ND	DN
Deposit Thickness, mean, nm			48.97	376.11		103.87	165.86		ND	DN
Deposit Volume x 10 ⁻⁵ , cm ³			2.72	27.7		5.78	9.23		9.5	14.81
Average of Runs 1 - 3										
Run Temperature			260	300		260	300		260	300
Deposit Thickness, minimum, nm			2.17	5.88		3.49	4.94		ND	ND
Deposit Thickness, maximum, nm			150.58	704.74		394.55	479.45		ND	ND
Deposit Thickness, mean, nm			51.34	399.55		109.98	173.93		ND	ND
Deposit Volume x 10^{-5} , cm ³			2.85	28.30		6.12	9.69		9.28	14.80

(continued)
A3.
Table

B100 Tested			Soy		ĺ	ellow Grease			Soy	
Sample Identification		AL-27102-F	CL05-0372	CL05-0378	AL-27097-F	CL05-0373	CL05-0379	AL-27144-F	CL06-0147	CL06-0150
Property	Method	Initial Value	Final 260°C	Final 300°C	Initial Value	Final 260°C	Final 300°C	Initial Value	Final 260°C	Final 300°C
Oil Stability Index @ 110°C, hr.	ISO 6886	9.11	7.98	7.30	1.03	1.25	1.09	5.04	4.57	4.7
Oxidation Stability, mg/100 ml	Modified ASTM D2274									
adherent insolubles, average		0.46	0.515	0.115	0.715	0.57	0.74	0.99	1.22	0.8
filterable insolubles, average		0.03	0.045	0	5.285	5.41	8.855	0.15	0.20	0.2
total insolubles, average		0.49	0.56	0.115	9	5.98	9.595	1.13	1.42	1.0
iso-octane insolubles, average		0	0	0.015	0	0.025	0.071	2.45	0.70	1.0
modified total insolubles, average		0.49	0.56	0.13	9	6.005	9.666	3.58	2.12	2.0
polymer content after D2274, average	BS EN ISO 16931	66.0	1.05	1.04	6.285	5.445	10.895	2.62	3.46	3.04
Total Acid Number after D2274, average	D664	0.485	0.505	ND	2.015	2.67	ΠN	1.13	1.34	1.3
JFTOT Results, average										
Run Temperature			260	300		260	300		260	30
Deposit Thickness, minimum, nm			2.17	5.88		3.49	4.94		ΠN	IN
Deposit Thickness, maximum, nm			150.58	704.74		394.55	479.45		ΠN	IN
Deposit Thickness, mean, nm			51.34	399.55		109.98	173.93		ΠN	IN
Deposit Volume x 10 ⁻⁵ , cm ³			2.85	28.30		6.12	69.6		9.28	14.8

Table A4. Oxidation Stability and JFTOT Performance of the Biodiesel Fuels

Table A5. Primary and Secondary Oxidation Analysis of the Biodiesel Fuels

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B100 lested			soy			ellow Grease			soy	
Sample Identification		AL-27102-F	CL05-0372	CL05-0378	AL-27097-F	CL05-0373	CL05-0379	AL-27144-F	CL06-0147	CL06-0150
Property	Method	Initial Value	Final 260°C	Final 300°C	Initial Value	Final 260°C	Final 300°C	Initial Value	Final 260°C	Final 300°C
Peroxide Value, meq O ₂ /kg	D3703	۲×	8	9	245	207	1.07	23	51	32
Conjugated Dienes	ISO 3656									
E ^{1%} _{1cm} (232)		1.86	5.72	2.13	13.30	13.71	12.89	4.10	4.08	4.11
E ^{1%} (268)		0.20	1.20	0.37	2.58	2.95	3.18	1.59	1.75	1.90
Anisidine Value	EN ISO 6885	1.5	4.7	4.5	33.8	53.6	93.6	4.4	14.7	25.7
τοτοχ		<3.5	10.7	16.5	523.8	467.6	95.74	150.4	116.7	89.7
Polymer Content, %(mass)	BS EN ISO 16931	0.64	0.59	0.68	1.08	1.28	1.34	1.33	1.21	1.29
Ester Content, %(mass)	BS EN ISO 16931	99.36	99.41	99.32	98.92	98.72	98.66	98.67	98.79	98.71
TAN, mg KOH/g	D664	0.38	95.0	0.45	0.69	0.66	0.66	86.0	0.39	0.40
TBN, mg KOH/g	D2896	0.13	0.11	0.14	0.14	0.12	0.13	DN	ND	ND
JFTOT Results, average										
Run Temperature			260	300		260	300		260	300
Deposit Thickness, minimum, nm			2.17	5.88		3.49	4.94		ΔN	ND
Deposit Thickness, maximum, nm			150.58	704.74		394.55	479.45		ND	ND
Deposit Thickness, mean, nm			51.34	399.55		109.98	173.93		ΔN	ND
Deposit Volume x 10 ⁻⁵ , cm ³			2.85	28.30		6.12	9.69		9.28	14.80

Table A6. I	nitial Compositiona	II Analysis	of the Biod	liesel Fu	els Relatin	g to Oxida	ation Suse	ceptibility		
B100 Tested			Soy		×	ellow Grease			Soy	
Sample Identification		AL-27102-F	CL05-0372 C	CL05-0378	AL-27097-F	CL05-0373	CL05-0379	AL-27144-F	CL06-0147	CL06-0150
Property	Method	Initial Value	Final 260°C F	inal 300°C	Initial Value	Final 260°C	Final 300°C	Initial Value	Final 260°C	Final 300°C
FAME Analysis	Pr EN 14103									
Ester Content, %		104.92	105.19	104.44	102.57	102.13	101.59	105.33	ND	ΠN
Methyl Palmitate (16:0), %		10.39	10.41	10.50	13.29	13.45	13.40	11.54	ND	ΠN
Methyl Stearate (18:0), %		4.30	4.30	4.28	8.64	8.61	8.41	4.44	ND	ΔN
Methyl Oleate (18:1), %		23.10	23.13	23.09	45.76	45.61	45.95	24.23	DN	DN
Methyl Linoleate (18:2), %		51.70	51.70	51.67	22.69	22.65	22.54	51.31	ND	ND
Methyl Linolenate (18:3), %		7.78	7.79	7.78	1.71	1.70	1.71	6.51	ND	ND
OX (Oxidizability)		0.68	0.68	0.68	0.27	0.27	0.27	0.65	ND	ND
Allylic Position Equivalent (APE)	Calculated from FAME	165.16	165.24	165.08	140.32	139.92	140.40	164.10	ND	ND
Bis-Allylic Position Equivalent (BAPE)	Calculated from FAME	67.26	67.28	67.23	26.11	26.05	25.96	64.33	ND	ND

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Figure A1. Effect of D2274 on Total Acid Number: Original Results



Figure A2. Effect of D2274 on Polymer Content: Original Results



Figure A3. Repeatability of JFTOT Deposit Volume, 260°C: Original Results



Figure A4. Repeatability of JFTOT Deposit Volume, 300°C: Original Results



Figure A5. Effect of Temperature on JFTOT Deposit Volume: Original Results



Figure A6. Effect of JFTOT on Rancimat Induction Period: Original Results



Figure A7. Effect of JFTOT on ASTM D2274 Total Insolubles: Original Results



Figure A8. Effect of JFTOT on Total Acid Number: Original Results



Figure A9. Effect of JFTOT on Polymer Content: Original Results



Figure A10. Effect of JFTOT on Post D2274 Polymer Content: Original Results



Figure A11. Effect of JFTOT on Peroxide Value: Original Results



Figure A12. Effect of JFTOT on Anisidine Value: Original Results



Figure A13. Effect of JFTOT on Conjugated Dienes Content: Original Results

APPENDIX B RE-EVALUATION OF TEST FUELS

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Overview

The initial evaluation of soy B100 AL-27102-F and yellow grease AL-27097-F was completed by August 2005. Initial evaluation of the third B100, soy-based AL-27144-F, was completed in April 2006. As previously mentioned, the AVFL-2b Committee decided to expand the remaining experimental project plan steps 7–11 to include evaluation of two B100's instead of the originally planned one B100. The two B100's selected for the remainder of the project work were the two soy-based B100's, AL-27102-F and AL-27144-F. The two reasons for this selection were:

- 1. The yellow grease sample was very low in stability (Rancimat IP = 1.0 hr.) and may not be representative of yellow greases;
- 2. The two soy B100's taken together would represent a wide range of initial stability with AL-27102-F representing unusually high stability (Rancimat IP = 9.1 hr.), and AL-27144-F representing typical stability (Rancimat IP = 5.0).

By the time this decision was made, significant time had elapsed since both soy-based B100's had been initially evaluated. Accordingly, both of the soy B100's were re-evaluated during November 2006. Prior to this re-evaluation, the two B100's had been purged with N_2 , sealed, and stored in their original 55-gallon drums under outside ambient temperature. Therefore, the re-evaluation represented a 14-month ambient temperature aging for AL-27102-F and a 6-month ambient aging for AL-27144-F.

The re-evaluation data for the two soy B100's is provided at the end of this appendix in Table B7 and Figures B14–B27. In the figures, the re-evaluation data is referred to as "before aging" since the primary reason for the re-evaluation was to provide more accurate baseline data for comparison to the agitated and quiescent aging data that would be generated in the remaining experimental project plan steps. Also, comparing the initial evaluation data (Appendix A, Figures A1–A13) with the re-evaluation data (Figures B14–B27) provides useful information on the effect of months of ambient aging on stability and JFTOT deposition tendency. These comparison graphs are provided in Figures B28–B36.

Most of the observations pertaining to the original evaluation data that were documented in Appendix A remained valid in the re-evaluation data. However, some noteworthy changes were observed. They are discussed in the following three sections.

Initial Biodiesel Stability

Comparing the initial evaluation data (Figure A6) to the re-evaluation data (Figure B20), both B100's experienced some minor reduction in stability as measured by Rancimat induction period (Figure B28).

Comparing the initial evaluation data (Figure A7) to the re-evaluation data (Figure B21-A), AL-27144-F (the less stable B100) experienced a small increase in D2274 total insolubles while AL-27102-F did not significantly change (Figure B29).

Comparing the initial evaluation data (Figures A1–A2) to the re-evaluation data (Figures B14 and B16), both B100's experienced no increase in initial TAN (Figure B30) or initial polymer content (Figure B31).

Comparing the initial evaluation data to the re-evaluation data, the less stable B100 AL-27144-F significantly increased in the D2274 iso-octane insolubles (Figure B32). Since the initial evaluation of D2274 iso-octane insolubles for AL-27102-F was not considered reliable, no meaningful comparison can be made for that property.

Comparing the initial evaluation data to the re-evaluation data, Post-D2274 TAN, post-D2274 polymer content, and initial peroxide value all experienced significant increases for the less stable AL-27144-F (Figures B30, B31, and B33, respectively). No significant change in these properties was observed for the more stable AL-27102-F.

Comparing the initial evaluation data (Figure A12) to the re-evaluation data (Figure B26), both B100's experienced only small changes in initial anisidine value (Figure B34).

Comparing the initial evaluation data (Figure A13) to the re-evaluation data (Figure B27), AL-27102-F experienced no change in initial conjugated diene level; AL-27144-F experienced a small increase (Figure B35).

JFTOT Deposition Tendency

JFTOT deposit volume repeatability in the re-evaluation results continued to be good at both test temperatures (Figures B17–B18), just as it was in the initial evaluation results (Figures A3–A4). However, there was a somewhat larger repeatability gap between 300°C deposit volume values for the less stable AL-27144-F, compared to the earlier repeatability for that B100.

Comparing the initial evaluation data (Figure A5) to the re-evaluation data (Figure B19), the JFTOT deposit volume of both B100's increased significantly at 260°C (Figure B36). However, the less stable AL-27144-F increased more than the more stable AL-27102-F. The JFTOT deposit volume of the less stable AL-27144-F also increased significantly at 300°C. The JFTOT deposit volume at 300°C for the more stable AL-27102-F did not significantly change. It should be mentioned that although the 260°C JFTOT deposit volumes for both B100's experienced an overall significant increase during the time between the original and current tests, the slopes of the two B100 lines relative to each other did not significantly change. The slope of the more stable AL-27102-F was originally much higher compared to the slope of AL-27144-F. This feature was unchanged in the re-evaluation JFTOT results.

As already noted in the previous section 3.2.1, only minor changes in Rancimat IP and D2274 total insolubles were experienced by the two soy B100's during their storage between the original evaluation and re-evaluation. The significant increase in JFTOT deposit volume experienced by both B100's during that period may indicate that subtle decreases in B100 stability data may result in significant increases in the tendency to form deposits on hot metal surfaces under conditions similar to those experienced in the JFTOT. Although the less stable

AL-27144-F did experience substantial increases in post-D2274 TAN, post-D2274 polymer content, and initial peroxide value, the more stable AL-27102-F did not. Therefore, any attempt to link the increase in JFTOT deposits for AL-27144-F to those test parameter increases is not consistent with the observed behavior of AL-27102-F.

It is interesting to note that if the usually stable AL-27102-F was indeed treated with an antioxidant, and if the stabilizing effect of that antioxidant was severely reduced at the higher JFTOT test temperature of 300°C, then the pattern of change in JFTOT deposit volume shown in Figure B36 is what might be expected. Note that in Figures B19 and B36, some individual data points representing average deposit volumes are bracketed so as to display their highest and lowest replicate values. This is done to provide a visual indication of repeatability and is done only for those data points where repeatability is of sufficient magnitude to make such a display meaningful. This convention will be used in the remaining figures where trends in deposit volumes are graphically compared.

Effect of JFTOT Stressing on Biodiesel Stability

The initial evaluation data (Figure A6) showed that JFTOT stressing at 260°C and 300°C caused a minor but progressive decrease in Rancimat induction period for the more stable AL-27102-F, but no significant reduction in Rancimat induction period for the less stable AL-27144-F. The re-evaluation data (Figure B20) shows no significant effect of JFTOT stressing on Rancimat induction period for either B100.

The initial evaluation data for the two soy B100's (Figure A7) showed that JFTOT stressing at 260°C and 300°C caused no significant change in D2274 total insolubles. Re-evaluation data (Figure B21-A) shows no significant effect of JFTOT at either stress temperature on D2274 total insolubles for AL-27102-F. For the less stable AL-27144-F, JFTOT stressing at 260°C and 300°C caused a progressive decrease in D2274 total insolubles. Similarly, with respect to the effect of JFTOT stressing at 260°C and 300°C caused a 260°C and 300°C con D2274 iso-octane insolubles, the re-evaluation data show no significant effect for the more stable AL-27102-F. For the less stable AL-27144-F, JFTOT stressing at 260°C and 300°C caused a substantial decrease in iso-octane insolubles (Figure B21-B). This may indicate that as a B100's stability decreases, short term, high temperature stressing from a hot metal surface may remove insolubles and insoluble precursors. This may correspond to insolubles and insoluble precursors being a source of JFTOT deposits.

With respect to the effect of JFTOT stressing at 260°C and 300°C on TAN, both the initial evaluation data (Figure A8) and the re-evaluation data (Figure B22-A) show the same effect: no significant effect on either B100 (Figure B30). However, the post-D2274 TAN re-evaluation data (Figure B22-B) for the less stable AL-27144-F did show a significant increase compared to initial evaluation data (Figure B30).

With respect to the effect of JFTOT stressing at 260°C and 300°C on peroxide value, both the initial evaluation data (Figure A11) and the re-evaluation data (Figure B25) show the same effect: no significant effect on the more stable AL-27102-F and a progressive decrease for the less stable AL-27144-F.

With respect to the effect of JFTOT stressing at 260°C and 300°C on anisidine value, both the initial evaluation data (Figure A12) and the re-evaluation data (Figure B26) show the same effect: a small increase for the more stable AL-27102-F and a more pronounced increase for the less stable AL-27144-F. Note that this trend for AL-27144-F is consistent with the decrease in peroxide value, since aldehydes are one of the known immediate decomposition products of hydroperoxides.

With respect to the effect of JFTOT stressing at 260°C and 300°C on conjugated dienes, both the initial evaluation data (Figure A13) and the re-evaluation data (Figure B27) show the same effect: no significant effect on the less stable AL-27144-F and an modest increase just at 260°C stressing for the less stable AL-27144-F. However, this increase in conjugated dienes after 260°C JFTOT stressing is much less pronounced in the re-evaluation data compared to the initial evaluation data. Comparing this trend for AL-27144-F with the previously described on for peroxide value, the implication is that hydroperoxides are not the only source of conjugated dienes in B100's.

B100 Tested			Soy			Soy	
Sample Identification			AL-27102-F			AL-27144-F	
Property	Method	Initial Value	Final 260°C	Final 300°C	Initial Value	Final 260°C	Final 300°C
Oxidation Stability Index (OSI) @ 110°C, hr.	ISO 6886						
replicate 1		7.85	7.19	7.68	4.47	4.32	4.33
replicate 2		8.02	7.43	7.78	4.39	4.43	4.29
replicate 3							
number of replicates		2	2	2	2	2	2
average value		7.94	7.31	7.73	4.43	4.38	4.31
Oxidation Stability, mg/100 ml	Modified ASTM D2274						
adherent insolubles, replicate 1		0.1	0.1	0.1	0.1	ΠN	0.0
filterable insolubles, replicate 1		0.2	0.2	0.2	1.4	ΔN	0.8
total insolubles, replicate 1		0.3	0.3	0.3	1.5	ΔN	0.8
iso-octane insolubles, replicate 1		0.4	0.7	0.6	2.3	ΔN	0.7
modified total insolubles, replicate 1		0.7	1.0	6.0	3.8	ΔN	1.5
polymer content after D2274, replicate 1	BS EN ISO 16931	1.14	1.04	1.17	4.70	ΠN	4.22
Total Acid Number after D2274, replicate 1	D664	0.59	0.66	0.61	1.86	ND	1.41
adherent insolubles, replicate 2		0.0	0.0	0.1	0.1	0.1	0.0
filterable insolubles, replicate 2		0.2	0.2	0.1	2.1	1.3	0.6
total insolubles, replicate 2		0.2	0.2	0.2	2.2	1.4	0.0
iso-octane insolubles, replicate 2		0.7	0.6	0.7	5.0	0.0	0.8
modified total insolubles, replicate 2		0.0	0.8	0.0	7.2	2.3	1.4
polymer content after D2274, replicate 2	BS EN ISO 16931	1.07	1.16	1.05	5.50	5.25	4.01
Total Acid Number after D2274, replicate 2	D664	0.62	0.61	0.62	2.12	1.96	1.34
adherent insolubles, average		0.1	0.1	0.1	0.1	0.1	0.0
filterable insolubles, average		0.2	0.2	0.2	1.8	1.3	0.7
total insolubles, average		0.3	0.3	0.3	1.9	1.4	0.7
iso-octane insolubles, average		0.6	0.7	0.7	3.7	0.9	0.8
modified total insolubles, average		0.8	0.9	0.0	5.5	2.3	1.5
polymer content after D2274, average	BS EN ISO 16931	1.11	1.10	1.11	5.10	5.25	4.12
Total Acid Number after D2274, average	D664	0.61	0.64	0.62	1.99	1.96	1.38

Aging
Before
Fuels
B100
of the
Re-Evaluation
Table B7.

B100 Tested			Soy			Soy	
Sample Identification			AL-27102-F			AL-27144-F	
Property	Method	Initial Value	Final 260°C	Final 300°C	Initial Value	Final 260°C	Final 300°C
Initial Iso-Octane Insolubles, mg/100 ml		0.7	ΠN	ΝD	1.6	ND	ΠN
Peroxide Value, meq O ₂ /kg	D3703	5.6	11.2	7.6	135	112	64.4
Conjugated Dienes	ISO 3656						
E ^{1%} (232)		1.84	2.67	2.11	5.36	5.43	5.07
E ^{1%} (268)		0.26	0.45	0.45	1.53	1.85	2.27
Anisidine Value	EN ISO 6885	1.0	3.6	6.1	4.7	20.2	51.1
τοτοχ		12.2	26	21.3	274.7	244.2	179.9
Polymer Content, %(mass)	BS EN ISO 16931	0.67	0.66	0.69	1.13	1.25	1.44
TAN, mg KOH/g	D664	0.38	0.39	0.38	0.40	0.42	0.43
JFTOT Results							
Run Number 1							
Run Temperature			260	300		260	300
Deposit Volume x 10 ⁻⁵ , cm ³			13.8	27.8		32.2	29.7
Run Number 2							
Run Temperature			260	300		260	300
Deposit Volume x 10 ⁻⁵ , cm ³			14.0	30.0		26.7	29.6
Run Number 3							
Run Temperature			260	300		260	300
Deposit Volume x 10 ⁻⁵ , cm ³			13.9	31.4		25.3	27.8
Average of Runs 1 - 3							
Run Temperature			260	300		260	300
Denosit Volume x 10 ⁻⁵ cm ³			13.0	206		28 1	0 00

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Figure B14. Effect of D2274 on Total Acid Number: B100's Before Aging



Figure B15. Effect of D2274 on Iso-Octane Insolubles: B100's Before Aging


Figure B16. Effect of D2274 on Polymer Content: B100's Before Aging



Figure B17. Repeatability of JFTOT Deposit Volume, 260°C: B100's Before Aging



Figure B18. Repeatability of JFTOT Deposit Volume, 300°C: B100's Before Aging



Figure B19. Effect of Temperature on JFTOT Deposit Volume: B100's Before Aging



Figure B20. Effect of JFTOT on Rancimat Induction Period: B100's Before Aging



Figure B21-A. Effect of JFTOT on ASTM D2274 Total Insolubles: B100's Before Aging



Figure B21-B. Effect of JFTOT on ASTM D2274 Iso-Octane Insolubles: B100's Before Aging



Figure B22-A. Effect of JFTOT on Total Acid Number: B100's Before Aging



Figure B22-B. Effect of JFTOT on Post-D2274 Total Acid Number: B100's Before Aging



Figure B23. Effect of JFTOT on Polymer Content: B100's Before Aging



Figure B24. Effect of JFTOT on Post-D2274 Polymer Content: B100's Before Aging



Figure B25. Effect of JFTOT on Peroxide Value: B100's Before Aging



Figure B26. Effect of JFTOT on Anisidine Value: B100's Before Aging



Figure B27. Effect of JFTOT on Conjugated Dienes Content: B100's Before Aging



Figure B28. Rancimat Induction Period for B100's: Original Results vs. Results Before Aging



Figure B29. ASTM D2274 Total Insolubles for B100's: Original Results vs. Results Before Aging



Figure B30. Total Acid Number for B100's: Original Results vs. Results Before Aging



Figure B31. Initial and Post D2274 Polymer Content for B100's: Original Results vs. Results Before Aging



Figure B32. ASTM D2274 Iso-Octane Insolubles for B100's: Original Results vs. Results Before Aging



Figure B33. Peroxide Value for B100's: Original Results vs. Results Before Aging



Figure B34. Anisidine Value for B100's: Original Results vs. Results Before Aging







Figure B36. Effect of Temperature on JFTOT Deposit Volume for B100's: Original Results vs. Results Before Aging

APPENDIX C INITIAL EVALUATION OF B20 BLENDS

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Overview

Each of two soy B100's was blended with the ULSD to obtain B20 blends. The two B20 blends were given the sample designations CL06-0663 (containing AL-27102-F) and CL06-0664 (containing AL-27144-F). Those B20 blends were initially evaluated to provide baseline data for the aging steps that would subsequently be performed on them. This data is given in Table C8 and in Figures C37–C46. It is discussed in the following three sections.

Initial Blend Stability

The more stable B100 AL-27102-F provided the more stable B20, relative to the B20 made from the less stable B100 AL-27144-F. This superior B20 stability was evidenced in the initial values of Rancimat induction period (Figure C41), peroxide value (Figure C44), and anisidine value (Figure C45).

ASTM D2274 total insolubles for the two B20's were leveled to essentially the same low value of about 0.4-mg/100 ml (Figure C42) despite the fact that the corresponding B100's were significantly different (Figure B21-1).

Both B20's had comparable initial TAN values (Figure C37). This is similar to what was observed for the two B100's (Figure B30). Both B20's also had comparable TAN values after D2274 stressing (Figure C37). This is in contrast to the B100 data where the less stable AL-27144-F had a much higher post-D2274 TAN compared to AL-27102-F (Figure B30).

Overall, the stability of the two initial B20's appeared closer to each other than did the stability of the corresponding initial B100's. This is likely due to the diluting effect of the non-polar ULSD. Also, this partial leveling effect suggests that at least for these two B100's there was no interactive effect between ULSD and B100 that magnified the resulting blend instability. Since neither B100 used to make the B20's was highly unstable, it cannot be determined from this data if a B100 and ULSD will always blend non-interactively with respect to instability-related properties.

JFTOT Deposition Tendency

As with the B100 JFTOT results, repeatability for the deposit volume was good (Figures C38–C39).

The relative trend in JFTOT deposit volume for the two B20's (Figure C40) was identical to the trend previously observed for the corresponding B100's (Figure B19). At least for the two B100's of this project, the relative deposit-forming tendencies of B20 blends appeared to be determined by the relative deposit-forming tendencies of the B100's from which they were made.

Also, the overall magnitude of JFTOT deposit volume for the initial B20's (Figure C40) was similar to the JFTOT deposit volume for the corresponding B100's before aging (Figure B19).

This will be discussed further in Appendix E in the section on the JFTOT deposition tendency of aged B20's.

Effect of JFTOT Stressing on Blend Stability

For both B20's, JFTOT stressing at 260°C and 300°C had little or no significant effect on Rancimat IP (Figure C41), D2274 total insolubles (Figure C42), TAN (Figure C43), and peroxide value (Figure C44). For the less stable CL06-0664, the peroxide values of the initial B20 and the B20 after JFTOT stressing were much less than what was observed for the corresponding B100 AL-27144-F (Figure B25).

For both B20's, JFTOT stressing at 260 and 300°C caused a modest increase in anisidine value (Figure C45). These increases in anisidine value mirror the trends caused by the JFTOT stressing in the corresponding B100's (Figure B26).

For both B20's, JFTOT stressing at 260 and 300°C had minimal impact on conjugated dienes (Figure C46). This trend is not the same as observed in the corresponding B100's (Figures A13 and B27). However, the order of magnitude increase in overall conjugated diene adsorption at 232 cm⁻¹ for the B20's compared to the B100's indicates that the ULSD component is greatly increasing and most likely leveling this test result.

B20 Tested		20% AL-27	102-F; 80% Al	27242-F	20% AL-27	144-F; 80% Al	27242-F
Sample Identification			CL06-0663			CL06-0664	
Property	Method	Initial Value	Final 260°C	Final 300°C	Initial Value	Final 260°C	Final 300°C
Oxidation Stability Index (OSI) @ 110°C, hr.	ISO 6886						
replicate 1		13.27	11.46	11.30	7.82	7.98	7.54
replicate 2		12.87	12.55	12.02	7.66	8.28	7.76
average value		13.07	12.01	11.66	7.74	8.13	7.65
Oxidation Stability, mg/100 ml	Modified ASTM D2274						
adherent insolubles, replicate 1		0.3	0.3	0.1	0.0	0.1	0.1
filterable insolubles, replicate 1		0.2	0.2	0.2	0.4	0.2	0.1
total insolubles, replicate 1		0.5	0.5	0.3	0.4	0.3	0.2
Total Acid Number after D2274, replicate 1	D664	0.12	0.11	0.12	0.11	0.11	0.11
adherent insolubles, replicate 2		0.2	0.2	0.1	0.0	0.1	0.1
filterable insolubles, replicate 2		0.2	0.3	0.2	0.4	0.1	0.2
total insolubles, replicate 2		0.4	0.5	0.3	0.4	0.2	0.3
Total Acid Number after D2274, replicate 2	D664	0.12	0.11	0.11	0.11	0.11	0.09
adherent insolubles, average		0.3	0.3	0.1	0.0	0.1	0.1
filterable insolubles, average		0.2	0.3	0.2	0.4	0.2	0.2
total insolubles, average		0.5	0.5	0.3	0.4	0.3	0.3
Total Acid Number after D2274, average	D664	0.12	0.11	0.12	0.11	0.11	0.10
Peroxide Value, meq O ₂ /kg	D3703	3.60	6.39	7.99	18.40	23.58	18.78
Conjugated Dienes	ISO 3656						
E ^{1%} _{1cm} (232)		19.91	19.87	20.64	23.09	24.56	22.88
E ^{1%} (268)		7.68	7.71	7.91	8.51	9.17	8.54
Anisidine Value	EN ISO 6885	0.6	1.2	2.7	1.5	4.4	7.7
ΤΟΤΟΧ		7.8	13.98	18.68	38.3	51.56	45.26
TAN, mg KOH/g	D664	0.10	0.10	0.11	0.09	0.10	0.10
JFTOT Results							
Run Number 1							
Run Temperature			260	300		260	300
Deposit Volume x 10 ⁻⁵ , cm ³			14.1	28.5		28.8	30.3
Run Number 2							
Run Temperature			260	300		260	300
Deposit Volume x 10 ⁻⁵ , cm ³			14.2	28.0		31.2	29.9
Run Number 3							
Run Temperature			260	300		260	300
Deposit Volume x 10 ⁻⁵ , cm ³			14.3	29.0		28.5	29.2
Average of Runs 1 - 3							
Run Temperature			260	300		260	300
Deposit Volume x 10 ⁻⁵ , cm ³			14.2	28.5		29.5	29.8

Table C8. Evaluation of the B20 Fuels Before Aging



Figure C37. Effect of D2274 on Total Acid Number: B20's Before Aging



Figure C38. Repeatability of JFTOT Deposit Volume, 260°C: B20's Before Aging



Figure C39. Repeatability of JFTOT Deposit Volume, 300°C: B20's Before Aging



Figure C40. Effect of Temperature on JFTOT Deposit Volume: B20's Before Aging



Figure C41. Effect of JFTOT on Rancimat Induction Period: B20's Before Aging



Figure C42. Effect of JFTOT on ASTM D2274 Total Insolubles: B20's Before Aging



Figure C43. Effect of JFTOT on Total Acid Number: B20's Before Aging



Figure C44. Effect of JFTOT on Peroxide Value: B20's Before Aging



Figure C45. Effect of JFTOT on Anisidine Value: B20's Before Aging



Figure C46. Effect of JFTOT on Conjugated Dienes: B20's Before Aging

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Overview

As indicated in the experimental project plan provided in section 2.1, each of the two B100's was stressed by two procedures: quiescent aging and agitated aging. The stressed fuels were then evaluated by the ORP tests as described in section 2.4 of this report. Test results of the quiescent aged fuels are provided in Table D9; test results of the agitated aged fuels are provide in Table D10. Test results of the quiescent and agitated aged fuels are compared to the corresponding results before aging and presented in Figures D47–D79. The results of this data are discussed in the following three sections.

Aged B100 Stability

Agitated aging was much more oxidatively severe than quiescent aging. For both B100's, there was a progressive deterioration from the "before aging" to the "after quiescent aging" to the "after agitated aging" test results for Rancimat IP (Figures D47–D49), D2274 total insolubles (Figure D50), D2274 Iso-Octane Insolubles (Figure D51), initial TAN (Figure D52), TAN after D2274 (Figure D53), initial polymer content (Figure D54), polymer content after D2274 (Figure D55), peroxide value (Figure D56), anisidine value (Figure D57), and conjugated dienes (Figure D58). The data provided in these figures also consistently confirms the fact that AL-27144-F is much less stable than AL-27102-F.

For agitated aged AL-27102-F, Rancimat IP dropped to 1.44 hours, compared to 7.94 hours before aging. The agitated aged AL-27144-F Rancimat IP dropped to 0 hours compared to 4.43 hours before aging (Figure D47). The fact that AL-27144-F after agitated aging has no remaining oxidative stability reserve will be significant in subsequent discussions.

For both B100's the pattern of increase for D2274 total insolubles after quiescent and agitated aging (Figure D50) is similar to the pattern of increase for D2274 iso-octane insolubles (Figure D51). Both B100's showed a dramatic increase in D2274 total and iso-octane insolubles after agitated aging. However, for the less stable AL-27144-F, D2274 total insolubles actually decreased in the quiescent aged fuel compared to the B100 before aging. The reason for this cannot be determined with certainty, but may be due in part to the fact that stressed fuels were pre-filtered before being evaluated by D2274.

For both B100's, the pattern of increase for TAN in the quiescent and agitated aged samples (Figure D52) was identical to the pattern of increase experienced in the polymer content (Figure D54). Similarly, the pattern of increase for post-D2274 TAN in the quiescent and agitated aged samples (Figure D53) was essentially identical to the pattern of increase experienced in the post-D2274 polymer content (Figure D55). This similarity between trends in TAN and polymer content was observed in the non-aged B100's. A more complete discussion of this is provided in Appendix F on global trends.

For both B100's the pattern of increase for peroxide value in the quiescent and agitated aged samples (Figure D56) was very similar to the pattern of increase experienced in the anisidine values (Figure D57) and the conjugated diene content (Figure D58). This is noteworthy since

previous data has shown that a decrease in peroxide value has often been accompanied by an increase in anisidine value. However, one must remember that for the oxidation of any fatty oilbased fluid, hydroperoxides are an intermediate species, and any trend in the overall concentration of hydroperoxides is the sum of the rate of their formation and the rate of their decomposition (to aldehydes and other compounds). The relationship between the increase in peroxide value and the similar increase in anisidine value simply shows that as hydroperoxides are forming from the direct oxidation of polyunsaturated fatty acid olefin groups. As shown in the Task 1 literature review, as hydroperoxides form in B100's the typical methylene-interrupted polyunsaturation is shifted to a conjugated configuration, thereby contributing to an increase in conjugated dienes. Apparently, under the conditions of the quiescent and (especially) the agitated aging, the hydroperoxide formation rate is significantly greater than the decomposition rate, thereby causing a net increase in the peroxide value, anisidine value, and conjugated diene content.

JFTOT Deposition Tendency

Repeatability for the deposit volume of the aged B100's (Figures D59–D62) was not as good as the B100's before aging (Figures B17–B18) or B20's before aging (Figures C38–C39). The repeatability of the JFTOT deposit volume appeared to be slightly worse for the more severely agitated B100's compared to the quiescent aged samples. Also, the repeatability of the JFTOT deposit volume was generally worse for tests run at 260°C compared to 300°C, as shown in the JFTOT deposit profile graphs of Figures D63–D66. The reason for the erratic nature of the deposit data cannot be determined, but may be partially due to the increased level of oxidative deterioration of the stressed B100's. This will be further discussed in Appendix F on global trends. The somewhat inconsistent JFTOT deposit data makes further observations concerning relative performance between B100's somewhat uncertain. However, based on the average JFTOT deposit data available the remaining observations are nonetheless made.

Effect of JFTOT Stressing on Aged B100 Stability

JFTOT stressing had no significant effect on the Rancimat IP of any of the quiescent and aged B100's (Figure D67–D68).

JFTOT stressing had no significant effect on the D2274 total insolubles of the quiescent or agitated aged AL-27102-F (Figures D69–D70). For the quiescent aged AL-27144-F, D2274 total insolubles increased significantly after JFTOT stressing at 300°C (Figure D69). For the agitated aged AL-27144-F, a small but progressive decrease in D2274 total insolubles was observed after JFTOT stressing at 260°C and 300°C (Figure D70). Note that only AL-27144-F after agitated aging has no oxidative reserve left, as evidenced by its zero Rancimat IP. Under those conditions, the effect of JFTOT stressing on subsequent D2274 total insolubles may simply reflect a balance of insolubles formation and insolubles deposition that favored deposition.

JFTOT stressing had no significant effect on the D2274 iso-octane insolubles of either of the quiescent aged B100's (Figure D71). However, for the agitated aged AL-27144-F there was a quite significant progressive decrease in D2274 iso-octane insolubles after JFTOT stressing at

260°C and 300°C (Figure 72). This trend is similar, but of a much larger magnitude, to the previously noted trend for D2274 total insolubles for the same B100 (Figure D70). It is also similar to the trend observed for the iso-octane insolubles of the same B100 before aging (Table C7). Since the agitated aged AL-27144-F had a Rancimat IP of essentially zero, it would be expected to be sensitive to the short term, high temperature stress of the JFTOT. The dramatic decrease in D2274 iso-octane insolubles may reflect an insolubles precursor formation rate that is less than the rate by which those precursors are either deposited in the JFTOT tube or converted to insolubles that are deposited.

JFTOT stressing at 260°C and 300°C caused a progressive decrease in peroxide value for all the quiescent and agitated aged B100's (Figure D73–D74). This is very similar to the trends seen before for the B100's initially and before aging (Figures A11 and B25), and is likely due to thermal decomposition of hydroperoxides by the hot steel surface of the JFTOT heater tube.

JFTOT stressing had no significant effect on the initial iso-octane insolubles (iso-octane insolubles before D2274 stressing) for the agitated aged AL-27102-F (Figure D75). For agitated aged AL-27144-F, JFTOT stressing at 260°C more than doubled the initial iso-octane insolubles. When JFTOT stressing was at 300°C, initial iso-octane insolubles decreased to an intermediate level. This behavior may represent the balance between the formation and decomposition of iso-octane insolubles in the agitated aged AL-27144-F during the JFTOT stressing at 260°C and 300°C. The relationship between the initial iso-octane insolubles, D2274 iso-octane insolubles, and D2274 total insolubles is obviously complex and insufficient data is available to define it. Measurement of initial iso-octane insolubles was not possible for the quiescent aged B100 samples before JFTOT stressing due to insufficient sample quantity. Accordingly, trends for these fuels could not be plotted. However, the data that is available suggests that initial iso-octane insolubles were low and insensitive to JFTOT stressing.

JFTOT stressing at 260°C and 300°C caused a progressive increase in anisidine value for all the quiescent and agitated aged B100's (Figure D76–D77). This is very similar to the trends seen before for the B100's initially and before aging (Figures A12 and B26), and is likely linked to the opposite (decreasing) effect observed for peroxide value (Figures D73–D74). Note that for the much more severe effect of agitated aging (in contrast with the mild JFTOT stressing), it was previously observed that both peroxide value and anisidine value increased. These two apparently contrasting trends are harmonized in a further discussion provided in Appendix F on global trends.

JFTOT stressing at 260 and 300°C had no significant effect on conjugated dienes for either of the quiescent aged B100's (Figure D78). Neither did it have any significant effect on the agitated aged AL-27102-F (Figure D79). However, for the agitated AL-27144-F, JFTOT stressing at 260°C and 300°C had a progressive decreasing effect on conjugated dienes. This is also likely linked to the very large decreasing effect on peroxide value for the same B100 (Figure D74).

B100 Tested			Soy			Soy	
Sample Identification			AL-27102-F			AL-27144-F	
Property	Method	Initial Value	Final 260°C	Final 300°C	Initial Value	Final 260°C	Final 300°C
Oxidation Stability Index (OSI) @ 110°C, hr.	ISO 6886						
replicate 1		6.20	6.04	6.56	3.59	3.22	4.32
replicate 2		6.18	5.97	6.41	3.48	3.25	4.18
average value		6.19	6.01	6.49	3.54	3.24	4.25
Oxidation Stability, mg/100 ml	Modified ASTM D2274						
adherent insolubles		0.0	0.0	0.1	0'0	0.1	0.1
filterable insolubles		0.2	0.2	0.2	0.2	0.1	1.1
total insolubles		0.2	0.2	0.3	0.2	0.2	1.2
iso-octane insolubles		0.4	0.6	0.5	0.5	0.5	0.6
modified total insolubles		0.0	0.8	8.0	2.0	2.0	1.8
polymer content after D2274	BS EN ISO 16931	1.45	2.00	1.90	4.97	6.16	5.76
Total Acid Number after D2274	D664	0.89	1.07	10.1	2.08	2.46	2.24
Initial Iso-Octane Insolubles, mg/100 ml		ΔN	0.5	0.8	ΠN	6.0	0.0
Peroxide Value, meq O ₂ /kg	D3703	69.1	73.2	6'6£	181	175	104
Conjugated Dienes	ISO 3656						
E ^{1%} _{1cm} (232)		2.99	3.21	3.14	10.7	69`2	7.19
E ^{1%} _{1cm} (268)		0.37	0.54	0.84	62.1	2.18	2.88
Anisidine Value	EN ISO 6885	2.7	10.2	12.5	10.4	29.7	71.1
τοτοχ		140.9	156.6	92.3	384.4	379.7	279.1
Polymer Content, %(mass)	BS EN ISO 16931	0.70	0.77	68.0	1.38	1.53	1.79
TAN, mg KOH/g	D664	0.49	0.45	0.50	0.58	0.58	0.58
Run Number 1							
Run Temperature			260	300		260	300
Deposit Volume x 10 ⁻⁵ , cm ³			27.5	29.7		27.3	28.9
Run Number 2							
Run Temperature			260	300		260	300
Deposit Volume x 10 ⁻⁵ , cm ³			14.1	29.4		24.0	27.2
Average of Runs 1 - 2							
Run Temperature			260	300		260	300
Deposit Volume x 10 ⁻⁵ , cm ³			20.8	29.6	0.0	25.7	28.1

Table D9. Evaluation of the B100 Fuels after Quiescent Aging

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B100 Tested			Soy			Soy	
Sample Identification			AL-27102-F			AL-27144-F	
Property	Method	Initial Value	Final 260°C	Final 300°C	Initial Value	Final 260°C	Final 300°C
Oxidation Stability Index (OSI) @ 110°C, hr.	ISO 6886						
replicate 1		1.47	1.62	1.65	00.00	0.00	00.00
replicate 2		1.41	1.64	1.63	00.00	00.00	00.0
average value		1.44	1.63	1.64	00.0	0.00	00.0
Oxidation Stability, mg/100 ml	Modified ASTM D2274						
adherent insolubles		0.4	0.6	0.5	1.1	0.5	0.7
filterable insolubles		4.4	5.3	5.1	9.6	9.2	8.3
total insolubles		4.8	5.9	5.6	10.7	9.7	0.0
iso-octane insolubles		31.0	46.3	33.8	100.1	54.1	40.8
modified total insolubles		35.8	52.2	39.4	110.8	63.8	49.8
polymer content after D2274	BS EN ISO 16931	10.23	12.01	12.13	16.46	17.33	19.02
Total Acid Number after D2274	D664	3.59	4.46	4.11	5.53	5.50	4.68
Initial Iso-Octane Insolubles, mg/100 ml		1.2	1.5	1.5	5.2	13.4	9.1
Peroxide Value, meq O ₂ /kg	D3703	986	658	363	3094	2268	266
Conjugated Dienes	ISO 3656						
E ^{1%} _{1cm} (232)		14.38	15.80	11.44	54.42	39.04	33.31
E ^{1%} _{1cm} (268)		0.69	1.63	4.14	3.00	6.29	12.30
Anisidine Value	EN ISO 6885	17.3	111.6	250.2	114.7	350.2	780.8
ΤΟΤΟΧ		1993.3	1427.6	976.2	6302.7	4886.2	2774.8
Polymer Content, %(mass)	BS EN ISO 16931	0.91	1.49	2.52	3.71	5.20	9.85
TAN, mg KOH/g	D664	0.59	0.74	0.72	1.89	1.98	2.21
JFTOT Results							
Run Number 1							
Run Temperature			260	300		260	300
Deposit Volume x 10 ⁻⁵ , cm ³			28.9	ND		28.2	30.1
Run Number 2							
Run Temperature			260	300		260	300
Deposit Volume x 10 ⁻⁵ , cm ³			14.2	30.7		14.0	28.4
Average of Runs 1 - 2							
Run Temperature			260	300		260	300
Deposit Volume x 10 ⁻⁵ , cm ³			21.6	30.7	0.0	21.1	29.3

Table D10. Evaluation of the B100 Fuels after Agitated Aging

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Figure D47. Effect of Aging on B100 Rancimat Induction Period



Figure D48. Effect of Aging on B100 Post-260°C JFTOT Rancimat Induction Period



Figure D49. Effect of Aging on B100 Post-300°C JFTOT Rancimat Induction Period







Figure D51. Effect of Aging on B100 D2274 Iso-Octane Insolubles



Figure D52. Effect of Aging on B100 Initial Total Acid Number



Figure D53. Effect of Aging on B100 Post-D2274 Total Acid Number







Figure D55. Effect of Aging on B100 Post-D2274 Polymer Content







Figure D57. Effect of Aging on B100 Anisidine Value



Figure D58. Effect of Aging on B100 Conjugated Dienes Content



Figure D59. Repeatability of JFTOT Deposit Volume, 260°C: B100's After Quiescent Aging



Figure D60. Repeatability of JFTOT Deposit Volume, 300°C: B100's After Quiescent Aging



Figure D61. Repeatability of JFTOT Deposit Volume, 260°C: B100's After Agitated Aging



Figure D62. Repeatability of JFTOT Deposit Volume, 300°C: B100's After Agitated Aging


Figure D63. Effect of Aging on JFTOT Deposit Volume for AL-27102-F



Figure D64. Effect of Aging on JFTOT Deposit Volume for AL-27144-F



Figure D65. JFTOT Deposit Volume for Quiescent Aged B100's



Figure D66. JFTOT Deposit Volume for Agitated Aged B100's



Figure D67. Effect of JFTOT on Rancimat Induction Period of Quiescent Aged B100's



Figure D68. Effect of JFTOT on Rancimat Induction Period of Agitated Aged B100's



Figure D69. Effect of JFTOT on D2274 Total Insolubles of Quiescent Aged B100's



Figure D70. Effect of JFTOT on D2274 Total Insolubles of Agitated Aged B100's



Figure D71. Effect of JFTOT on D2274 Iso-Octane Insolubles of Quiescent Aged B100's



Figure D72. Effect of JFTOT on D2274 Iso-Octane Insolubles of Agitated Aged B100's



Figure D73. Effect of JFTOT on Peroxide Value of Quiescent Aged B100's



Figure D74. Effect of JFTOT on Peroxide Value of Agitated Aged B100's



Figure D75. Effect of JFTOT on Initial Iso-Octane Insolubles of Agitated Aged B100's



Figure D76. Effect of JFTOT on Anisidine Value of Quiescent Aged B100's



Figure D77. Effect of JFTOT on Anisidine Value of Agitated Aged B100's



Figure D78. Effect of JFTOT on Conjugated Dienes Content of Quiescent Aged B100's



Figure D79. Effect of JFTOT on Conjugated Dienes Content of Agitated Aged B100's

APPENDIX E EVALUATION OF B20 BLENDS AFTER AGING

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Overview

Each of the two B20 blends was stressed by the quiescent aging and agitated aging procedures. The stressed fuels were then evaluated by the ORP tests as described in section 2.4 of this report. Test results of the quiescent aged B20's are provided in Table E11; test results of the agitated aged fuels are provided in Table E12. Test results of the quiescent and agitated aged fuels are compared to the corresponding results before aging and presented in Figures E80–E106. The information revealed in this data is discussed in the following three sections.

Aged B20 Blend Stability

Overall, the effects of quiescent and agitated aging appear to be less for the B20 blends compared to what was observed for the corresponding B100's.

The progressive deterioration of stability-related test results observed for quiescent and agitated aged B100's was not as consistently observed for the aged B20's. This can be seen by comparing the aged B20 results for total insolubles (Figure E83), initial TAN (Figure E84), TAN after D2274 (Figure E85), and conjugated dienes (Figure E88) with the corresponding results for the aged B100's (Figures D50, D52, D53, and D58, respectively).

For both B20's, quiescent and agitated aging did not produce any significant change in total insolubles (Figure E83) or initial TAN (Figure E84) when compared to the non-aged B20's. This is in contrast to the corresponding data for the aged B100's which showed significant increases in both those properties (Figures D50 and D52), especially for the less stable AL-27144-F. TAN after D2274 did sharply increase for only the agitated aged CL06-0664 compared the non-aged value (Figure E85).

For both B20's, quiescent and agitated aging did produce a moderate and progressive reduction in Rancimat IP relative to the non-aged blends (Figures E80–E82). However, the amount of reduction in Rancimat IP in going from the non-aged to the agitated aged B20's is not as large as what was observed for the corresponding B100's (Figures D47–D49).

Similarly, both B20's when quiescent and agitated aged did produce a moderate and progressive increase in peroxide value relative to the non-aged blends (Figure E86). However, the actual values and the amount of increase in peroxide value in going from the non-aged to the agitated aged B20's was very small compared to what was observed for the corresponding B100's (Figure D56). This suggests that the ULSD component was not making a large contribution to the net formation of hydroperoxides for these two B20 blends under the conditions of quiescent and agitated aging. On the basis of the data it cannot be determined if the ULSD is interacting with biodiesel-originated hydroperoxides to promote their decomposition.

For both B20's, anisidine value increased after quiescent and agitated aging compared to the non-aged values. However, the less severe quiescent aging process produced the largest increase for both B20's (Figure E87). This suggests that for the two B20's the more severe agitated aging promoted hydroperoxide decomposition more than it promoted hydroperoxide formation. A more complete discussion of this is given in Appendix F on global trends.

JFTOT Deposition Tendency

Repeatability for the deposit volume of the aged B20's (Figures E89–E92) was roughly comparable to that of the aged B100's (Figures D59–D62). It was not as good as the B100's before aging (Figures B17–B18) or B20's before aging (Figures C38–C39). Like the aged B100's, the repeatability of the JFTOT deposit volume appeared to be somewhat worse for the more severely agitated B20's compared to the quiescent aged samples, as shown in the JFTOT deposit profile graphs of Figures E93–E96. As already mentioned in the case of the B100's after aging, the reason for the erratic nature of the deposit data cannot be determined, but may be partially due to the increased level of oxidative deterioration of the stressed B20's. This will be further discussed in the Appendix F on global trends. The somewhat inconsistent JFTOT deposit data makes further observations concerning relative performance between B20's uncertain.

Despite the poor repeatability of the data, the overall JFTOT deposit volumes for the aged B20's appear to be of similar magnitude to the JFTOT deposit volumes of the corresponding aged B100's. This is exactly what was previously observed when comparing the JFTOT deposit volumes for the non-aged B100's with the non-aged B20's. This is noteworthy, since the B20's have only 20% the amount of oxidatively unstable material. Since the JFTOT deposit tendency of the ULSD was not determined, the exact cause of this is not discernable. However, additional comments will be provided in section 3.6 on Global Trends.

Effect of JFTOT Stressing on Aged B20 Blend Stability

JFTOT stressing at both temperatures had the same effect on the Rancimat IP of the quiescent and agitated aged B100's: JFTOT stressing at 260°C caused a small reduction in Rancimat IP compared to the initial aged B20; JFTOT stressing at 300°C caused the Rancimat IP to either remain unchanged or slightly increase compared to the initial aged B20 (Figure E97–E98). This pattern was not observed for the non-aged B20's (Figure C41). There is not enough information to determine the cause of this minor but apparently real effect.

For both quiescent aged B20's, D2274 total insolubles were very low, and JFTOT stressing did not cause a significant change (Figure E99). Likewise, for the agitated aged CL06-0663 there was not significant effect on D2274 total insolubles. However, for CL06-0664 there was a significant increase in D2274 total insolubles for the 260°C stressed sample (Figure E100).

JFTOT stressing at 300°C caused a decrease in peroxide value for all the quiescent and agitated aged B20's compared to the initial aged B20's (Figure E101–E102). JFTOT stressing at 260°C caused a small increase in peroxide value for all aged fuels except for the agitated aged CL06-0664, where a decrease was observed (Figure E102). Apparently, for the 300°C JFTOT stressing, the overall effect on the aged B20's is to provide a net decomposition of hydroperoxides, just as was observed for the aged B100's (Figures D73–D74). At the lower 260°C JFTOT stressing, the amount of hydroperoxides formed in most cases was greater than or equal to the amount that was decomposed, resulting in either no significant change or a net increase. The difference in this pattern cannot be determined with certainty, but may be partially due to the effect of the JFTOT stressing on the ULSD component.

JFTOT stressing at 260°C and 300°C caused a progressive increase in anisidine value for all the quiescent and agitated aged B20's (Figure E103–E104). This is very similar to the trends seen before for the non-aged B20's (Figure C45), the non-aged B100's (Figure B26), and the aged B100's (Figures D76–D77). These trends will be further discussed in Appendix F on global trends.

JFTOT stressing at 260 and 300°C had no significant effect on the conjugated diene content of any of the quiescent or agitated aged B20's (Figure E105–E106). This is the same effect observed for the B20's before aging (Figure C46) and the B100's before aging (Figure B27). It is also similar to the effect observed on the quiescent aged B100's (Figure D78). However, it is not the same as the decreasing trend observed for the JFTOT stressing of the agitated aged B100's (Figure D79).

B20 Tested		20% AL-27	102-F: 80% AI	-27242-F	20% AL-27	7144-F: 80% AI	-27242-F
Sample Identification			CL06-0663			CL06-0664	
Property	Method	Initial Value	Final 260°C	Final 300°C	Initial Value	Final 260°C	Final 300°C
Oxidation Stability Index (OSI) @ 110°C, hr.	ISO 6886						
replicate 1		8.23	7.07	9.01	6.15	5.65	7.23
replicate 2		9.20	6.81	9.67	6.03	5.27	7.03
average value		8.72	6.94	9.34	60.9	5.46	7.13
Oxidation Stability, mg/100 ml	Modified ASTM D2274						
adherent insolubles		0.0	0.1	0.1	0.0	0.0	0.1
filterable insolubles		0.2	0.1	0.0	0.1	0.1	0.1
total insolubles		0.2	0.2	0.1	0.1	0.1	0.2
Total Acid Number after D2274	D664	0.19	0.19	0.15	0.14	0.22	0.16
Peroxide Value, meq O ₂ /kg	D3703	23.5	61.0	40.7	12	72.7	45.1
Conjugated Dienes	ISO 3656						
E ^{1%} (232)		18.76	19.80	20.36	24.77	23.54	22.89
E ^{1%} (268)		7.21	7.72	80.8	91.0	8.86	8.86
Anisidine Value	EN ISO 6885	1.9	7.1	17.8	3.2	9.3	22.5
τοτοχ		108.9	129.1	99.2	144.2	154.7	112.7
TAN, mg KOH/g	D664	0.13	0.13	0.14	0.13	0.13	0.14
JFTOT Results							
Run Number 1							
Run Temperature			260	300		260	300
Deposit Volume x 10 ⁻⁵ , cm ³			28.4	31.5		35.4	28.3
Run Number 2							
Run Temperature			260	300		260	300
Deposit Volume x 10 ⁻⁵ , cm ³			28.9	29.4		29.0	30.1
Average of Runs 1 - 2							
Run Temperature			260	300		260	300
Deposit Volume x 10 ⁻⁵ , cm ³			28.7	30.5	0.0	32.2	29.2

Table E11. Evaluation of the B20 Fuels After Quiescent Aging

B20 Tested		20% AL-27	'102-F; 80% AI	27242-F	20% AL-2	7144-F; 80% AI	L-27242-F
Sample Identification			CL06-0663			CL06-0664	
Property	Method	Initial Value	Final 260°C	Final 300°C	Initial Value	Final 260°C	Final 300°C
Oxidation Stability Index (OSI) @ 110°C, hr.	ISO 6886						
replicate 1		8.20	7.40	8.26	4.20	3.77	11.4
replicate 2		8.20	7.20	8.43	4.17	3.72	4.71
average value		8.20	7.30	8.35	4.19	3.75	4.41
Oxidation Stability, mg/100 ml	Modified ASTM D2274						
adherent insolubles		0.0	0.0	0.0	0.1	0.4	0.0
filterable insolubles		0.2	0.2	0.1	0.3	1.0	0.4
total insolubles		0.2	0.2	0.1	0.4	1.4	0.4
Total Acid Number after D2274	D664	0.15	0.15	0.14	0.81	1.52	0.92
Peroxide Value, meq O ₂ /kg	D3703	52.0	55.9	38.0	102	91.2	63.2
Conjugated Dienes	ISO 3656						
E ^{1%} _{1cm} (232)		21.08	19.26	19.13	21.98	23.29	22.47
E ^{1%} _{1cm} (268)		8.19	7.59	69'.	8.01	8.81	8.84
Anisidine Value	EN ISO 6885	1.3	6.8	14.8	2.9	11.5	28.1
τοτοχ		105.3	118.6	8.06	206.9	193.9	154.5
TAN, mg KOH/g	D664	0.11	0.12	0.13	0.12	0.13	0.14
JFTOT Results							
Run Number 1							
Run Temperature			260	300		260	300
Deposit Volume x 10 ⁻⁵ , cm ³			27.8	31.6		31.1	27.9
Run Number 2							
Run Temperature			260	300		260	300
Deposit Volume x 10 ⁻⁵ , cm ³			14.3	15.1		29.8	34.0
Average of Runs 1 - 2							
Run Temperature			260	300		260	300
Deposit Volume x 10 ⁻⁵ , cm ³			21.1	23.4		30.5	31.0

Table E12. Evaluation of the B20 Fuels After Agitated Aging



Figure E80. Effect of Aging on B20 Rancimat Induction Period







Figure E82. Effect of Aging on B20 Post-300°C JFTOT Rancimat Induction Period







Figure E84. Effect of Aging on B20 Initial Total Acid Number



Figure E85. Effect of Aging on B20 Post-D2274 Total Acid Number



Figure E86. Effect of Aging on B20 Peroxide Value







Figure E88. Effect of Aging on B20 Conjugated Dienes Content



Figure E89. Repeatability of JFTOT Deposit Volume, 260°C: B20's After Quiescent Aging



Figure E90. Repeatability of JFTOT Deposit Volume, 300°C: B20's After Quiescent Aging



Figure E91. Repeatability of JFTOT Deposit Volume, 260°C: B20's After Agitated Aging



Figure E92. Repeatability of JFTOT Deposit Volume, 300°C: B20's After Agitated Aging



Figure E93. Effect of Aging on JFTOT Deposit Volume for CL06-0663



Figure E94. Effect of Aging on JFTOT Deposit Volume for CL06-0664



Figure E95. JFTOT Deposit Volume for Quiescent Aged B20's



Figure E96. JFTOT Deposit Volume for Agitated Aged B20's



Figure E97. Effect of JFTOT on Rancimat Induction Period of Quiescent Aged B20's



Figure E98. Effect of JFTOT on Rancimat Induction Period of Agitated Aged B20's



Figure E99. Effect of JFTOT on D2274 Total Insolubles of Quiescent Aged B20's



Figure E100. Effect of JFTOT on D2274 Total Insolubles of Agitated Aged B20's



Figure E101. Effect of JFTOT on Peroxide Value of Quiescent Aged B20's



Figure E102. Effect of JFTOT on Peroxide Value of Agitated Aged B20's



Figure E103. Effect of JFTOT on Anisidine Value of Quiescent Aged B20's



Figure E104. Effect of JFTOT on Anisidine Value of Agitated Aged B20's







Figure E106. Effect of JFTOT on Conjugated Dienes Content of Agitated Aged B20's

APPENDIX F GLOBAL TRENDS

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Overview

Further analysis of the previously discussed results provides insight into trends that span all or significant parts of the data. These trends accordingly shed light on the chemistry of biodiesel oxidation as it applies to the relationships between various stability indicators (ORP test results) and deposition tendency (JFTOT results). In order to accomplish this, ORP test data spanning the initial (Table A3), before aging (Table B7), quiescent aged (Table D9), and agitated aged (Table D10) B100 test results were plotted in Figures F107–F121. Similarly, all before aging (Table C8), quiescent aged (Table E11), and agitated aged (Table E12) B20 test results were plotted in Figures E122–E131. Figures E132–E135 provide additional insight into the overall trends found in the JFTOT deposition tendency of the B100's and B20's. This information is discussed in the following three sections.

Trends Concerning Stability-Related Test Results for B100

A general relationship was observed between the Rancimat IP and D2274 total insolubles for B100's, as indicated in Figure F107. For both B100's whether evaluated initially, just prior to aging, or after the two aging processes, a relationship somewhat similar to an exponential decay pattern is observed in the data. For B100's with Rancimat IP values less than 2 hours, D2274 total insolubles are very high. As the Rancimat IP increases, the D2274 total insoluble level rapidly decreases. When the Rancimat IP approaches 6 hours, the D2274 total insoluble level has essentially reached its low asymptotic value. Although a simple exponential function as available by Excel software only provides an R² value of 0.6707, a more involved exponential equation would certainly yield a better fit. A simple quadratic fit of the Figure F107 data provides an excellent R² value of 0.9439. However, this is an intrinsically flawed approach since the resulting curve increases parabolically just at the high end of the plotted Rancimat values, a trend that should not happen in real B100 samples.

It is interesting to note that the data from the both B100's appear to mesh together to form one unified trend despite the fact that the initial stabilities of these fuels were quite different from each other. Also, as already discussed, the more stable AL-27102-F shows consistent signs of containing a significant dose of a synthetic antioxidant, while the less stable AL-27144-F does not. If this is indeed the case, then the way that the data from these two B100's fit together is even more remarkable. If AL-27102-F does not contain an antioxidant, but instead has extremely atypical initial stability for some unknown reason not suggested by the overall data and the prior stability literature, then the result is still the same: the apparent unifying trend in Figure 62 is noteworthy. However, this trend spans only two fuels. It remains to be seen whether a much larger group of B100's similarly evaluated would have conformed to the plot provided in Figure F107.

The general features of the exponential decay curve observed in Figure F107 were repeated when other stability indicators were plotted as a function of Rancimat IP. These include TAN (Figure F108), TAN increase after D2274—hereafter referred to as delta TAN—(Figure F109), initial polymer content (Figure F110), increase in polymer content after D2274—hereafter referred to as delta polymer—(Figure F111), peroxide value (Figure F112), anisidine value (Figure F113), TOTOX (Figure (F114), and conjugated diene content (Figure F115). The rate of decrease with

increasing Rancimat IP varied depending on which stability indicator was plotted. For instance, TAN and initial polymer content dropped very rapidly and leveled off quickly as Rancimat IP increased from zero (Figures F108 and F110, respectively). However, delta TAN and delta polymer dropped off much more gradually (nearly linearly) before leveling off (Figure F109 and F111, respectively). These figures show that as the oxidation stability reserve as indicated by Rancimat IP decreases, other stability indicators tend to increase. The point at which a given stability indicator will increase and the rate by which that increase occurs will depend on which stability indicator is considered.

Delta TAN and delta polymer appear to be an advanced indicator of the onset of gross instability. Delta TAN began to increase when Rancimat IP was reduced to about 6 hours (Figure F109); delta polymer showed exactly the same behavior (Figure F111). In contrast, other stability indicators such as TAN, polymer content, initial peroxide value, anisidine value, and conjugated dienes did not begin to increase until Rancimat IP dropped to about 2 hours. D2274 total insolubles began to increase as Rancimat IP decreased from 6 hours to 4 hours. This behavior is consistent with the previously observed effect of agitated aging (D2274 stressing) on Rancimat IP for the two B100's (Figure D47): for the more stable AL-27102-F Rancimat IP dropped by more than 6 hours after agitated aging; for the less stable B100 AL-27144-F Rancimat IP dropped by more than 4 hours, resulting in a final Rancimat IP of zero after agitated aging. Therefore, the effect of D2274 stressing was to dramatically reduce the oxidative stability reserve. This was reflected in delta TAN and delta polymer increasing more rapidly as Rancimat IP decreased compared to TAN and polymer content.

The most striking correlation of stability indicator data is the relationship between polymer content and TAN (Figure F116-A). This linear plot provides an R² value of 0.9500. This is consistent with what has been reported in previous work, as documented in the Task 1 literature survey. The linear relationship between polymer content and TAN shows that the polymeric materials formed as B100 oxidizes are either the primary source of TAN increase, or else the acidic materials are tightly linked byproducts of the same process that forms the polymeric material. This result, combined with the information outlined in the previous item 3, suggest that initial TAN combined with delta TAN may be an excellent indicator of B100 stability, perhaps more reliable than D2274 total insolubles. Certainly, TAN and delta TAN are much easier to obtain since all filtrations and gravimetry are avoided. Unfortunately, previously reported work where D2274 testing was done has almost always not included TAN after D2274, despite the extreme ease by which this additional determination could be obtained.

The relationship between iso-octane insolubles content and TAN is given in Figure F116-B. Both initial iso-octane insolubles data and D2274 iso-octane insolubles data are plotted against their corresponding TAN values for all B100's for which that data is available. This figure is the exact analog to Figure F116-A. As can be seen, the linear correlation for TAN vs. iso-octane insolubles ($R^2 = 0.7734$) is significantly less defined than that previously noted for TAN vs. polymer content ($R^2 = 0.9500$). This difference points to a very significant fact. Iso-octane insolubles, either in the initial B100 or in the D2274-stressed B100, are an indicator of total insoluble precursors. That is, higher molecular weight material, although still soluble in the B100, may precipitate out when the B100 is blended with a non-polar fluid such as an ULSD. The polymer content is a measure of the actual compounds that have a molecular size (and molecular weight)

much greater than the fatty acid methyl esters. Actual polymer test results show what appear to be dimers and trimers of the methyl esters. Because of the nature of the chromatographic polymer test procedure (see section 2.4), all polymeric material will be indicated in the test result. However, it is routinely observed that when B100 samples with high iso-octane insolubles are diluted with the iso-octane, and when the resulting turbid solution is filtered, the turbidity of the filtrate is never significantly reduced. This implies that much of the precipitated material formed during the iso-octane insolubles test is not caught by the 0.8 micron filter used in the test. It has already been observed that TAN is a reliable indicator of the formation of polymeric material during B100 oxidation. Therefore, Figures F116-A and F116-B show that TAN and delta TAN (or polymer content and delta polymer content) may be potentially superior stability indicators compared to initial iso-octane insolubles and D2274 iso-octane insolubles.

A general display of all anisidine values as a function of peroxide value is provided in Figure F117. At first glance, no apparent correlation is visible. However, separating the data according to individual B100 both before and after aging provides illuminating insight into the mechanism of biodiesel oxidation. Figure F118 shows just the values of anisidine value vs. peroxide value for the more stable AL-27102-F. The data points represent the initial evaluation done as is, after JFTOT stressing at 260°C, and after JFTOT stressing at 300°C. Also represented in this plot are the same B100 similarly evaluated after 14 months of outside ambient aging just prior to the quiescent and agitated aging processes. As with the general plot of all data points, there does not appear to be any correlation. However, when the anisidine value vs. peroxide value is plotted for the quiescent and agitated aged AL-27102-F, a decreasing linear correlation is observed for the agitated aged samples (Figure F119). When the values before aging and after aging are plotted for the less stable AL-27144-F, similar decreasing linear correlations are observed for all fuels (Figures F120 and F121).

Each of the linear sets of three points represents the corresponding B100 just before JFTOT stressing, after JFTOT stressing at 260°C, and after JFTOT stressing at 300°C. As already discussed previously, the less stable AL-27144-F gave progressively decreasing peroxide values as it was JFTOT stressed at 260°C and 300°C. As this occurred, anisidine values correspondingly increased. This was observed in the AL-27144-F before aging, after quiescent aging, and after agitated aging. This trend is the result of the well-known fact that the first product of biodiesel oxidation is hydroperoxides (as measured by peroxide value). One of the primary compounds formed by the decomposition of hydroperoxides are aldehydes (as measured by anisidine value). Therefore, as AL-27144-F is progressively stressed in the JFTOT at 260 and 300°C, some of the hydroperoxides already present are thermally decomposed into primary products, including aldehydes. This occurs for the non-aged AL-27144-F (Figure F120) as well as the same B100 after quiescent and agitated aging (Figure F121).

For the more stable AL-27102 the relationship between anisidine value and peroxide value is more complex. The very low level of initial hydroperoxides in the initial and before aging AL-27102-F provides almost no baseline from which to form primary hydroperoxide decomposition products. Only after the very severe agitated aging is the oxidative reserve of AL-27102-F reduced to the point where significant levels of hydroperoxides have been formed. This provides the baseline needed for the relatively mild short duration thermal stressing of the JFTOT that results in decomposition of some of those hydroperoxides and the formation of aldehydes.

When looking at a given B100 or B20 just before aging, after quiescent aging, and after agitated aging, a general trend of decreasing peroxide value and increasing anisidine value is not observed. This is because the prolonged aging, especially the agitated aging is very severe compared to the mild JFTOT stressing. Hydroperoxides are both formed and decomposed. The decomposition products of the hydroperoxides have sufficient time to further react, thereby partially depleting them even as they are formed. Therefore, it is not surprising that a universal single trend between peroxide value and anisidine value is not observed among B100's or B20's as they are quiescent aged and agitated aged.

Trends Concerning Stability-Related Test Results for B20 Blends

The general relationship observed between the Rancimat IP and D2274 total insolubles for B100's was not observed for the B20's (Figure F122). This was due to the leveling effect that blending B100 with ULSD apparently has on ASTM D2274 total insolubles. All values except one had D2274 total insolubles of 0.5 mg/100 ml or less regardless of observed Rancimat IP range of 13.07 hours to 3.75 hours.

When other B20 stability indicators were plotted as a function of Rancimat IP results were varied. TAN values only ranged from 0.09 to 0.14 mg KOH/g regardless of Rancimat IP (Figure F123). The delta TAN vs. Rancimat IP plot (Figure F124) was the only B20 relationship between stability indicators that showed a exponential curve similar to what was observed for most of the B100 data. However, only the three points with Rancimat IP values below 5 hours had dramatically increasing delta TAN values. These three data points represent the CL06-0664 (made from the less stable AL-27144-F) after agitated aging, i.e, the least stable B20 blend after the most severe oxidative stress.

The plot of peroxide value vs. Rancimat IP was roughly linear with an R2 value of 0.7556 (Figure F125). Although the plot of anisidine value vs. Rancimat IP showed no discernable trend (Figure F126), the plot of TOTOX (a weighted linear sum of peroxide value and anisidine value) gave a linear trend with an R2 value of 0.7893 (Figure F127). This simply showed that the effect of the somewhat linear relationship between Peroxide Value and Rancimat IP predominated when the TOTOX sum values were plotted against Rancimat IP.

Conjugated diene content vs. Rancimat IP gave a roughly linear relationship, but with very little sensitivity, since the range of conjugated diene adsorption levels ranged from 18.76 to 24.77 cm⁻¹ (Figure F128).

The interesting relationships observed between anisidine value and peroxide value in the B100's were not observed for the B20's (Figures F129–F131).

Overall, the B20 data indicated that the differentiation observed between the two B100's was eliminated or minimized for the B20's in all but the most severe oxidative environments.
Trends Concerning JFTOT Deposition Tendency

The overall repeatability of the JFTOT deposit data for both B100's became worse as the fuels were progressively aged as shown in Figures F132–F133. Also, repeatability was worse for the quiescent aged B100's compared to the agitated aged B100's. Comparing the two B100's with each other, neither appeared to be clearly superior to the other in terms of deposit volume repeatability.

Deposit volumes for both fuels as they were aged appear to top out at about 30×10^{-5} cm³. As already mentioned, this amount of deposit is very large compared to what is typically observed when testing jet fuels (using aluminum instead of steel JFTOT heater tubes).

As already discussed in Appendix D, the deposit volumes of the two B100's appear to converge as they are more severely stressed (comparing Figures F132 and F133). Also, the deposit volumes of the two B100's may be more similar to each other when tested at 300°C compared to 260°C.

The previous observations are consistent with the idea that biodiesel deposit formation can reach a maximum level beyond which discrimination between fuels of significantly differing stability is lost. This loss of discrimination apparently occurs when the B100's are increasingly aged with concomitant reduction in stability. For sufficiently unstable B100's, discrimination can also be lost or reduced when the JFTOT stressing occurs at 300°C compared to 260°C. Mechanistically, this loss of discrimination may be due to the heater tube metal surface being so deeply covered that deposit precursors within the adjacent fuel layer are unable to be affected by the metal surface. Also, a thermal insulating effect may reduce further deposits after a certain deposit thickness is achieved. In effect, the available JFTOT heater tube surface apparently becomes saturated with deposits to the point that test sensitivity is lost. In retrospect, running the JFTOT test with a smaller sample volume might have reduced the overall deposit volumes and increased discrimination between fuels of differing stability.

The overall repeatability of the JFTOT deposit data for both B20's is similar to that of the B100's in that repeatability became worse as the fuels were aged. However, unlike the B100's, overall deposit volume repeatability for the B20's did not appear to greatly differ when comparing results measured at 260°C and 300°C.

As already discussed, the JFTOT deposit volumes for the B20's (non-aged and aged) were of a similar magnitude to the JFTOT deposit volumes for the B100's (non-aged and aged). This behavior is consistent with the idea that deposit formation is topping out due to the extremely unstable nature of biodiesel fuel relative to more conventional fuels that are evaluated on the JFTOT (i.e., jet fuels).

Since the effect of the ULSD on JFTOT deposit volume was not determined, it is difficult to completely interpret the B20 deposit data in relation to the corresponding B100 data. However, any improvements to the JFTOT test procedure that increases the discriminating power for B100's will likely also be beneficial to biodiesel blends.



Figure F107. Correlation of B100 D2274 Total Insolubles vs. Rancimat IP



Figure F108. Correlation of B100 Initial Total Acid Number vs. Rancimat IP



Figure F109. Correlation of Increase in Total Acid Number After D2274 vs. Rancimat IP



Figure F110. Correlation of B100 Initial Polymer Content vs. Rancimat IP



Figure F111. Correlation of B100 Increase in Polymer Content After D2274 vs. Rancimat IP



Figure F112. Correlation of B100 Initial Peroxide Value vs. Rancimat IP



Figure F113. Correlation of B100 Anisidine Value vs. Rancimat IP



Figure F114. Correlation of B100 TOTOX vs. Rancimat IP



Figure F115. Correlation of B100 Conjugated Diene Content vs. Rancimat IP



Figure F116-A. Correlation of B100 Total Acid Number vs. Polymer Content



Figure F116-B. Correlation of B100 Total Acid Number vs. Iso-Octane Insolubles



Figure F117. Correlation of B100 Anisidine Value vs. Peroxide Value: All Data



Figure F118. Correlation of B100 Anisidine Value vs. Peroxide Value: AL-27102-F Before Aging



Figure F119. Correlation of B100 Anisidine Value vs. Peroxide Value: AL-27102-F After Aging



Figure F120. Correlation of B100 Anisidine Value vs. Peroxide Value: AL-27144-F Before Aging



Figure F121. Correlation of B100 Anisidine Value vs. Peroxide Value: AL-27144-F After Aging



Figure F122. Correlation of B20 D2274 Total Insolubles vs. Rancimat IP



Figure F123. Correlation of B20 Initial Total Acid Number vs. Rancimat IP



Figure F124. Correlation of B20 Increase in TAN after D2274 vs. Rancimat IP



Figure F125. Correlation of B20 Initial Peroxide Value vs. Rancimat IP



Figure F126. Correlation of B20 Anisidine Value vs. Rancimat IP



Figure F127. Correlation of B20 TOTOX vs. Rancimat IP



Figure F128. Correlation of B20 Conjugated Diene Content vs. Rancimat IP



Figure F129. Correlation of B20 Anisidine Value vs. Peroxide Value: Before Aging



Figure F130. Correlation of B20 Anisidine Value vs. Peroxide Value: CL-06-0663 After Aging



Figure F131. Correlation of B20 Anisidine Value vs. Peroxide Value: CL-06-0662 After Aging



Figure F132. Effect of Progressive Aging on JFTOT Deposit Volume: AL-27102-F



Figure F133. Effect of Progressive Aging on JFTOT Deposit Volume: AL-27144-F



Figure F134. Effect of Progressive Aging on JFTOT Deposit Volume: CL-06-0663



Figure F135. Effect of Progressive Aging on JFTOT Deposit Volume: CL-06-0664