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An Evaluation and Comparison of Test Methods to Measure the Oxidation Stability of Neat Biodiesel

September 2003 — May 2005

S.R. Westbrook
Southwest Research Institute
San Antonio, Texas

Subcontract Report
NREL/SR-540-38983
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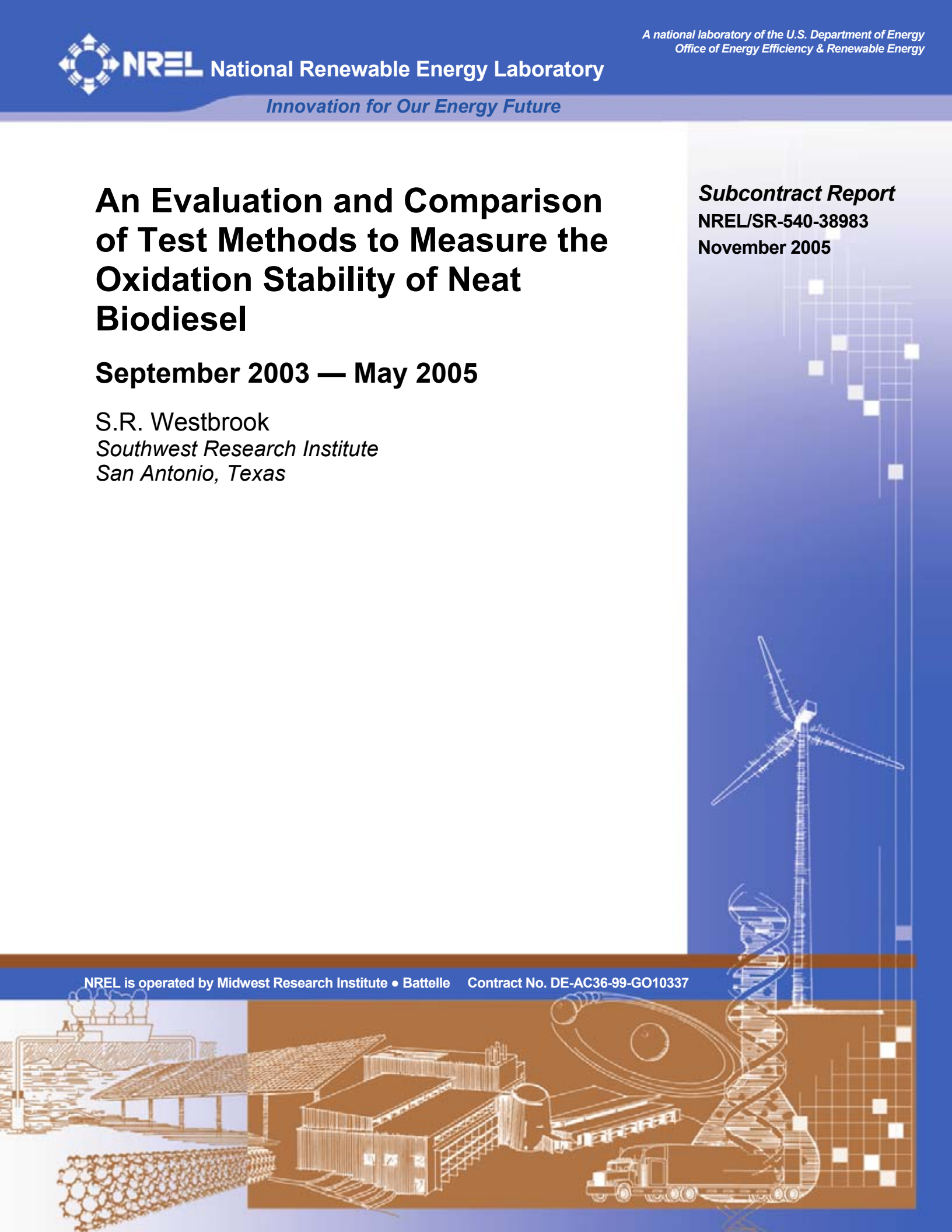

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NREL Technical Monitor: R. McCormick

Prepared under Subcontract No. ACE-3-33075-01

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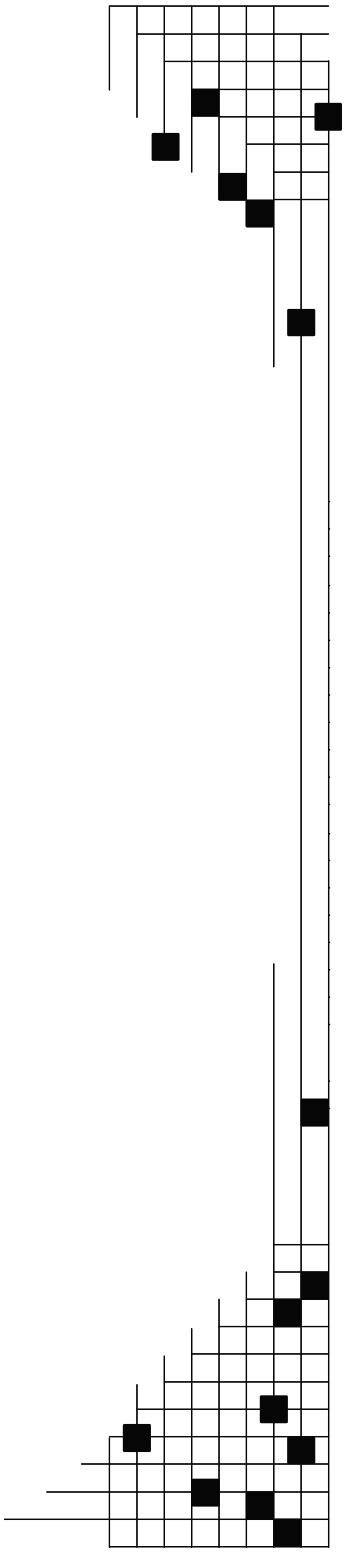

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Executive Summary

Oxidation stability is one of the most important properties of fatty-acid methyl esters (biodiesel) used as a blend stock with petroleum diesel to make biodiesel blends. Even so, at the time of this writing, there is no oxidation stability requirement in ASTM Standard Specification D6751, the specification for biodiesel. The primary reason for the absence of an oxidation stability requirement is a lack of agreement on which oxidation stability test method to specify. The European biodiesel specification incorporates the Rancimat test as a measure of oxidation stability. The Rancimat test is one of the methods under consideration for the ASTM specification along with several other stability tests traditionally used for petroleum fuels.

The purpose of this project was to compare and evaluate several candidate test methods. The information gathered from this work will be available to aid in the selection of a test method for inclusion in D6751.

The test methods evaluated during this project were:

- ASTM[1] D4625, Standard Test Method for Middle Distillate Fuel Storage Stability at 43°C (110°F).
- ASTM D6468, Standard Test Method for High Temperature Stability of Distillate Fuels. Modified for gravimetric determination of insoluble formation (as described in this report).
- ASTM D2274, Standard Test Method for Oxidation Stability of Distillate Fuel Oil (Accelerated Method). Modified, specifically for use with biodiesel, as described later in this report.
- ASTM D3241, Standard Test Method for Thermal Oxidation Stability of Aviation Turbine Fuels (JFTOT Procedure).
- EN 14112, the Rancimat Test, Fat and oil derivatives. Fatty Acid Methyl Ester (FAME). Determination Of Oxidation Stability (Accelerated Oxidation Test).
- Modified IP 306, Determination Of Oxidation Stability Of Straight Mineral Oil.
- ASTM D5483, Standard Test Method for Oxidation Induction Time of Lubricating Greases by Pressure Differential Scanning Calorimetry.

The test methods were evaluated for their ease of use, applicability to the measurement of biodiesel, ability to discern additive effects, and ability to discriminate between biodiesel samples of various levels of oxidation stability.

Two test methods emerged as the most likely choice for inclusion in D6751. They were the Rancimat test and a modified version of D2274. For D2274, modification to include collection of isooctane insolubles (or other non-polar solvent) may improve precision and accuracy. Other modifications to filtration procedures may also be necessary. Additional evaluation of these test methods is proposed in order to make a final decision for specification purposes.

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1.0 Objective

The objectives of this project are to compare several stability test methods using biodiesel typical of the U.S. market:

a. Using the currently accepted tests (D2274 and EN14112) as well as other tests that might provide additional or more accurate information.
b. To examine the effect of common anti-oxidants.
c. Verify these results using a subset of the test methods on commercial biodiesel samples produced from soybean oil and yellow grease.

2.0 Background

An important goal of the United States Department of Energy (US DOE) Fuels Technologies Program is to develop renewable diesel blending-components in order to displace imported petroleum and to reduce emissions of global warming gases. Biodiesel is an important renewable diesel blending component. Because of its chemical structure, biodiesel can be very sensitive to oxidative and thermal degradation. The sensitivity varies depending on the feedstock and the presence of naturally occurring antioxidants in the finished fuel. The oxidation stability characteristics of biodiesel can also be improved through the use of commercially available antioxidant additives. Oxidation can lead to the formation of corrosive acids and deposits that may cause increased wear in engine fuel pumps and fuel injectors.

ASTM International (American Society of Testing and Materials, ASTM) Standard Specification D6751 is the quality specification for neat (100%) biodiesel or B100 that is to be used for blending with petroleum diesel. This specification does not currently contain a requirement for fuel stability. The lack of a stability requirement in D6751 is a major barrier to increased acceptance of biodiesel by engine and fuel injection equipment manufacturers, and thus to increased markets for this fuel. In order to include such a requirement, a suitable test method must first be identified, as well as possible alternate test methods. Presently available stability tests have been developed for petroleum-derived fuels. Biodiesel is chemically different enough that these tests do not produce meaningful results. Under this study basic data on how biodiesel is oxidatively and thermally degraded under the conditions of various stability test methods was acquired. These data will point to appropriate test method modifications, and ultimately lead to improved tools for studies of biodiesel stability and improved stability test methods for inclusion in standard specifications.

Prior work under National Renewable Energy Laboratory (NREL) subcontract number ACG-7-17066-01 has shown that a modified version of ASTM Test Method D2274 may distinguish between stable and unstable B100 samples in some cases.

In this earlier study, results from the long term D4625 storage test were compared to results of an accelerated stability test based on ASTM D2274. D2274 was modified via the following procedures:

- Use Whatman type GF/F glass fiber filters (because of incompatibility of cellulose ester filters with biodiesel)
- Retain aged and filtered fuel and analyze it for viscosity and total acid number

The results of the study were used to determine appropriate time and temperature for aging.

Thermal stability was examined using ASTM D6468 (also called the DuPont F21 test) modified to include filtration and gravimetric analysis for insolubles.

2.1 B100 Stability

For comparison of long-term fuel storage and accelerated oxidation tests the following fuels were employed:

- CL00-288 (soy-biodiesel)
- CL00-289 (soy-biodiesel)
- CL00-290 (a 50/50 blend of CL00-288 and CL00-289)
- AL-25842 (a soy-biodiesel treated with 200 ppm of Tenox-21 antioxidant)

Results of ASTM D4625 for 16 weeks are shown in Figure 1. With the exception of the Tenox-21 treated fuel, all fuels can be considered unstable based on either insoluble formation or acid formation during long term storage. There may be some question regarding the insolubles data for CL00-289 as an increase followed by a decrease was observed, but this fuel was clearly unstable based on acid number. All of the fuels would meet the viscosity requirements of D6751, although CL00-289 and CL00-290 exhibited significant increases.

Based on these results it is clear that no one measure of instability (i.e. insolubles, acid value, or viscosity) will be adequate for measuring or predicting stability of B100 fuels. At a minimum, measurement of insolubles and either acid value or viscosity will be required.

The fuels tested above were also tested using ASTM D2274 over a range of times and at three different temperatures. The objective of these tests was to select a time and temperature that distinguishes between stable and unstable fuels. Results are summarized in Figure 2 for the three unstable fuels. One approach to selecting an appropriate accelerated oxidation test is to use the mildest conditions (lowest temperature and shortest time) that reveal instability. For fuel CL00-288 instability is only revealed at 95°C and for times of 16 hours or longer, suggesting that for this set of fuels these are the required conditions. Figure 3 shows a similar data set for the Tenox-21 treated fuel (AL-25842) as well as for a tallow-based biodiesel (AL-25954) and a yellow-grease-based biodiesel (AL-25843). All test conditions predict the Tenox-21 treated fuel to be stable. Both the tallow- and yellow grease-based biodiesels are predicted to be unstable using the 95°C/16 hr test condition, as well as at milder test conditions. Based on these results the selection of 95°C and 16 hours would appear to be appropriate for the ASTM D2274 test.

The tallow-based sample was analyzed using these test conditions to provide a preliminary measure of test repeatability and results are listed in Table 1. The coefficient of variation for these measurements is roughly 13% for insolubles and acid number, and 1% for viscosity. For this sample the insoluble, acid, and viscosity levels rose well above the upper limits in D6751

and thus repeatability is adequate for determining stability. For samples that are less obviously unstable improved repeatability may be required.

In summary, the results of oxidative stability testing for B100 samples indicate that the D2274 test can predict if a fuel is stable or not. The most appropriate testing conditions are 95°C for 16 hours. However, additional method development for determination of the mass of insolubles and for determination of acid number may be needed in order to reduce experimental error to acceptable levels.

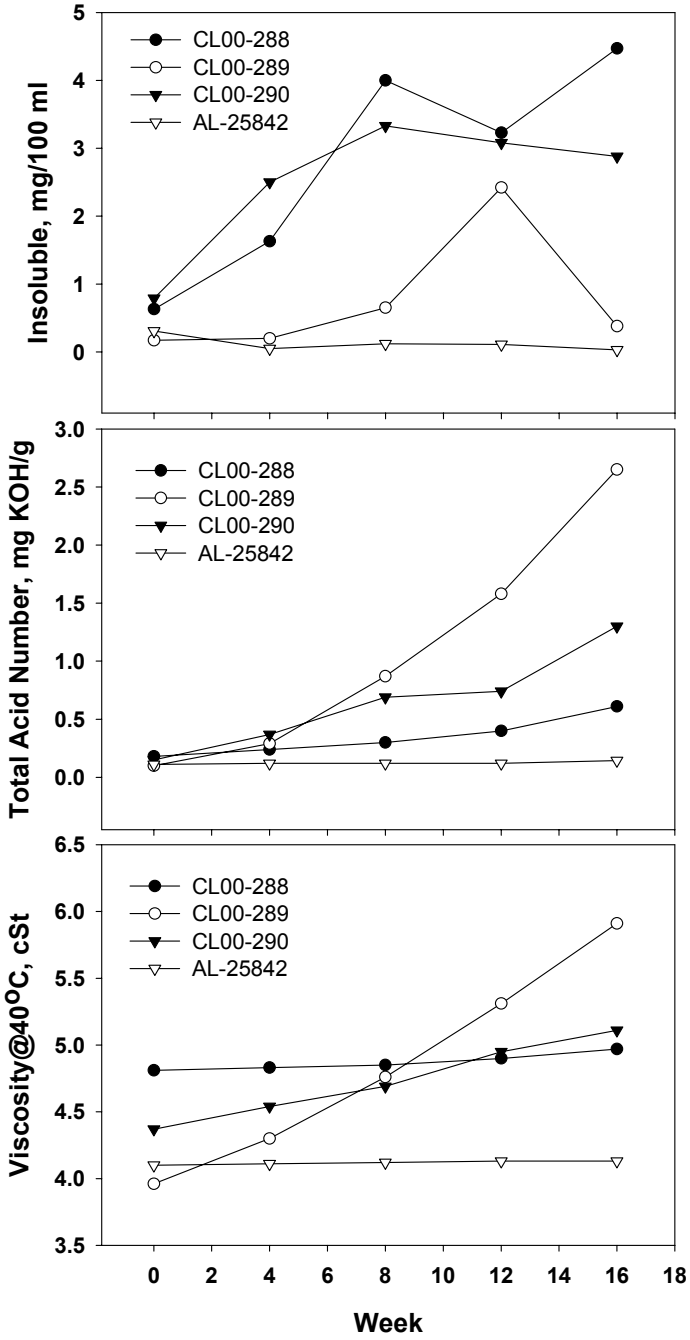

Figure 1. Results Of Long-Term Storage Stability Testing For Several B100 Biodiesel Samples Via ASTM D4625 (43°C).

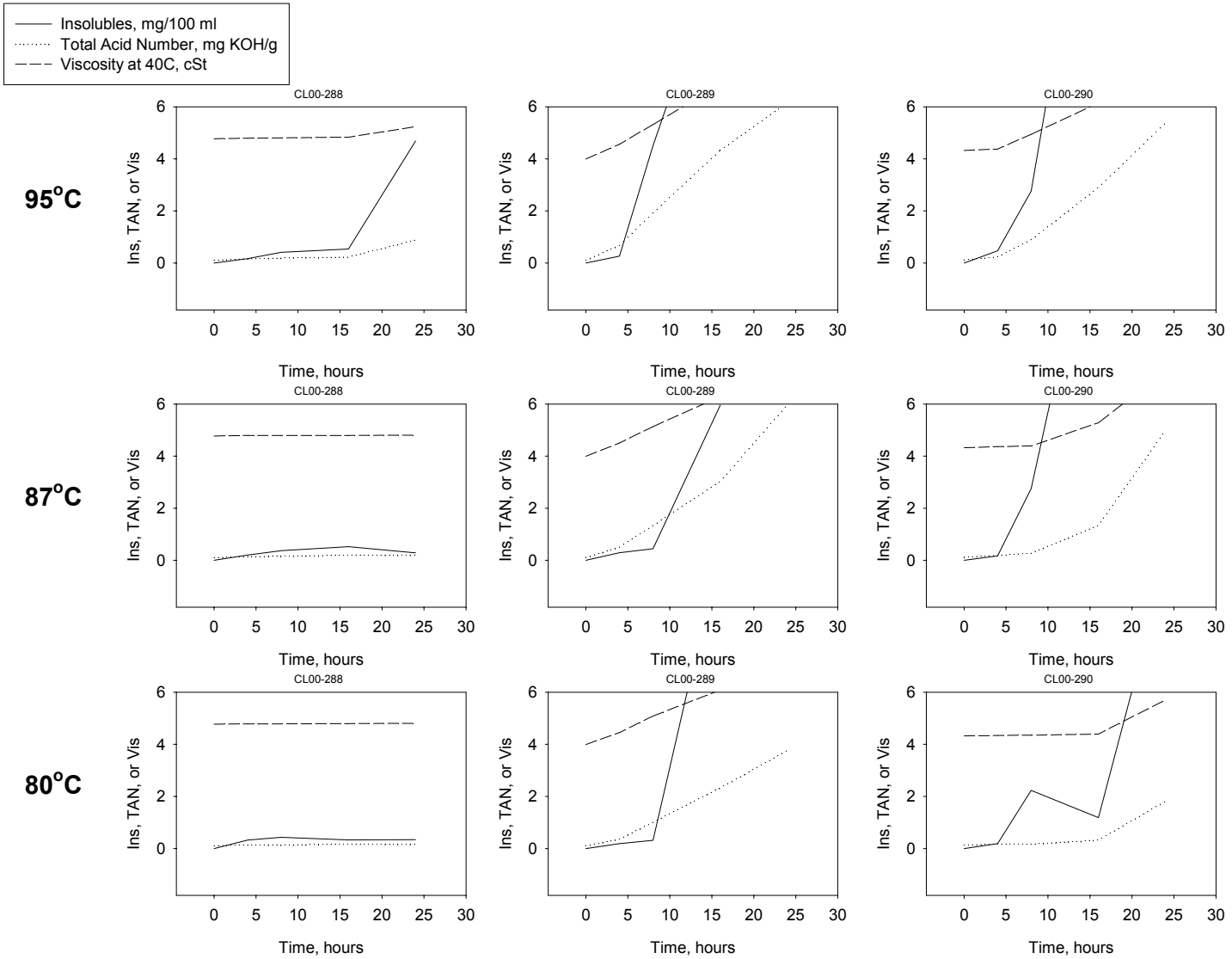

Figure 2. Results Of Accelerated Oxidation Stability Testing For B100 Samples Using ASTM D2274 At Different Times And Temperatures.

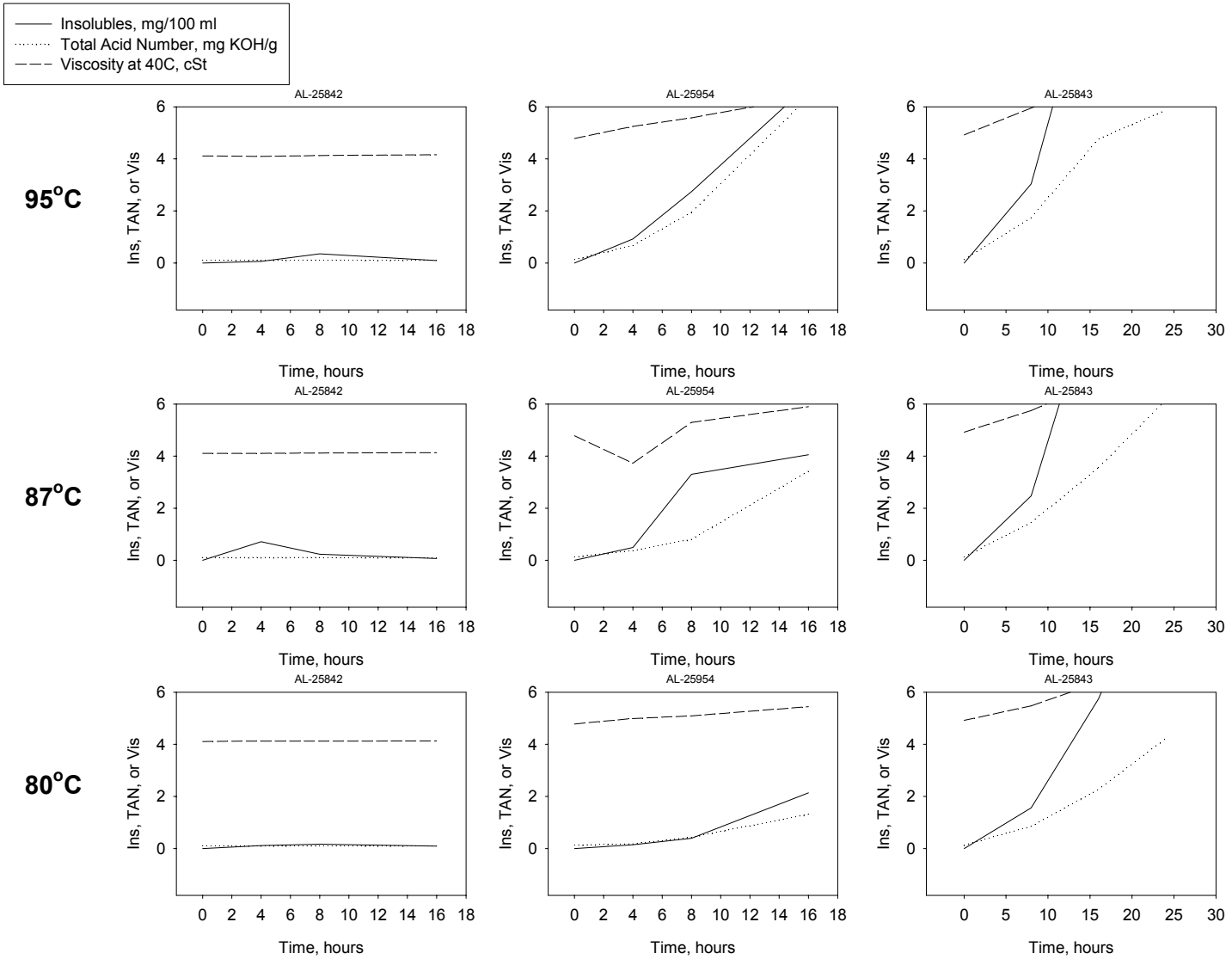

Figure 3. Results Of Accelerated Oxidation Stability Testing For B100 Samples Using ASTM D2274 At Different Times And Temperatures.

Table 1. Results of Repeated ASTM D2274 Tests at 95°C, 16 hours on Tallow-based Biodiesel (Sample AL-25954)			
Run	**Total Insolubles, mg/100 ml**	**Total Acid Number, mg KOH/g**	**Viscosity @40°C, cSt**
1	7.77	6.97	6.43
2	5.92	5.77	6.32
3	6.55	5.10	6.24
4	7.80	5.57	6.27
Mean	7.010	5.853	6.315
Standard Deviation	0.9312	0.7962	0.0835
Coefficient of Variation	13.3%	13.6%	1.32%
95% conf	1.4814	1.2666	0.1328
Upper Limit*	0.05	0.8	6.0

*Upper limit for these properties based on specifications in D6751 for B100. Runs 1 and 2 from SwRI report for Task 8A, November 23, 1999. Runs 3 and 4 from SwRI report to NBB dated August 3, 2001.

2.2 Effect of Anti-Oxidants

A task was conducted to determine if ASTM D2274 at 80°C and for 24 hours would reveal the effect of antioxidants on stability for fuel CL00-289. While subsequent results suggest that 80°C is not the best temperature for this test, it was selected based on results of another study[2] that indicated lower temperatures were required to reveal the impact of antioxidants. Additionally, for this fuel a temperature of 80°C was adequate to reveal instability in the accelerated test. The test fuels were:

- CL00-289
- CL00-289 plus 200 ppm BHT
- CL00-289 plus 200 ppm TBHQ
- CL00-289 plus 1000 ppm Tenox-21

Figure 4 shows the results for total insolubles, acid number, and viscosity following the modified D2274 procedure for these fuels. The unadditized fuels are again predicted to be unstable by this test. The addition of 200 ppm of BHT is very effective at stabilizing the fuel under these conditions with essentially no change in acid number or viscosity and only a small formation of insolubles. Both TBHQ and Tenox-21 improve stability substantially.

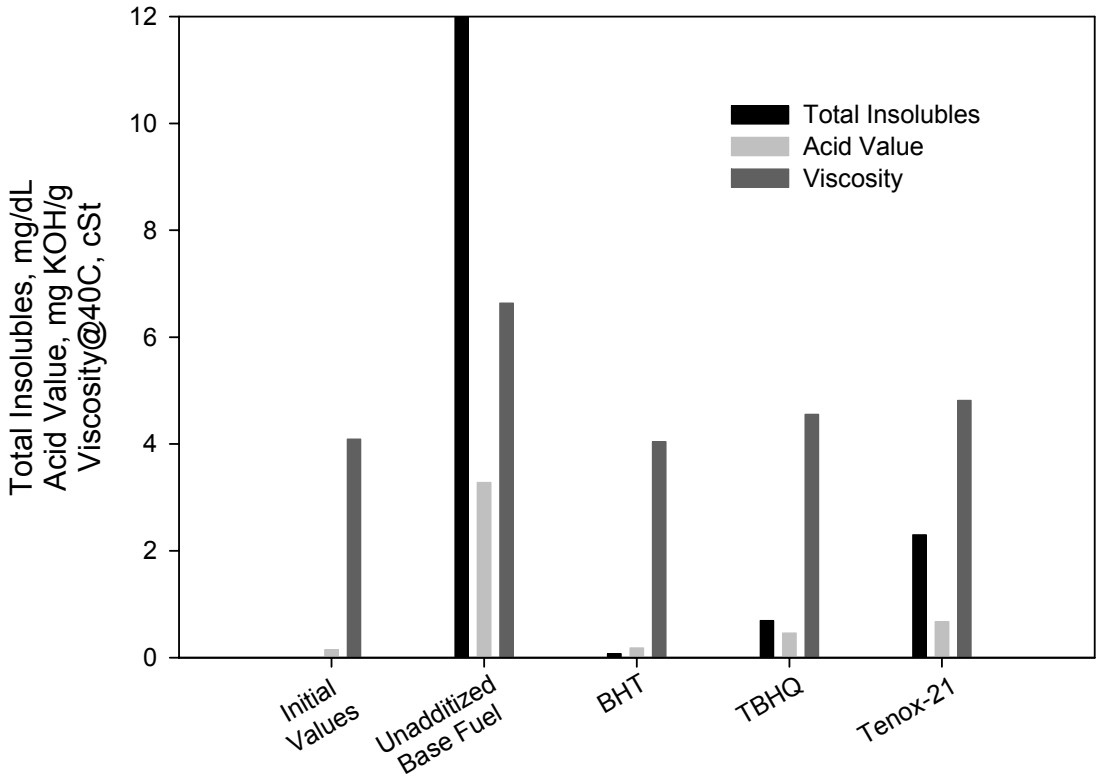

Figure 4. Results Of Accelerated Stability Determination By ASTM D2274 At 80°C For 24 Hours For CL00-289 Treated With Several Antioxidants.

It is interesting to note that in this case 1,000 ppm of Tenox-21 did not produce a completely stable fuel, while the results shown above in Figure 1 indicate that only 200 ppm of Tenox-21 was adequate to accomplish this in the long term test (ASTM D4625). It seems clear that additional test data are required to understand the impact of antioxidants in the accelerated test. More specifically, it is desirable to test an unstable biodiesel over a range of antioxidant blending levels and temperatures using several food and refinery antioxidants.

2.3 Thermal Stability

Thermal stability of three B100 samples and two petroleum diesel samples was assessed using ASTM D6468 (duPont F21 test). Both the standard version of D6468 and a modified version were used. In the standard version the fuel is filtered following high temperature exposure and the reflectance of the filter is measured. Reflectance decreases with increasing levels of insolubles. A modified method where insolubles are determined gravimetrically was also used. Table 2 reports results for both approaches. Note that none of the B100 fuels showed any appreciable degradation under any of the test conditions.

Table 2. Results of D6468 Using Both Standard And Modified Methods for Three Biodiesel Fuels (B100) And Two Petroleum Diesel Fuels [a]						
	90 minutes		180 minutes		360 minutes	
Sample	% Reflectance	Gravimetric mg/dL	% Reflectance	Gravimetric mg/dL	% Reflectance	Gravimetric mg/dL[b]
CL00-288	93.10	-0.80	93.40	-1.20	91.40	-0.09
	98.00	-0.26	90.00	0.06	91.00	-1.60
CL00-289	99.70	-0.09	99.40	-0.23	98.70	-0.34
	99.60	-0.23	99.40	-0.54	99.30	-0.63
CL00-290	95.90	-0.03	95.80	0.03	94.20	-0.63
	94.70	-0.91	95.70	-0.17	93.10	-1.06
AL-25844	7.50	1.86	4.10	1.91	2.90	3.09
	15.70	1.00	3.80	2.03	2.60	2.80
AL-22662	4.10	5.60	2.80	6.23	1.80	9.80
	4.10	5.83	2.80	7.51	1.90	10.00

[a]AL-25844 is a stable petroleum diesel and AL-22662 is an unstable petroleum diesel.
[b]Negative values indicate that the filter lost mass and are an indication of the error of this test.

2.4 Summary

The results of this prior study clearly show the potential of biodiesel to exhibit oxidation instability in different environments. As a follow on to this work, the current study was conducted with the goal of comparing a wider range of test methods for use in measuring biodiesel stability and the effect of antioxidants.

3.0 Procedure

3.1 Tasks

3.1.1 Comparative Testing with Unstable Biodiesel

The objective of this task is to compare results using a variety of oxidative and thermal stability test methods using two highly characterized unstable biodiesels. Based on these results, a more limited set of tests and conditions were selected for further examination. The following subtasks were also performed:

3.1.2 Effect of Antioxidants

The objective of this task is to examine the performance of common anti-oxidant chemistries as well as the sensitivity of selected test methods to the effects of these additives.

3.1.3 Testing of Commercial Biodiesels

This task will determine if what was learned in the above two tasks can be generalized to other soy-based biodiesels (containing natural antioxidants), as well as biodiesels produced from waste cooking oil and animal fat.

3.2 Test Fuels

The test fuels are listed in Table 3. Neither test fuel contained any additives as received. The fuels were tested against ASTM Standard Specification D6751. The detailed requirements of the specification are shown in Figure 5. Inspection test results are listed in Table 4. The test fuels meet all requirements with the exception of the acid number for soy-derived fuel. The limit on acid number is 0.8 mg KOH/g. The measured value of 1.46 indicates that some oxidation of this material has already begun to occur.

Table 5 gives the results of Fatty Acid Methyl Ester (FAME) analysis for the two B100 test fuels. Also contained in the table is the typical composition for soy-derived B100. It is not meaningful to give typical results for yellow grease since it is derived from numerous different feedstocks. The FAME analysis indicates that the soy-derived test fuel is atypical of soy biodiesel with 60% oleic acid (C18: 1) and almost no C18: 3. Nevertheless, this material contained very low levels of natural antioxidants[3] and was not found to be particularly stable on various stability tests.

Table 3. Test Fuels

Laboratory Identification	Description
27007 -- Soy (CL03-842)	Distilled Soy Methyl Ester Biodiesel
27008 -- Yellow Grease (CL03-843)	Low Sulfur, Yellow Grease Biodiesel

Property	Test Method[B]	Grade S15 Limits	Grade S500 Limits	Units
Flash point (closed cup)	D 93	130.0 min	130.0 min	°C
Water and sediment	D 2709	0.050 max	0.050 max	% volume
Kinematic viscosity, 40°C	D 445	1.9-6.0[C]	1.9–6.0[C]	mm^2/s
Sulfated ash	D 874	0.020 max	0.020 max	% mass
Sulfur[D]	D 5453	0.0015 max (15)	0.05 max (500)	% mass (ppm)
Copper strip corrosion	D 130	No. 3 max	No. 3 max	
Cetane number	D 613	47 min	47 min	
Cloud point	D 2500	Report[E]	Report[E]	°C
Carbon residue[F]	D 4530	0.050 max	0.050 max	% mass
Acid number	D 664	0.80 max	0.80 max	mg KOH/g
Free glycerin	D 6584	0.020	0.020	% mass
Total glycerin	D 6584	0.240	0.240	% mass
Phosphorus content	D 4951	0.001 max	0.001 max	% mass
Distillation temperature, Atmospheric equivalent temperature, 90 % recovered	D 1160	360 max	360 max	°C

[A] To meet special operating conditions, modifications of individual limiting requirements may be agreed upon between purchaser, seller, and manufacturer.
[B] The test methods indicated are the approved referee methods. Other acceptable methods are indicated in 5.1.
[C] See X1.3.1. The 6.0 mm^2/s upper viscosity limit is higher than petroleum based diesel fuel and should be taken into consideration when blending.
[D] Other sulfur limits can apply in selected areas in the United States and in other countries.
[E] The cloud point of biodiesel is generally higher than petroleum based diesel fuel and should be taken into consideration when blending.
[F] Carbon residue shall be run on the 100 % sample (see 5.1.10).

Figure 5. Detailed Requirements for Biodiesel per ASTM D6751

Table 4. Characterization Data for Test Fuels		
Property	**Soy**	**Yellow Grease**
Copper Strip Corrosion, D130	1A	1A
Water and Sediment, vol%, D2709	< 0.005	<0.005
Flash Point, °C, D93	172	176
Kinematic Viscosity @ 40°C, mm^2/s, D445	4.72	4.64
Cloud Point, °C, D2500	8	13
Cetane Number, D613	65	64
Sulfated Ash, D874, mass%	<0.01	<0.01
Carbon Residue, D4530, mass%	0.02	0.007
Free Glycerin, D6584, mass%	0.007	0.008
Total Glycerin, D6584, mass%	0.051	0.063
Phosphorus Content, D4951, ppm	<5	<5
Water and Sediment, D2709, volume%	<0.005	<0.005
Total Sulfur, D5453, ppm	<5	6.7
Total Acid Number, D664, mg KOH/g	1.46	0.59
Vacuum Distillation, D1160, °C		
IBP		
10%	362	348
50%	381	380
90%	381	401
99%	386	408
Residue	435	422
Loss	0.5	1

Table 5. Fatty Acid Methyl Ester Content of Test Fuels (As Measured by GCMS)[4]				
FAME	**Name**	**Soy, mass %**		**Yellow Grease, mass %**
		Typical Soy	Test Fuel	
C12:0	Methyl Laurate			
C14:0	Methyl Myristate	0	0.17	0.22
C14:1		0	---	
C15:0		0	---	
C16:0	Methyl Palmitate	12	14.21	12.26
C16:1	Methyl Palmitoleate	0	---	
C16:2		0	---	
C17:0		0	---	
C17:1		0	---	
C18:0	Methyl Stearate	4	12.02	5.70
C18:1	Methyl Oleate (9)	23	58.24	30.27
C18:2	Methyl Linoleate (9,12)	55	13.56	47.69
C18:3	Methyl Linolenate (6,9,12)	7	0.94	3.28
C20:0	Methyl Arachidate	1	0.68	0.32
C22:0	Methyl Behenate		0.09	0.27
C24:0	Methyl Lignocerate		0.09	

3.3 Test Methods

Although there is an oxidation stability requirement in the European biodiesel specification (EN 14214), there is not one in the ASTM specification. The results of this project will be used as part of the selection of a test method for the ASTM specification. Several candidate test methods were selected for evaluation, as follows:

3.3.1 ASTM D4625

Standard Test Method ASTM D4625 is the most widely accepted test method for assessing the storage stability of middle distillate, petroleum fuels. The fuel is stored at 43°C for selected periods up to 24 weeks. One week of storage in this test is generally accepted as equivalent to one month of storage at 17°C (65°F). Typically a sample is filtered to determine total insolubles on a weekely basis. For testing of biodiesel Whatman GF/F filters (47 mm diameter) were used. After filtering the aged sample the filtrate was analyzed for total acid number (ASTM D664) and kinematic viscosity at 40°C (ASTM D445).

As an additional analysis, 100 ml of the aged, filtered fuel was mixed with 400 ml of *iso*-octane to precipitate any polar polymeric materials that may have formed as a result of ageing. The aged fuel/*iso*-octane mixture was filtered through a separate pair of filters. This was done to investigate a previous study that concluded that ageing of B100 under these conditions does not result in the formation of insolubles because the oxidized and polar polymers that are formed are soluble in the biodiesel. Dilution with a non-polar solvent, such as *iso*-octane, was shown to result in precipitation of these polymers. [5]

3.3.2 ASTM D2274

A 350 ml volume of filtered middle distillate fuel is aged at 95°C (203°F) for 16 h. Oxygen is bubbled through the sample at a rate of 3 L/h. After aging, the sample is cooled to approximately room temperature before filtering to obtain the filterable insolubles quantity. Adherent insolubles are then removed from the oxidation cell and associated glassware with trisolvent (a mixture of equal parts toluene, acetone, and methanol). The trisolvent is evaporated to obtain the quantity of adherent insolubles. The sum of the filterable and adherent insolubles, expressed as milligrams per 100 ml, is reported as total insolubles. As with the D4625 analyses, 100 ml of the aged, filtered fuel was mixed with 400 ml of *iso*-octane and filtered.

Whatman GF/F filters (47 mm diameter) were used.

After filtering the aged sample, but prior to solvent washing of the filters, an aliquot of the filtrate was obtained for additional testing. The aliquot was analyzed for total acid number (ASTM D664) and kinematic viscosity at 40°C (ASTM D445).

As an additional analysis for biodiesel-soluble polymers, 100 ml of the aged, filtered fuel was mixed with 400 ml of *iso*-octane. The aged fuel/*iso*-octane mixture was also filtered through a separate pair of filters.

3.3.3 ASTM D6468 at 150°C, 3 hours

Two 50-mL volumes of filtered middle distillate fuel were aged for 90 or 180 minutes at 150°C in open tubes with air exposure. After aging and cooling, the fuel samples were filtered and the average amount of filterable insolubles is estimated by measuring the light reflectance of the filter pads. An unused filter pad and a commercial black standard define the 100 and 0 % extremes of the reflectance rating range, respectively.

The reflectance measurement works well with petroleum diesel fuel because the particles formed during the aging are typically brown or black. Hence, increased amounts of particles result in decreased reflectance. With biodiesel, the particles and polymers formed have almost no visible color. Therefore, increased amounts of biodiesel particles/polymers result in little or no change in reflectance. This means that the test gives best results when the biodiesel particles/polymers are measured gravimetrically.

3.3.4 EN 14112 (Rancimat)

The Rancimat test instrument is pictured in Figure 6. This is the required stability method in the European biodiesel specification. The induction period prior to the onset of rapid oxidation is measured.

A stream of purified air is passed through the sample, which is heated to a specified temperature. The gases released during the oxidation process, together with the air, are

passed into a flask containing deionized water. The flask also contains an electrode to measure conductivity. The electrode is connected to a measuring and recording device. The time at which the conductivity begins to increase rapidly is defined as the induction time. Acids produced during the oxidation process and absorbed in the water cause this accelerated increase. The volatile acids are primarily formic acid, but also include lower levels of acetic and other acids.[6] A plot of a typical Rancimat test is shown in Figure 7. This figure shows the deionized water conductivity versus time for the Rancimat test. For this particular sample conductivity remains unchanged or very low for roughly 4.5 hours. At this point in time the conductivity of the water begins to increase rapidly because of oxidation of the biodiesel sample yielding volatile acids that are carried by the flowing air into the water bath. The first derivative of the conductivity curve shows the inflection point (maxima in the first derivative) that defines the induction time. Recent results show that Rancimat induction times correlate well with induction times measured by ASTM D525, Standard Test Method for Oxidation Stability of Gasoline.[7]

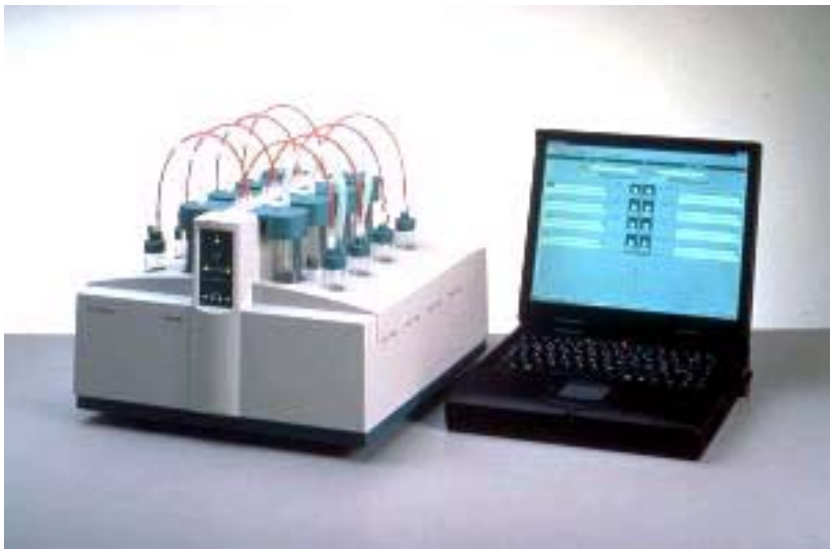

Figure 6. Rancimat Instrument Connected to Notebook Computer. The Standard Rancimat Can Analyze Eight Samples at One Time

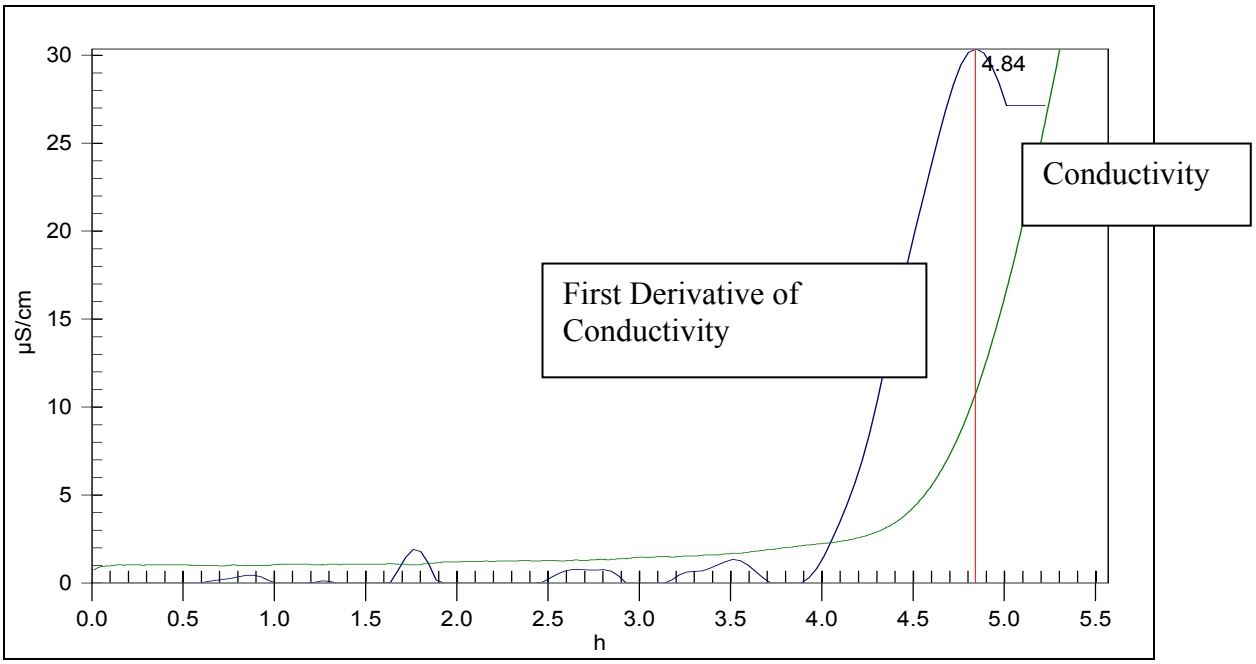

Figure 7. Typical Rancimat Test Data Trace for a Sample with an Induction Period of 4.84 Hours

3.3.5 ASTM D3241, JFTOT Procedure

This test method for measuring the high temperature stability of gas turbine fuels uses the Jet Fuel Thermal Oxidation Tester (JFTOT) that subjects the test fuel to conditions that can be related to those occurring in gas turbine engine fuel systems. The fuel is pumped at a fixed volumetric flow rate through a heater after which it enters a precision stainless steel filter where fuel degradation products may become trapped. For the work in this project, the precision filter had to be removed because it plugged too quickly. The apparatus uses 450 mL of test fuel ideally during a 2.5 h test. The essential data derived are the amount of deposits on an aluminum heater tube as determined by ellipsometry (an optical technique for measuring the thickness of thin films), and the rate of plugging of a 17µ nominal porosity precision filter located just downstream of the heater tube.

3.3.6 HPDSC - High Pressure Differential Scanning Calorimeter

These tests were conducted using a modification of ASTM D5483, Standard Test Method for Oxidation Induction Time of Lubricating Greases by Pressure Differential Scanning Calorimetry. A small quantity of sample is weighed into a sample pan and placed in a test cell. The cell is heated to a specified temperature and then pressurized with oxygen to 500 pounds per square inch. The cell is held at a regulated temperature and pressure until an exothermic reaction occurs. The extrapolated onset time is measured and reported as the oxidation induction time for the sample under the specified test temperature.

3.3.7 Institute of Petroleum Method 306[8] (Modified)

This test method is similar to D2274. The sample size is only 25 grams as opposed to 350 mL for D2274. The oxidation tubes are correspondingly smaller. Dry oxygen is passed into the reaction tubes (containing the B100) for 16 hours. The IP 306 method calls for an oxidation catalyst (copper wire) in one sample during aging but no catalyst was used in any of the tubes during this testing. The heating block is held at a temperature of 120°C. The volatile acids driven off by the flowing oxygen were absorbed in de-ionized water. The volatile and oil-soluble acidities produced in the B100 were measured at the end of the test. The insoluble polymers were also measured gravimetrically. A solvent of equal parts toluene, acetone, and methanol was used in place of chloroform wherever it was called for in the test method.

IP 306 is a viable alternative test method to D2274 although more work has been done with D2274. The largest disadvantage of IP 306 is the small sample size. Based on experience with other test methods (such as D6217, D2276, and D2274) it is very likely that the 25 g sample size significantly reduces the sensitivity of the polymer measurement.

4.0 Results and Discussion of Data

The results of analyses with each test are discussed below.

4.1 ASTM D4625

The results for the D4625 test are presented in Table 6. In general, each of the properties showed an increase with storage time, as expected. The degree of change varied with the fuels. This is in agreement with an earlier project, which found that D4625 is sensitive to stability differences in the fuels.[9] While the soy biodiesel tested here exhibited an atypical fatty acid composition, results for this test are similar and in line with what has been observed previously for relatively unstable soy biodiesel (see Figure 1). Note that the yellow grease sample had a significant increase in iso-octane insoluble material (dissolved polymers) between weeks 4 and 8. Yet, there was almost no change in the viscosity of the fuel. This indicates that perhaps viscosity is not sufficiently sensitive to changes in polymer formation. Also, the conditions of this test are very mild compared to some of the other test methods often used to measure oxidation stability. This test is more representative of changes in the biodiesel during longer periods of quiescent storage, typically at temperatures below 30°C. It is not representative of the higher temperatures and greater oxygen exposure found in a diesel vehicle fuel system.

Although it is a generally accepted test for the storage stability of petroleum fuels, similar correlations to the storage of biodiesel have yet to be demonstrated. Until those correlations have been demonstrated, the ability of this test to measure storage stability is unclear. The milder conditions and very long test times used in this method make it a poor choice as a convenient and predictive measure of oxidation stability.

Table 6. Results of ASTM D4625 Tests					
Biodiesel	**Weeks**	**Total Insolubles (mg/L)**	**Total Acid Number (mg KOH/g)**	**Kinematic Viscosity @ 40°C, mm^2/s**	***iso*-octane Insoluble Material (mg/L)**
Soy	4	3.0	1.6	5.0	0.1
	8	0.3	1.9	5.2	4.2
	12	1.7	2.5	5.4	2.8
Yellow Grease	4	0.1	0.7	4.7	3.8
	8	0.4	0.7	4.7	2.8
	12	7.5	0.9	4.8	12.2

4.2 ASTM D2274

The D2274 test has been used in various, non-ASTM, diesel fuel specifications for over 30 years. During that entire period, numerous researchers have spent countless hours, and dollars, attempting to improve the precision of the method and determine its correlation to long-term storage. Many of the sources of imprecision were identified and corrected. Still, the published precision for the method is less than most users consider acceptable (see below for published precision).

Precision and Bias Statement from ASTM D2274-03a

14. Precision and Bias [7]

14.1 *Precision*—The precision (see Table 1) of this test method as determined by statistical examination of interlaboratory results is as follows:

14.1.1 *Repeatability*—The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

$$0.54\ (\sqrt[4]{\text{total insolubles, mg/100 mL}}) \quad (4)$$

14.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

$$1.06\ (\sqrt[4]{\text{total insolubles, mg/100 mL}}) \quad (5)$$

14.2 *Bias*—Since there is no accepted reference material suitable for determining the bias for this test method no statement on bias is being made.

For petroleum diesel fuel, it has been demonstrated that there is no correlation between the results of D2274 and long-term storage under normal conditions. The general consensus is that the test can discriminate between very stable fuels and very unstable

fuels. The marginal fuels tend to give mixed results compared to long-term storage. It is assumed that the poor correlation is because the high test temperature and constant oxygen replenishment initiate reactions that would not normally occur at the lower temperatures and quiescent storage.

The test conditions that make D2274 a poor predictor of storage stability are the very conditions that make the test a promising candidate for measuring biodiesel oxidation stability. Because the chemistry of biodiesel degradation is almost entirely oxidation chemistry, higher temperatures and constant oxygen replenishment are realistic parameters for a biodiesel test method. Indeed, all the test methods that have either been adopted or seriously considered have these parameters in common with D2274.

Most of the previous work with D2274 as a test for biodiesel has centered on selection of an appropriate test temperature and test time. The standard temperature is 95°C and the standard test time is 16 hours. More recently, some researchers have begun to study the solubility factor of biodiesel. This issue was identified and first studied under the European Biostab project. Under that project, studies of stability test methods produced the following as one of the observations from the work:

> "…no significant insoluble formation was observed. The conclusion was that polymer formed during storage of biodiesel in controlled conditions are soluble in oxidised biodiesel, thanks to its high polarity and become insoluble only when oxidised biodiesel is mixed with diesel fuel..."

It is now understood that the solubility factor plays a significant role in the oxidation stability of biodiesel. Also, it is now assumed that test methods such as D2274, which measure insolubles formation, must also incorporate a measurement of the polymers that are insoluble when the B100 is mixed with a non-polar solvent.

As such, consideration of D2274 for biodiesel oxidation stability means selection of three parameters:

1. Test temperature.
2. Test time.
3. Ratio of aged B100 to non-polar solvent for measuring solubility effects.

Of the three parameters listed above, items 1 and 2 have been studied in greatest detail. Test temperatures from 80°C to 110°C have been proposed and studied. The results are mixed and no clear choice stands out. Stavinoha and Howell showed data that indicated temperatures above 80°C could mask the effects of antioxidants. This conclusion was based on very limited data (shown in Table 7). However, it is a significant observation and is deserving of further study. The effects of test temperatures above 110°C are not yet known but temperatures that high have been known to decompose natural inhibitors.[10]

Table 7. Effect of Antioxidant at Different Temperatures on total insolubles (mg/100 ml) in the AST D2274 test (data from Stavinoha and Howell, reference 2)		
BHT Conc., ppm	B100 (1) 80°C	B100 (1) 95°C
0	17.2	12.1
120	8.1	16.5
240	1.2	16.5

Test times ranging from 4 hours to 8 hours have been evaluated. Since there is no established correlation of this test with long-term storage and no data with which to draw such a correlation, selection of a test time rests on other criteria. The main criteria are ease of use and sufficient time to allow discrimination between fuels of various qualities. For the purposes of a specification test/quality control, shorter test times are desirable. Longer test times typically provide more information on the degradation of the sample. In a previous study, Westbrook and Stavinoha examined a large matrix of test times and temperatures. A plot of total insolubles data from that study is shown in Figure 8. As would be expected, the best discrimination between fuels comes at higher temperatures and longer test times. These experiments did not, however, include an examination of solubility effects or antioxidant additives. As such, it is difficult to make test condition selections on those results.

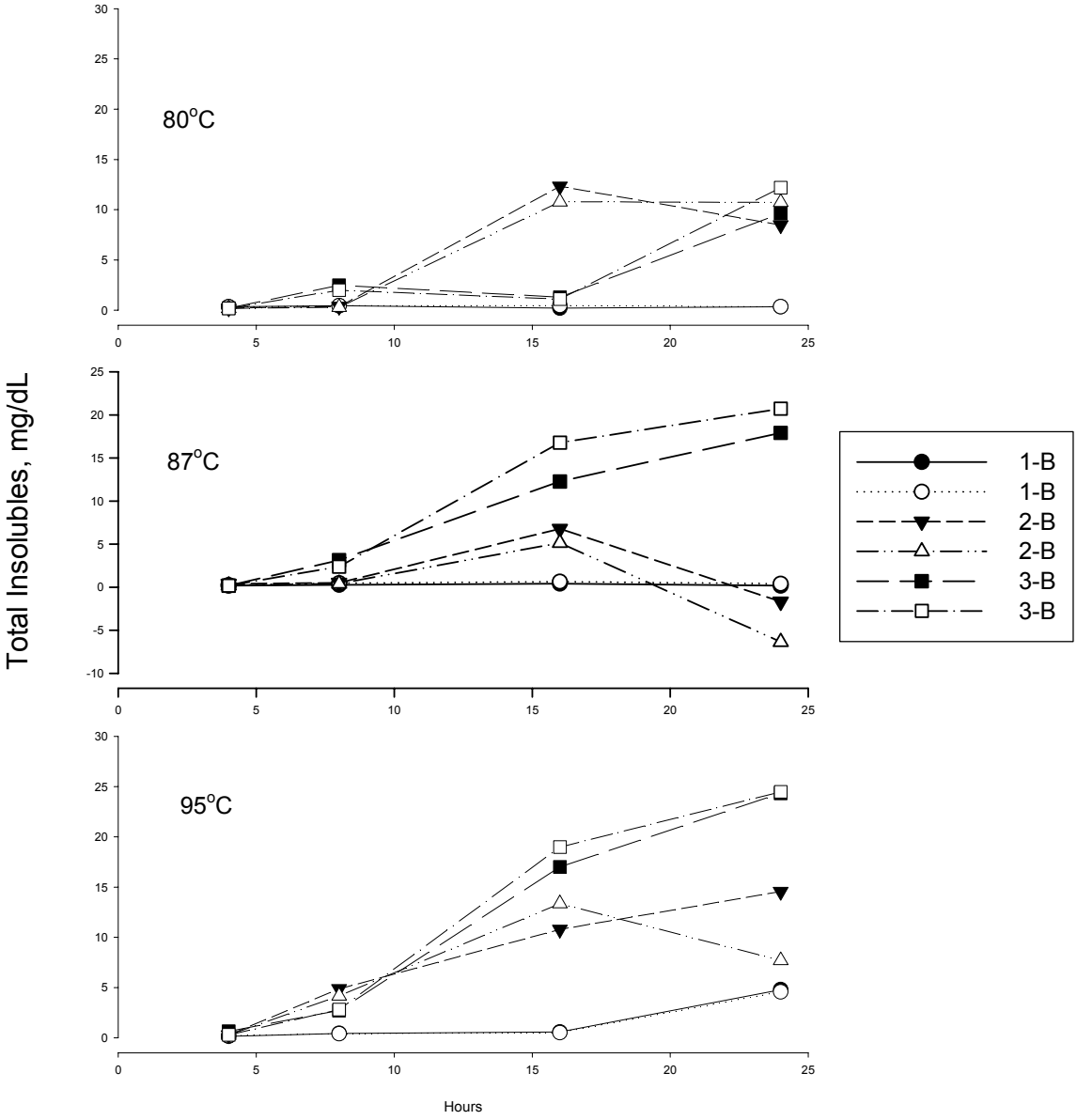

Figure 8. D2274 Time and Temperature Study Results

For the purposes of the current study, we ran tests at 95°C and 110°C. The focus of this work however, was on the solubility factor rather than test temperature or test duration. The data presented in Table 8 are for the fuels tested by the modified D2274 at 95°C. The data presented in Table 9 are for the modified D2274 conducted at 110°C. From the data in these two tables, it is interesting to note the difference in the amount of iso-octane insolubles at the two temperatures. Note that each of the fuels tends to form similar amounts of total insolubles, irrespective of the temperature. The amounts of iso-octane insolubles, however, differ significantly, depending on the temperature. For each of the fuels, the higher test temperature results in higher levels of iso-octane insoluble polymers.

This demonstrates the significant effect that the solubility of B100 can have on the amount of measured total insolubles. These results are especially significant when one remembers that most biodiesel is used in a blend with petroleum diesel fuel, a significantly less polar solvent than B100. And, we can expect that this solubility difference will grow as more ultra-low sulfur diesel fuel appears in the marketplace as removal of heteroatoms and aromatics will make this fuel a less polar solvent. These results support the inclusion of a measurement of iso-octane insolubles in any oxidation test that measures insolubles formation.

Table 8. Results for Testing of B100 by Modified D2274 (95°C)

Biodiesel	Total Insolubles (mg/100 ml)	Total Acid Number (mg KOH/g)	Kinematic Viscosity @ 40°C, mm^2/s	*iso*-octane Insoluble Material (mg/100 ml)
Soy	7.7	7.1	6.6	2.1
Yellow Grease	4.1	1.5	5.3	1.4

Table 9. Modified D2274 (110°C) of B100 and B100 plus Antioxidant

		mg/100 ml			
Sample	**Tube**	**Filt. Insols**	**Adh. Insols**	**Tot. Insols**	**Iso-octane Insols**
Soy	1	0	3.4	3.4	19.4
	2	10.7	2	12.7	15.7
Soy + 500 ppm TBHQ	1	0	2.8	2.8	16.1
	2	7.9	2.1	10	18.2
Soy + 500 ppm Pet AO 203	1	17.3	1.9	19.2	15.3
	2	19.7	3.2	22.9	13.2
Yellow Grease	1	0	2.2	2.2	48.0
	2	0	2.6	2.6	40.2
Yellow Grease + 500 ppm TBHQ	1	0	1.9	1.9	38.2
	2	0	1.5	1.5	35.8

At this higher temperature, the soy-derived B100 tended to form more total insolubles but less iso-octane insolubles as compared to the yellow grease B100. Also, there seems to be little measurable effect of addition of antioxidant. The only exception is the marked increase in filterable insolubles when the petroleum antioxidant was added.

One interesting observation from these D2274 results is presented in Table 10. Note that raising the test temperature from 95°C to 110°C had almost no effect on the measured total insolubles but a very marked effect on the amount of iso-octane insolubles. These data further demonstrate the significant ability of B100 to solubilize polymers formed during oxidation. If this relationship holds true for most biodiesel fuels, it has direct effect on the selection and use of this test in a biodiesel specification. It means that the results of this test can probably not be used to predict insolubles or deposit-forming tendencies at some specific time in the future. Solubility, especially in a biodiesel blend, will have a large effect. This test does not measure an induction period or "antioxidation-

capacity" of any type. It does, however, provide a measure of the insoluble/polymer forming characteristics of the B100. At this time, though, there is no correlation between these test results and insoluble/polymer concentrations at any given time in the future.

Table 10. Modified D2274 – Polymer Solubility				
	Tot. Insols, mg/dl		Iso-octane Insols, mg/dl	
Test Temperature, °C	95	110	95	110
Soy	7.7	8	2.1	19
Yellow Grease	4.1	2.4	1.4	48

If a more detailed time/temperature matrix study is conducted, including the solubility factor, it should be possible to select a time and temperature suitable for this application. Since some previous work has shown that temperatures above 80°C can mask additive effects, the study should include B100 samples both with and without antioxidants.

4.3 ASTM D6468

The results are presented in Table 11. These results support the widely held assertion that the thermal stability of B100, as measured by this test, is very good. Figure 9 presents similar results obtained in an earlier program. In that project, both B100 and petroleum diesel samples were tested. The B100 samples had very little thermal degradation as measured either by reflectance or filter weight. The petroleum diesel samples, however, showed significant differences in their thermal stability characteristics.

Table 11. Results for D6468 Tests				
Sample	**90 minutes**	**180 minutes**	**90 minutes**	**180 minutes**
	% Reflectance		**Gravimetric, mg/100 mL**	
Soy	96	96	0.8	1.2
Yellow Grease	96	96	0.4	0.7

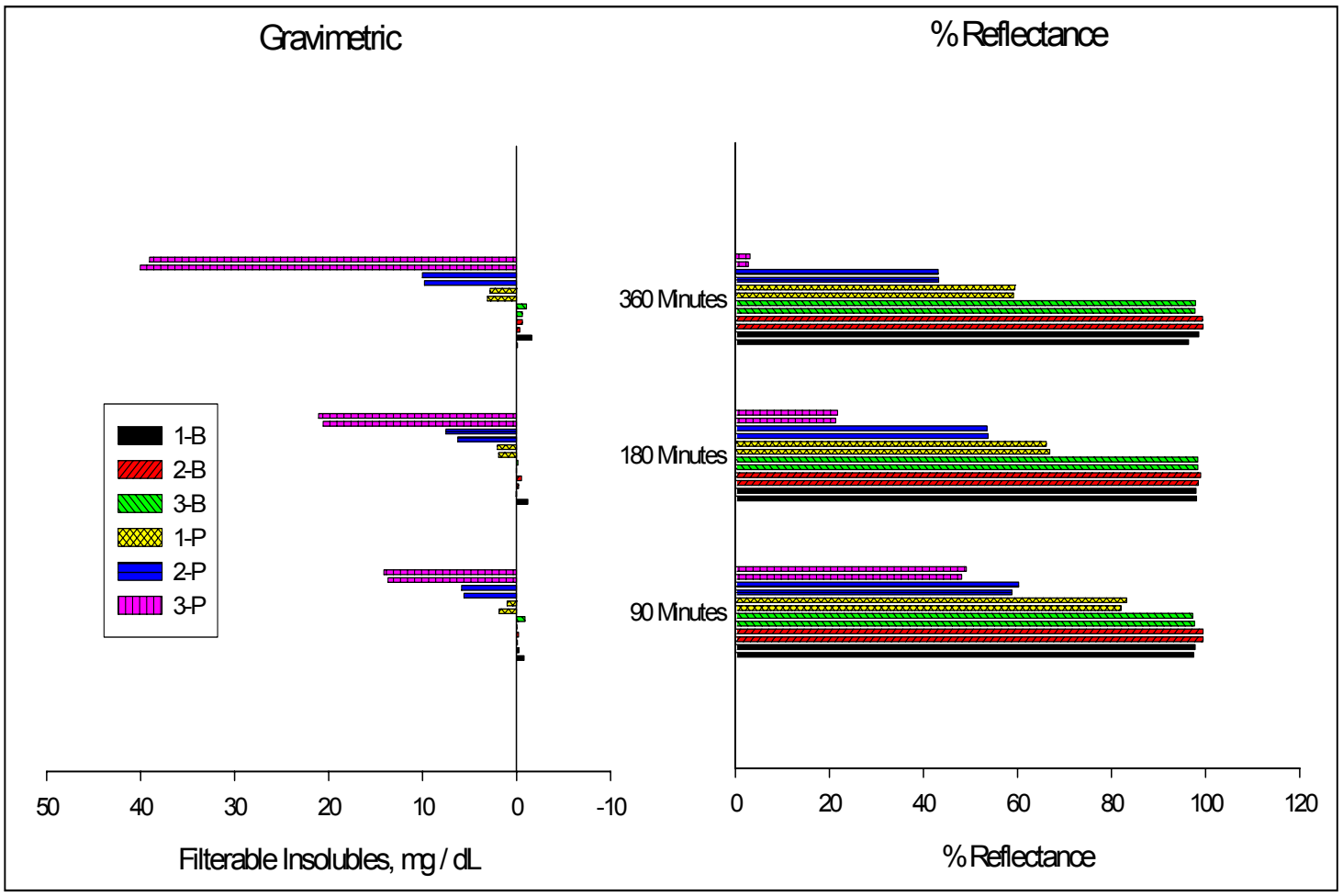

Figure 9. Thermal Stability D6468, Test Results for B100 and Petroleum Diesel Samples (See Reference 9).

4.4 EN 14112 (Rancimat)

There are two new European standards for biodiesel: EN 14213, for home heating fuel and EN 14214 for automotive diesel fuel. Both of these standards contain stability requirements based on the Rancimat test.

- Heating fuels - Fatty acid methyl esters (FAME) - Stability Requirement: Rancimat Induction Period @ 110°C ≥ 4 hours.
- Automotive fuels - Fatty acid methyl esters (FAME) for diesel engines - Stability Requirement: Rancimat Induction Period @ 110°C ≥ 6 hours.

Because the Rancimat test is included in these two European specifications, it is in much wider use in Europe as compared to the United States. Also, the amount of data from running the test on biodiesel samples is greater in Europe.

One significant difference regarding the use of the Rancimat test in Europe vs. the U.S. is that most of the B100 produced in Europe is rapeseed-based. Most of the biodiesel produced in the U.S. is made from soybeans or yellow grease. Because of its composition (lower polyunsaturated content), the rapeseed methyl ester (RME) tends to have significantly longer Rancimat induction periods than either soy or yellow grease. Typical induction periods for RME are 4-6 hours as compared to 1-2 hours for soy and yellow grease. The Rancimat induction periods for the test fuels, at several temperatures, are presented in Table 12.

These much shorter induction periods mean that the sensitivity of the Rancimat is greatly reduced when testing typical U.S. B100. Two possible ways to increase the sensitivity when testing U.S. B100 are:

- Treat the B100 with antioxidant to increase the measured induction period. However, it is not yet certain that additive effects are linear with different fuels.
- Run the test at a temperature below the 110°C temperature currently used in the European specifications and proposed for U.S. specifications. This approach will only work if the oxidation reactions of the methyl esters, are unchanged by temperature changes in the range suggested.

Table 12. Rancimat Test Results

Sample	Temperature, °C	Induction Period, h
Soy	120	0.45, 0.48, 0.50, 0.51
Yellow Grease	120	2.19, 2.30, 2.31, 2.40
Soy	110	0.67, 0.61, 0.77, 0.65
Yellow Grease	110	4.81, 5.02, 5.11, 4.80
Soy	100	0.88, 0.89
Yellow Grease	100	10.01, 10.24
Soy	130	0.43, 0.42
Yellow Grease	130	1.07, 0.87
Soy/Yellow Grease Blends	110	
25/75		1.63, 1.42
50/50		1.18, 1.23
75/25		0.94, 0.92

Figure 10 is an Arrhenius Plot of the Rancimat results for several samples of B100. Note the significant changes in induction period, for some of the samples, as the temperature decreases. This plot suggests that, for the 100°C to 130°C range, it should be possible to change the test temperature of the Rancimat without significantly changing the reaction mechanisms.

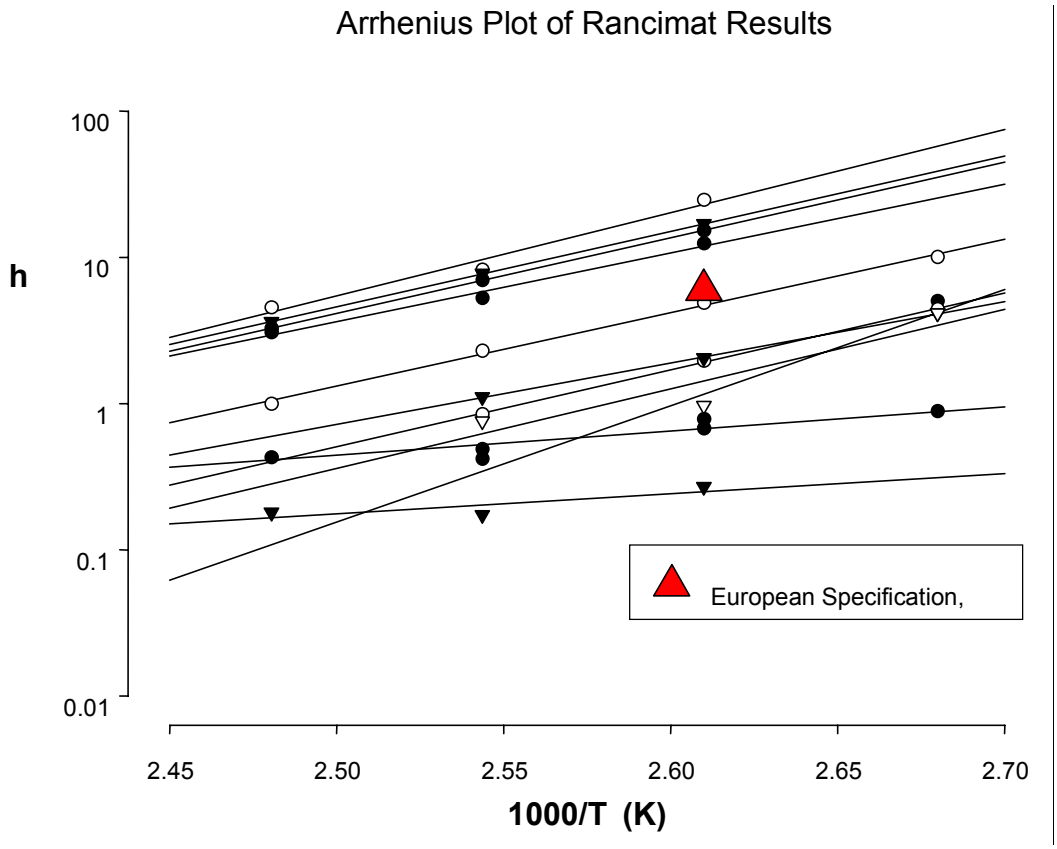

Figure 10. Arrhenius Plot of Rancimat Induction Periods at Selected Temperatures

4.5 ASTM D3241 (JFTOT)

The JFTOT results are presented in Table 11 and plotted in Figure 11. The soy sample shows a steady increase in deposit formation as temperature rises. It is unknown whether deposit volume would reach a maximum at some higher temperature. The yellow grease appears to have reached a maximum at some temperature below 225°C and is decreasing slightly between 225°C and 230°C, at which temperature the deposit volume appears to remain constant with increasing temperature.

Because of the small sample size, the data are inconclusive. Further study to evaluate this test method is warranted. The JFTOT could be a significant tool for studying high temperature deposit formation with B100. However, the JFTOT is not likely to be useful as an oxidation stability test for specification purposes. Multiple tests would be required to establish the induction period of a given B100; the time and cost of which could be prohibitive.

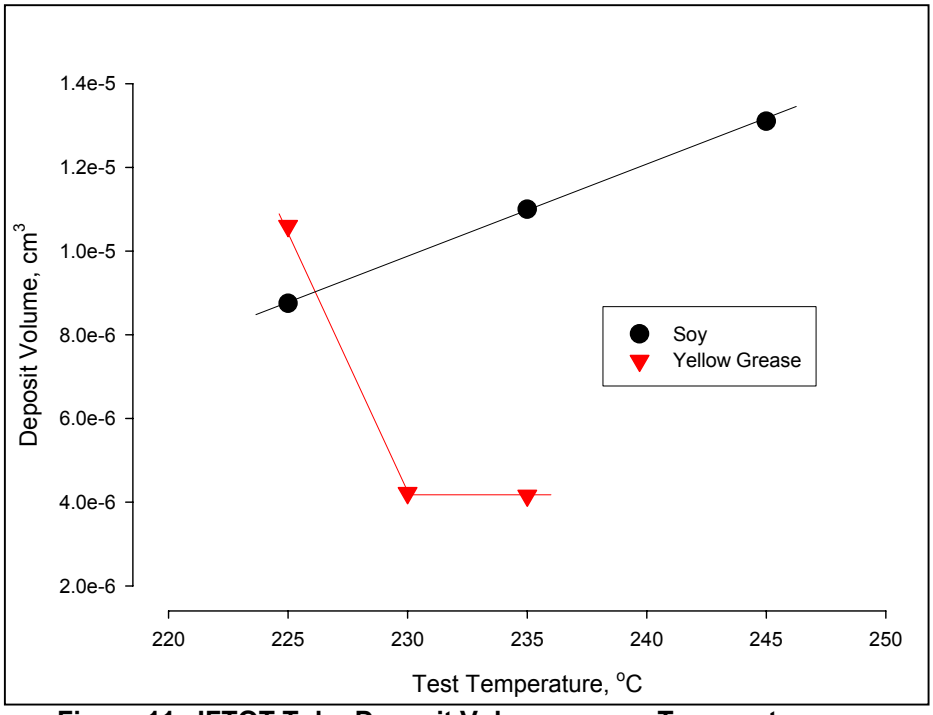

Figure 11. JFTOT Tube-Deposit Volume versus Temperature

Table 13. Results of Testing B100 Samples by ASTM D3241 (JFTOT)			
Sample	Test Temperature, °C	Deposit Rating	Deposit Volume±, cm^3
Soy	225	1A*	8.75×10^{-6}
	235	1A	1.10×10^{-5}
	245	1A	1.31×10^{-5}
Yellow Grease	225	2	1.06×10^{-5}
	230	2	4.22×10^{-6}
	235	2	4.16×10^{-6}
*A= Abnormal deposit as compared to typical petroleum jet fuel deposits.			
± Deposit volume was measured with an ellipsometric, tube-deposit, measuring instrument.			

4.6 HPDSC

The biodiesels were analyzed using a modified version of ASTM D5483, ramped-temperature method. The results obtained are presented in Table 14. The analyses indicate that this test does not give useful results regarding the oxidation stability of B100. There is insufficient differentiation between the samples under the conditions used. The heating started at room temperature and increased at 5°C/min up to 200°C.

Table 14. HPDSC Results for Biodiesel Plus Antioxidants (Temperature Ramp = 10°C/min)		
Biodiesel	**Additive, 500 ppm (See Table 11 for Additives)**	**Oxidation Induction Time, OIT, min**
Soy	None	15.24
	04-202	14.66
	04-203	14.48
	04-204	14.77
	04-205	14.93
Yellow Grease	None	14.92
	04-202	15.70
	04-203	15.35
	04-204	15.23
	04-205	15.34

4.7 IP Method 306 (Modified)

The results for this testing, given in Table 15, are similar to those for the modified D2274. They again demonstrate the effect of solubility on the measured results, with relatively high levels of iso-octane insolubles because of the relatively high test-temperature of 120°C. This method could be used in lieu of D2274 although it is not as familiar in the U.S. diesel fuel community as is D2274. Also, the work-up procedures for this test are slightly more involved than D2274.

Table 15. Results for Testing of B100 by Modified IP 306				
Biodiesel	**Total Insolubles, mg/L (Filt/Adh)**	**Soluble Acidity (mg KOH/g)**	**Volatile Acidity (mg KOH/g)**	***iso*-octane Insoluble Material (mg)**
Soy	15.6 / 8.4	2.5	2.3	30
Yellow Grease	11.2 / 8.9	2.0	1.8	135

4.8 Antioxidant Additives

Because of the questions regarding test temperatures and additive response with the D2274 test (See Section 4.2 above), the decision was made to use the Rancimat method for the antioxidant efficacy study. In addition to the food grade antioxidants traditionally used in B100 (such as BHT and TBHQ) we obtained 4 petroleum antioxidants from a petroleum additive supplier for evaluation. The additives are described in Table 16. The Rancimat test results are presented in Tables 17 and 18. Of the food grade additives, only TBHQ caused a significant increase in the induction time for the soy B100. The food grade additives gave a slight improvement in the induction times of the yellow grease. The petroleum additives caused a significant increase in the induction period of the yellow grease. Selected test results are also plotted in Figures 12 and 13. Figure 12 demonstrates that additive effects tend to be linear but not equivalent. This relationship could allow biodiesel suppliers to determine necessary treat rates, with a given additive, to reach a pre-selected Rancimat induction period. That is especially useful if the

Rancimat test is selected for D6751 specification purposes. These results demonstrate that the Rancimat can discriminate antioxidant additives. However, it is possible that a lower test temperature, say 90°C or 100°C will be required when evaluating the effects in some biodiesel samples.

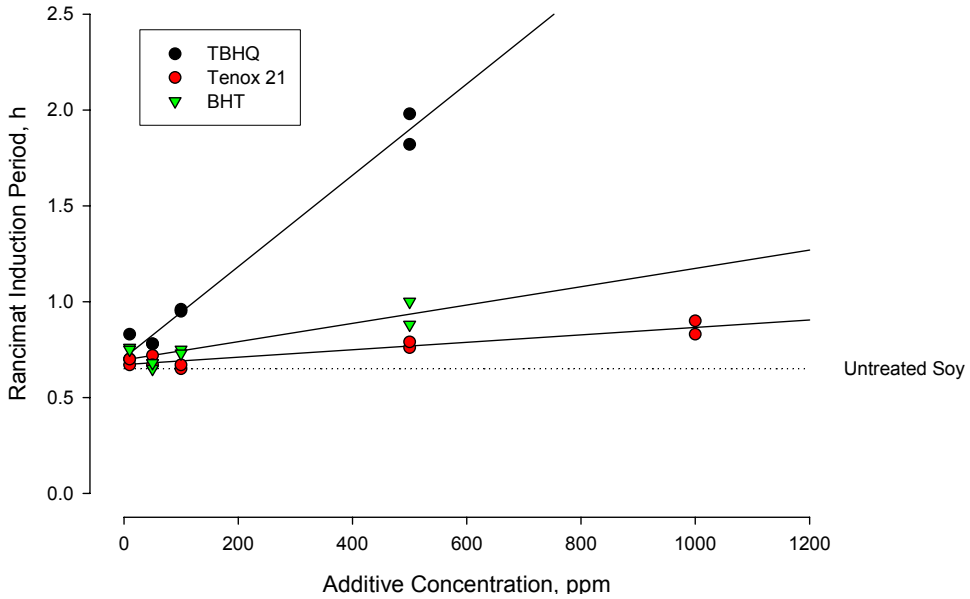

Figure 12. Antioxidant Efficacy for Three Food-Grade Additives via Rancimat at 110°C, soy based biodiesel

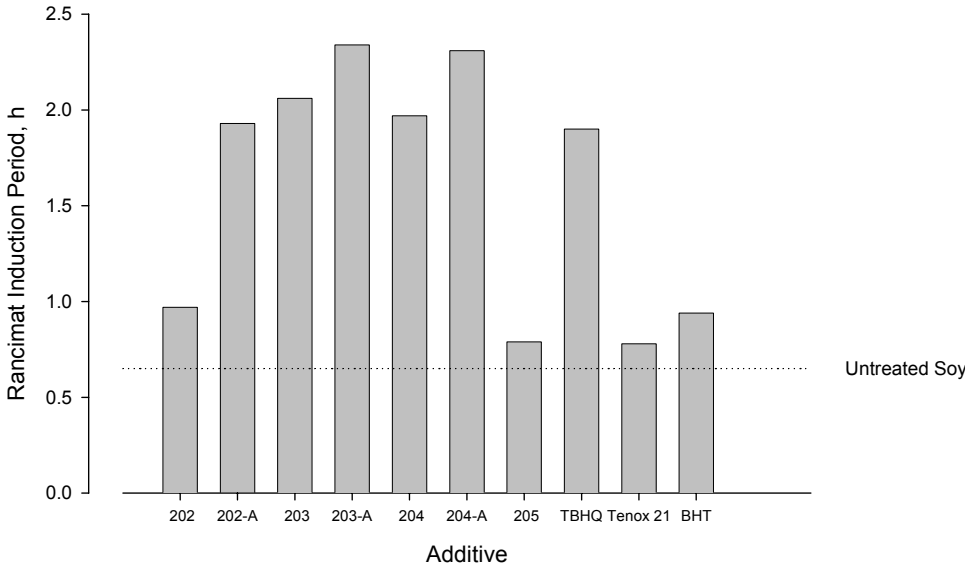

Figure 13. Comparison of Antioxidant Effects for Selected Petroleum and Food-Grade Additives, Rancimat at 110°C.

Table 16. Description of Additives Used	
Additive	**Description**
BHT	Butylated phenol
TBHQ	Hindered phenol
Tenox 21	20% TBHQ+1% citric acid
04-202	Substituted phenol liquid
04-203	Butylated phenol
04-204	Alkylated phenol, functionalized
04-205	Mixture phenol/amine types

Table 17. Effect of Food-Grade Antioxidants -- Rancimat Testing		
Sample	**Test Temperature**	**Induction Period, h**
Soy + TBHQ	110	10 ppm: 0.83,0.70 50 ppm: 0.75, 0.78 100 ppm: 0.95, 0.96 500 ppm: 1.98, 1.82
Soy + Tenox 21	110	10 ppm: 0.67, 0.70 50 ppm: 0.72, 0.67 100 ppm: 0.65, 0.67 500 ppm: 0.76, 0.79 1000 ppm: 0.83, 0.90
Soy + BHT	110	10 ppm: 0.76, 0.75 50 ppm: 0.65, 0.68 100 ppm: 0.75, 0.73 500 ppm: 1.00, 0.88

Table 18. Effect of Petroleum Antioxidants -- Rancimat Testing			
B100	**Additive @ 500 ppm**	**Induction Period, h**	
		110°C	**120°C**
Soy (04-200)	04-202	0.92, 1.02	0.45
	04-203	2.03, 2.08	0.99, 1.23
	04-204	2.26, 1.67	0.83, 0.87
	04-205	0.77, 0.80	0.43, 0.41
Yellow Grease (04-201)	04-202	16.12, 14.47	3.86, 5.83
	04-203	12.65, 12.33	5.11, 5.48
	04-204	24.56, 25.14	7.77, 8.71
	04-205	17.07, 16.82	7.86, 7.65

4.9 Oxidation Stability of Commercially Available B100 Fuels

The Rancimat results presented in Tables 19 and 20 are for B100 samples taken from various sources. The samples in Table 19 were obtained from a survey of commercially available B100 throughout the United States. The samples in Table 20 are a mix of samples on-hand at SwRI during this project. More complete descriptions of any of these samples were not readily available. Taken all together, these results demonstrate the varied range of results typical of current U.S. biodiesel. The most significant point is that

nearly all of these samples have induction periods well below the European specification of 6 hours, minimum.

Table 19. Rancimat Test Results for B100 Fuel Quality Survey Samples		
Lab ID (No Description was Available)	**Induction Period, h**	
	110°C	**120°C**
04-132	0.66, 0.68	0.49, 0.50
04-133	0.55, 0.39	0.14, 0.18
04-135	1.64, 1.57	0.74, 0.86
04-136	0.52, 0.51	0.39, 0.40
04-137	1.21, 1.24	0.54, 0.60

Table 20. Rancimat Results for Samples of Commercially Available B100 Fuels from Various Sources	
Sample Description	**Rancimat Induction Period, h**
CL04-395, Soy B100 plus antioxidant	5.12, 5.05
CL04-396, Y.G., 2763-001C	5.37, 5.32
CL04-397, Soy B100	0.18, 0.55
CL04-398, Canola B100	4.86, 4.81
B 100	0.9
B 100 + antioxidant	1.3
Rapeseed Methyl Ester	1.5
Rapeseed Methyl Ester plus 100 ppm BHT	4.9

4.10 Tests of B20 by D2274 and Rancimat

B20 blends with low sulfur diesel and kerosene were prepared using both the soy and yellow grease biodiesel samples. The modified D2274 and Rancimat results are presented in Table 21. This limited set of data suggests a correlation between the results of these two tests for B20 blends. Further investigation is warranted. As ultra-low sulfur diesel fuel becomes more available on the open market, there should be some specific studies of B20 blends with these fuels.

Table 21. Rancimat Test (110°C) Results for B20 Blends		
Sample	**Modified D2274, mg/100mL Filt/Adh/Total**	**Rancimat Induction Period, h**
CL04-221, Soy / Low Sulfur Diesel	3.1/0.3/3.4 2.7/0.3/3.0	11.23
CL04-222, YG / Low Sulfur Diesel	0.0/0.1/0.1 0.0/0.1/0.1	> 24
CL04-223, Soy / Kerosene Fuel	0.0/0.2/0.2 0.0/0.2/0.2	> 24
CL04-224, YG / Kerosene Fuel	0.0/0.1/0.1 0.0/0.1/0.1	> 24

5.0 Conclusions on Selection of an Oxidation Stability Test Method for B100

5.1 Test Methods

The test methods evaluated during this project were:

- ASTM D4625, Standard Test Method for Middle Distillate Fuel Storage Stability at 43°C (110°F).
- ASTM D6468, Standard Test Method for High Temperature Stability of Distillate Fuels. Modified for gravimetric determination of insoluble formation.
- ASTM D2274, Standard Test Method for Oxidation Stability of Distillate Fuel Oil (Accelerated Method). Modified, specifically for use with biodiesel, as described in this report.
- ASTM D3241, Standard Test Method for Thermal Oxidation Stability of Aviation Turbine Fuels (JFTOT Procedure).
- EN 14112, the Rancimat Test, Fat and oil derivatives. Fatty Acid Methyl Ester (FAME). Determination Of Oxidation Stability (Accelerated Oxidation Test).
- Modified IP 306, Determination Of Oxidation Stability Of Straight Mineral Oil.
- ASTM D5483, Standard Test Method for Oxidation Induction Time of Lubricating Greases by Pressure Differential Scanning Calorimetry.

The test methods were evaluated for their applicability to the measurement of biodiesel, ability to discern additive effects, and ability to discriminate between biodiesel samples of various levels of oxidation stability.

ASTM D4625 is an excellent method for estimating the long-term storage stability of middle distillate petroleum fuels. One week of storage at 43°C is widely accepted as equivalent to 4 weeks at 15°C (underground, ambient storage). While the same relationship has yet to be proven for B100, most researchers have tended to accept that the correlation holds. This makes D4625 an excellent research method but it is not acceptable as a specification test.

ASTM D6468 has existed in nearly the same form (albeit different names) for over 60 years. Its very short 90-minute test time makes it a very attractive test for quality assurance and quality control. The 150°C test temperature makes this test quite severe. There is no active addition of air or oxygen to the fuel during testing so this test is not as useful for measuring oxidation stability. Also, this test method has historically relied on estimating the amount of insolubles formed based on the darkness of the material trapped on a filter pad. Biodiesel insolubles tend to be far less dark in color than petroleum diesel; and, as such, are more difficult to quantify using optical methods. Gravimetric measurement of insolubles provides more reliable quantification. Biodiesel tends to be very thermally stable but less oxidatively stable when compared to petroleum diesel. This test method does not provide a useful discrimination between biodiesel fuels of varying quality. This test may, however, be useful for B20 but more work is needed.

ASTM D3241 (JFTOT) will require additional study to determine if it can be used to measure the oxidation stability of biodiesel. This test is quick and simple to perform. There are numerous methods for quantifying the deposits formed although most are visual so not as useful. The ellipsometric tube-rating instrument shows promise since deposit color does not affect the measurement. This test method is a specification test for aviation fuel so there is already acceptance of the results for specification purposes. The greatest strength of this test may be as a measure of the tendency of a biodiesel to form deposits on a hot metal surface. In general, there is currently insufficient data to recommend this test as a specification test but it deserves additional study.

IP 306 is a strong candidate for a specification test. It is oxidizing and it measures both total and iso-octane insoluble material. It uses a relatively small 100-mL sample size, which tends to reduce the precision and sensitivity of the method. Also, it is not as widely used in diesel fuel test laboratories so the glassware is not as commonly found. This test method could be used in a specification but is so similar to the more commonly run D2274 that D2274 is probably a better choice.

ASTM D5483 as used in this study, failed to give useful results regarding the relative stabilities of various fuels. Still, research into the use of DSC continues and it is reasonable to assume that a suitable method can be developed. At such time, the method should be considered a viable candidate for inclusion in a specification.

At this time, there are two likely choices for an oxidation stability test for B100 (D6751). Those two choices are the Rancimat test and some modification of ASTM D2274.

5.1.1 Rancimat Test

This test is well established in Europe and is included in several European specifications. It is quick and simple to run and could be completed in a single work shift (a plus for using it as a specification requirement). It provides a repeatable measure of the antioxidant capacity of the biodiesel although the relationship of that measure to the field has not been established.

This test does not give any measure of polymer forming tendencies. It is believed that some types of B100 are more prone to forming polymers (and insolubles) than others. This could be a factor when some formation of insolubles is considered acceptable.

5.1.2 Modified D2274

Unlike the Rancimat, this test gives no measure of induction period. It is presumed that all antioxidant capacity in the B100 is consumed during the test. Hence, this test is more a measure of the tendency of the B100 to form polymers and insolubles. For those concerned about the formation of these materials, D2274 is probably a better screening tool/test.

The current versions of the test are at least 16 hours long but it may be possible to shorten the aging period to allow completion within a single shift. Doing so would require substantial additional work.

It may also be necessary to change the test temperatures of both of these tests to allow better discrimination between samples and also additives.

5.2 Specification Limits

The European specification for B100 includes a 6-hour minimum Rancimat induction period. The vast majority of U.S. biodiesels have Rancimat induction periods that range between 1 and 4 hours. Limited testing has shown that excessive amounts of currently used antioxidants would be required before most U.S. fuels could meet the European specification. Additionally, to date there has been no controlled study of the minimum induction period required to minimize the chance of problems in the field. Many in the industry point to the lack of reported problems, linked to unstable biodiesel, as proof that U.S. fuels are for the most part acceptably stable. As such, it is expected that any ASTM specification that uses the Rancimat will probably have a lower minimum induction period, perhaps 4 hours rather than 6.

In contrast, biodiesel tends to form more insolubles in tests like D2274 when compared to petroleum diesel. Historically, specifications that include D2274 have set limits of 1.5 to 2.5 mg/100mL, maximum. This would likely be too restrictive for U.S. biodiesel (and perhaps European fuels as well). A slightly relaxed requirement of perhaps 4.0 mg/100, maximum, may be more appropriate. However, inclusion of iso-octane insolubles measurement will alter that limit. Additional work is needed to find an acceptable limit with this test method.

5.3 Antioxidants

In general, each of the test methods showed the relative efficacy of various antioxidants. The relative ranking was similar but not always exactly the same. Test times and temperatures seem to have a significant effect with some of the tests, such as D2274.

Historically, food-grade antioxidants have been the additives of choice for biodiesel. This project was able to show that petroleum antioxidants can give equal or greater protection against oxidation. Antioxidant efficacy in biodiesel blends, especially with ultra-low sulfur diesel, must be studied further. It is assumed that ULSD will be far more susceptible to oxidation since natural inhibitors are removed along with the sulfur compounds. Some combination of food-grade and petroleum additives may be required in the near future.

List of Acronyms

ASTM	American Society of Testing and Materials, ASTM International, a standards setting organization
B100	100% Biodiesel
B20	A blend of 20% biodiesel in petroleum diesel
BHT	Butylated hydroxy toluene
DSC	Differential scanning calorimetry
EN	European Normalization
FAME	Fatty acid methyl ester
GCMS	Gas chromatography mass spectrometry
HPDSC	High pressure differential scanning calorimetry
IP	Institute of Petroleum
JFTOT	Jet fuel thermal oxidation test
NREL	National Renewable Energy Laboratory
RME	Rapeseed methyl ester
TBHQ	Tert-butyl hydroquinone
ULSD	Ultralow sulfur diesel (15 ppm S in the US).
USDOE	United States Department of Energy

References

[1] All ASTM Methods Published by ASTM International, West Conshohocken, PA; www.astm.org

[2] Stavinoha, L.L. and Howell, S. "Potential Analytical Methods for Stability Testing of Biodiesel and Biodiesel Blends" SAE Technical Paper No. 1999-01-3520 (1999).

[3] McCormick, R.L. personal communication, 2005.

[4] FAME Analyses conducted and provided by NREL, Golden, CO.

[5] Bondioli, P, Gasparoli, A., Della Bella, L., Tagliabue, S. "Evaluation of Biodiesel Storage Stability Using Reference Methods" *Eur. J. Lipid Sci. Technol.* 104 777-784 (2002).

[6] de Man, J.M., Tie, F., and de Man, L. "Formation of Short Chain Volatile Organic Acids in the Automated AOM Method: *J. Am. Oil Chem. Soc.* 64 993-996 (1987).

[7] Miyata, I., Takei, Y., Tsurutani, K., and Okada, M. "Effects of Bio-Fuels on Vehicle Performance: Degradation Mechanism Analysis of Bio-Fuels" SAE Technical Paper No. 2004-01-3031 (2004).

[8] "Determination of Oxidation Stability of Straight Mineral Oil," [Formerly Institute of Petroleum, now Energy Institute] Standard Test Method 306.

[9] Westbrook, S.R. and Stavinoha, L.L., 'Biodiesel And B20 Blends: Stability Test Methods And Stability Characteristics," *IASH 2003, the 8th International Conference on Stability and Handling of Liquid Fuels,* Steamboat Springs, Colorado, September 14-19, 2003.

[10] Fang, H. L., "Deposit Formation of Biodiesel," Presentation, August 2004.

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