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Thermal and Oxidative Instability in Biodiesel Blends During Vehicle Use and Onboard Fuel Storage

Final Report

August 2016



COORDINATING RESEARCH COUNCIL, INC. 5755 NORTH POINT PARKWAY • SUITE 265 • ALPHARETTA, GA 30022

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FINAL REPORT

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EXECUTIVE SUMMARY

This report covers CRC Project AVFL-17c to study the thermal and oxidative stability of biodiesel blends during vehicle use and onboard storage. The CRC considers the work reported herein as Phase I of a potentially larger-scope project. The objective of this first phase was to examine the impacts of various aspects of fuel stability (temperature, pressure, oxidation, free radical formation, acid formation, etc.) on biodiesel blends during onboard vehicle use and storage conditions. More specific goals included:

- Identify the environmental conditions and chemical processes which influence thermal and oxidative instability (via a literature review).
- Investigate the relationship between such processes and a measurable property of the fuel such as the onset/presence of free radicals, peroxide formation, acid number, oxidation induction period, etc.
- Develop a surrogate process or performance test to simulate those impacts similarly to the effect of fuel stored in a light duty vehicle operated on a daily basis.
- Create oxidized biodiesel blends according to a given oxidation stability requirement.

The project was divided into 6 different tasks:

Task 1 – Conduct a literature review of oxidation and thermal fuel stability parameters as pertains to vehicle use and storage. The review also included looking for possible fuel stability screening tools or test methods.

Task 2 – Based on the results of Task 1, input from technical contacts, and SwRI experience, make selections of pertinent vehicle technology pertaining to possible stability parameters. This task also included gathering available information regarding fuel residence time, fuel temperatures, and system pressures in actual light duty vehicles operating in hot, summer-time conditions.

Task 3 – Identify and obtain test fuels.

Task 4 – Vehicle testing to collect fuel system condition data and effects on biodiesel degradation.

Task 5 – Develop bench-scale, fuel-stressing methodology to mimic the conditions that fuel experiences in HPCR fuel systems.

Task 6 – Provide recommendations for Phase II (fuel effects testing) to CRC.

Information and conclusions from each task are given below:

Task 1: Literature Review – Thirty three reports and papers were reviewed for information relevant to this study. Nine of the documents contained information useful to the current project and are summarized in the body of the report.

Task 2: Test Vehicles – Two different light duty vehicles were used in this study. They were a 2013 Chevrolet Silverado pickup truck and a 2012 Mercedes ML350 Blue Tec. These two vehicles were used in order to have a light duty truck and a passenger automobile. It was thought that these vehicle types would offer some differences in the fuel systems; which would, in turn, have different effects on the fuel. Each vehicle was instrumented to collect various data during the testing. Of primary concern was fuel temperature and pressure data that could be helpful in the design of a fuel-stressing apparatus.

Task 3: Test Fuels – Initially, two hydrocarbon-only diesel fuels and two B100 biodiesels were selected as candidate fuels for the study. The project called for preparing three final test fuels, B0, B5, and B20, using two of the candidates. It was decided to use a commercially available ULSD and a soy-derived B100 as the blend components. The ULSD was thought to be more widely used than the TX-LED fuel and the soy biodiesel was chosen because it was more commonly used commercially in the US than mixed-fats biodiesel.

Task 4: Vehicle Testing – The objectives of the vehicle testing were: 1) Mimic the degradation of specification-quality biodiesel blends seen by CRC AVFL members in other vehicle studies. 2) Identify analytical methods capable of detecting degradation of the test fuels during vehicle operation. 3) Determine the maximum temperatures and pressures that occur in the vehicle fuel systems. These parameters could then be used in designing non-vehicle, fuel-aging rigs. 4) Measure the conditions of fuel temperature and pressure in a light duty vehicle operating in summer. 5) Expose fuel(s) to these conditions and evaluate the effect on the fuel as measured by numerous candidate fuel stability test metrics.

The B0 and B5 blends were run in both vehicles in an on-road evaluation and in a heated dynamometer facility. Vehicles data such as temperatures and pressures were collected from numerous locations throughout the testing. Fuel samples were collected at pre-determined times and submitted for analysis. Fuel analyses included oxidation stability tests, total acid number, peroxides, and thermal stability. A B20 blend was also tested in the Silverado in the heated dynamometer facility. Air-sparging of the B20 was conducted during the testing to investigate effects of increased oxygen mixing in the fuel.

The fuel analyses indicated that the fuels underwent relatively mild oxidative degradation during the vehicle operation. The two oxidation stability tests, Rancimat and Rapid Small Scale Oxidation Test were the most sensitive to changes in the fuel. These two methods also exhibited good repeatability. Thermal stability of the fuel remained virtually unchanged throughout the vehicle testing.

Task 5: Bench Scale Fuel-Stressing Methodology – The fuel-stressing capability was designed to provide a means to realistically stress test fuels in quantities up to about 50 gallons. The stressed fuels would then be available for other testing in the laboratory or in vehicles. This task used a newly-developed (by SwRI) test technique based on the High Reynolds Number Thermal Stability (HiReTS) tester. The HiReTS is the equipment used in ASTM D6811, Standard Test Method for Measurement of Thermal Stability of Aviation Turbine Fuels under Turbulent Flow Conditions. Two test fuels were used in this task. Both were B20 blends made from the B0 and B100 used for all the test fuels in this project. Test fuel 1 was the B20, as prepared. Test fuel 2 was the same B20 with added water (200 ppm, total) and added vegetable oil (3 wt%). Each test fuel was stressed according to a strict protocol designed to mimic conditions seen during the vehicle testing. Fuels reached a high temperature of 110 °C and 500 psi pressure. Samples were taken at pre-set intervals for laboratory testing. Each of the fuel samples taken during the fuel stressing process was analyzed by test methods including oxidation stability tests, distillation, peroxides, total water, total acid number, jet fuel thermal oxidation test (ASTM D3241), and high temperature stability. The Rapid Small Scale Oxidation Tester was the most consistent indicator of changes in the fuel, followed closely by the Rancimat test. Samples analyzed by the D3241 test were found to give varying amounts of deposits on a heated metal tube. Measurements of the deposits using an ellipsometric technique provided useful information. Remaining test results were less indicative.

Task 6: Recommendations for Phase II (fuel effects testing) to CRC – A more detailed study of the effects of various fuels, blend components, vehicle environments (such as metals, elastomers, and available oxygen) and additives is needed. Emphasis should be placed on testing a variety of fuels and fuel blend components. The aged fuels should be tested using the RSSOT, Rancimat, and D3241/ellipsometer as indicators of change in the fuel. The ellipsometer also provides a reliable indication of relative deposit forming characteristics.

It is recommended that efforts be made to improve the usefulness of the ellipsometric analysis of heater tubes when testing diesel fuel. These could include investigation of using a different temperature profile, to possibly cause deposits elsewhere on the tube, or a new ellipsometer designed to measure more of the heater tube surface.

Use of a D3241-type analysis for the study of diesel and biodiesel blends could provide very valuable information about fuel, additive, and contaminant effects. A breakpoint approach, currently applied to aviation fuel, would give researchers a tool to quantify some of these effects.

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ACRONYMS & ABBREVIATIONS

0	degree
%	percent
μm	micrometer
AET	Atmospheric Equivalent Temperature
С	Celsius
CFR	Cooperative Fuel Research
EN 15751	Automotive fuels. Fatty acid methyl ester (FAME) fuel and blends with diesel fuel,
	Determination of oxidation stability by accelerated oxidation method.
EPA	Environmental Protection Agency
F	Fahrenheit
FAME	Fatty Acid Methyl Ester (biodiesel)
FBP	Final Boiling Point
g	grams
GC-MS	Gas Chromatography-Mass Spectrometry
GTL	Gas-to-Liquid
h	hour(s)
HFRR	High Frequency Reciprocating Rig
HPCR	High Pressure Common Rail
IBP	Initial Boiling Point
IP	Induction Period
min	minute(s)
NREL	National Renewable Energy Laboratory
OBD	On Board Diagnostics
RSSOT	Rapid Small-Scale Oxidation Test; Apparatus used in ASTM D7545; this
	instrument is also known as the PetroOxy
SwHiReTS	SwRI Designed "SwRI High Reynolds Number Thermal Stability Tester"
SwRI	Southwest Research Institute
TAN	Total Acid Number
Tx-LED	Texas Low Emission Diesel
USLD	Ultra-low sulfur diesel fuel
UV	Ultraviolet

LIST OF ASTM STANDARDS CITED IN THIS REPORT

Designation	Title			
D975	Specification for Diesel Fuels			
D2274	Test Method for Oxidation Stability of Distillate Fuel Oil (Accelerated Method)			
D2709	Test Method for Water and Sediment in Middle Distillate Fuels by Centrifuge			
D3241	Test Method for Thermal Oxidation Stability of Aviation Turbine Fuels			
D4625	Test Method for Distillate Fuel Storage Stability at 43 $^{\circ}$ C (110 $^{\circ}$ F)			
D5304	Test Method for Assessing Distillate Fuel Storage Stability by Oxygen Overpressure			
D5500	Test Method for Vehicle Evaluation of Unleaded Automotive Spark- Ignition Engine Fuel for Intake Valve Deposit Formation			
D6304	Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fisher Titration			
D6468	Test Method for High Temperature Stability of Middle Distillate Fuels			
D6584	Test Method for Determination of Total Monoglycerides, Total Diglycerides, Total Triglycerides, and Free and Total Glycerin in B-100 Biodiesel Methyl Esters by Gas Chromatography			
D6751	Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels			
D6811	Test Method for Measurement of Thermal Stability of Aviation Turbine Fuels under Turbulent Flow Conditions (HiReTS Method)			
D7467	Specification for Diesel Fuel Oil, Biodiesel Blend (B6 to B20)			
D7545	Test Method for Oxidation Stability of Middle Distillate Fuels – Rapid Small Scale Oxidation Test (RSSOT)			

1.0 BACKGROUND AND OBJECTIVES

As diesel engines for light-duty vehicles have evolved, the fuel burned in the engine has been exposed to increasingly severe levels of heat, pressure, and oxidation. These conditions can cause chemical changes (degradation) in the fuel resulting in undesirable, even damaging, consequences to the fuel system. The resistance of fuel to these changes is the stability of the fuel.

The commercial diesel fuel specification, ASTM D975¹, contains no requirement, only guidance (Appendix X3), regarding the stability of diesel fuels. Much of the guidance, as it relates to vehicles and fuel systems, was developed for older technology engines. More modern, common-rail fuel systems expose fuel to significantly higher temperatures and pressures compared to these older technologies. Additionally, the D975 guidance was prepared prior to the allowance for up to 5% biodiesel (B5) and so may not adequately represent that potential concern.

As such, existing stability test methods and specification guidance do not adequately address stability of diesel fuel for modern diesel-powered vehicles. The Coordinating Research Council (CRC) solicited proposals for an investigation of diesel fuel stability to address these concerns.

As mentioned above, fuel stability is typically defined as "the resistance of the fuel to physical and chemical changes brought about by the interaction of the fuel with its environment.²" Most research has divided the general topic of fuel stability into three, broad categories: thermal, oxidation, and storage. Thermal stability is the resistance of fuel to change caused by thermal stress. Oxidation stability is the resistance to change under oxidizing conditions. Storage stability is the resistance to change of fuel, prior to burning it in an engine. For most of the years that diesel fuel has been used, the need to measure, predict, and control the stability of the fuel has resulted in many studies. Some of those studies resulted in the development of standardized stability test methods. Within the United States, the most commonly used test methods are published by ASTM International. A partial listing of diesel fuel stability test methods is given below:

- Standard Test Method for High Temperature Stability of Distillate Fuels, ASTM D6468
- Standard Test Method for Oxidation Stability of Distillate Fuel Oil (Accelerated Method), ASTM D2274
- Standard Test Method for Distillate Fuel Storage Stability at 43 °C, ASTM D4625
- Standard Test Method for Assessing Distillate Fuel Storage Stability by Oxygen Overpressure, ASTM D5304
- Standard Test Method for Oxidation Stability of Middle Distillate Fuels Rapid Small Scale Oxidation Test (RSSOT), ASTM D7545

Some test methods are published by other organizations, such as ISO:

¹ Standard Specification for Diesel Fuel Oils, ASTM Designation D975, ASTM International, West Conshohocken, PA.

² Fuels and Lubricants Handbook: Technology, Properties, Performance, and Testing, G.E. Totten, S.R. Westbrook, and R.J. Shah, eds. Manual 37, p. 125, ASTM International, West Conshohocken, PA. 2003.

• EN 15751, Fatty acid methyl esters (FAME) fuel and blends with diesel fuel – Determination of oxidation stability by accelerated oxidation method. [This test method is more commonly referred to as the Rancimat test.]

Since the introduction of the high-pressure, common-rail (HPCR) fuel system for diesel engines, there has been a growing acknowledgement within the industry that the stability tests listed above do not adequately account for the conditions experienced by the fuel in the fuel system. The temperatures and pressures within the HPCR system are far greater than those in the older technology fuel systems. For the above reasons, it has become necessary to develop new stability test methodology. And, that new methodology must be based on an accurate understanding of the conditions to which diesel fuel is exposed in a modern, diesel-powered, vehicle.

The CRC considers the work reported herein as Phase I of a potentially larger-scope project. The objective of this first phase is to examine the impacts of various aspects of fuel stability (temperature, pressure, oxidation, free radical formation, acid formation, etc.) on biodiesel blends during onboard vehicle use and storage conditions. More specific goals include:

- Identify the environmental conditions and chemical processes which influence thermal and oxidative instability.
- Investigate the relationship between such processes and a measurable property of the fuel such as the onset/presence of free radicals, peroxide formation, acid number, oxidation induction period, etc.
- Develop a surrogate process or performance test to simulate those impacts similarly to the effect of fuel stored in a light duty vehicle operated on a daily basis.
- Create oxidized biodiesel blends according to a given oxidation stability requirement.

2.0 APPROACH

The project was conducted in several tasks, as detailed below.

- Task 1 Conduct a literature review of oxidation and thermal fuel stability parameters as pertains to vehicle use and storage. The review will also include looking for possible fuel stability screening tools or test methods.
- Task 2 Based on the results of Task 1, input from technical contacts, and SwRI experience, make selections of pertinent vehicle technology pertaining to possible stability parameters. This task will also include gathering available information regarding fuel residence time, fuel temperatures, and system pressures in actual light duty vehicles operating in hot, summer-time conditions.
- Task 3 Identify and obtain test fuels.
- Task 4 Vehicle Testing to collect fuel system condition data and effects on biodiesel degradation.
- Task 5 Develop bench-scale, fuel-stressing methodology (mimic the conditions that fuel experiences in HPCR fuel systems)
- Task 6 Provide recommendations for Phase II (fuel effects testing) to CRC.

2.1 Task 1 Literature Review

Appendix A contains a listing of the publications reviewed under this task. Below are several key points of relevant information taken from selected publications listed in Appendix A. These key points were especially useful in guiding the work conducted under this project.

Publication 2. Waynick, J.A., "Characterization of Biodiesel Oxidation and Oxidation Products, Technical Literature Review" CRC Project No. AVFL-2b, August 2005.

The lack of any significant body of adequately controlled engine equipment test results makes it impossible to tie the existing understanding of biodiesel chemistry to the real world. If such adequate controlled engine equipment test results did become available, the needed ties between it and the chemistry aspects could probably be made without further chemistry research except in the area pertaining to the relationship between insolubles formation and other stability-related parameters.

In the absence of actual (and extremely costly) diesel engine equipment testing, specialized test rig programs designed to reasonably simulate engine equipment dynamics may provide valuable information to assist in defining the potential real world problems associated with using biodiesel and the solutions to those problems.

Publication 3. Waynick, J.A., "Characterization of Biodiesel Oxidation and Oxidation Products, Experimental Investigation of Biodiesel Oxidation and Deposition Tendency – Task 2 Results" CRC Project No. AVFL-2b, August 2005.

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.

Using the D3241 test apparatus, 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 D3241 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 D3241 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. With an optimized D3241-type test method, it is likely that the relationship between stability indicators and deposition tendency can be determined if sufficient research is performed. [Author's Note: During the review process for this report, one of the reviewers raised the question of whether the modified D3241 testing conducted in the AVFL-17c project was done with a lower test fuel volume. The testing conducted under AVFL-17c was done with the standard 600 ml sample size. Use of a smaller sample size remains a possible solution to gaining additional sensitivity with diesel fuels that can produce more deposit than conventional D3241 heater-tube rating methods can quantify.]

Publication 17. S.R. Westbrook, An Evaluation and Comparison of Test Methods to Measure the Oxidation Stability of Neat Biodiesel. Subcontract Report. National Renewable Energy Laboratory, NREL/SR-540-38983, 2005.

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-min 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 (D3241) 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.

Publication 23. Bouilly, J., et. al., "Biodiesel Stability and its Effects on Diesel Fuel Injection Equipment," SAE No. 2012-01-0860.

Increasing injector body heating temperature accelerates the formation of deposit and lead to a quicker injection failure.

B20 degradation can lead to injection failure when its IP drop below 3 hr. However peroxide number and total acid number could not be correlated with injection failure time.

Injection failures with B20 fuels occurred only after their oxidation stability (IP) was significantly below the minimum limit specified for current B7 market fuel (EN590:2009)

Publication 25. Velaers, A.J. and Goede, S., "The Properties and Injector Nozzle Fouling Performance of Neat GTL and GTL/EN590 Diesel Blends in Various Diesel Engines," SAE No. 2012-01-1692.

The stability of the neat and blended diesel fuels, as determined by the ASTM D6468, Standard Test Method for High Temperature Stability of Middle Distillate Fuels, stability method, were very good and similar in stability amongst the series of blends.

The ASTM D3241 procedure, as used for the thermal stability measurement of jet fuel, was applied to diesel. Measuring the break point of the fuels gave an indication of the inherent stability of the fuels under specific conditions. In the D3241 testing, EN590 diesel had the lowest stability, while gas-to-liquid (GTL) diesel had far superior stability. The break points of the blends showed a nonlinear relationship between the stabilities of the neat components.

Publication 27. Dodos, G. et. al., "Impact of Oxidation on Lubricating Properties of Biodiesel Blends," SAE No. 2013-01-2596.

The oxidized biodiesel B7 blends, in general, exhibited higher tribological wear and friction coefficient in comparison to their non-oxidized counterparts. On the other hand oxidation of conventional ULSD resulted in enhanced lubricity and considerably improved friction coefficient.

Publication 30. Dodos, G., et. al., "Assessment of the Oxidation Stability of Biodiesel Fuel using the Rancimat and the RSSOT methods," SAE No. 2014-01-2758.

The RSSOT measurements showed that the addition of FAME on conventional ULSD fuel affects the latter's oxidation stability and generally gives rise to higher oxidation rate. However this is not always the case. Castor oil methylester (CAME) not only demonstrated higher induction time from two out of three ULSD fuels but also when added to the corresponding B7 blends it acted cumulatively since the latter were found to be considerably more stable compared to the base fuels. From the rest of the utilized FAMEs, overall palm oil methyl ester (PALME), pomace olive oil methyl ester (POME) and sesame oil methyl ester (SEME) appeared to give rise to less reduction in the oxidation stability of the base fuel. On the other hand cotton seed oil methyl ester (COME) and sunflower methyl ester (SUNME) substantially decreased the oxidative resistance of ULSD fuels.

Nevertheless the base ULSD fuel composition might also play a role. For pure diesel fuel samples it was shown in the RSSOT determinations that the ULSD fuel from the hydrodesulphurization unit has improved - but not significantly - oxidation stability compared to the hydro cracked ones. However, this was not always mirrored in the B7 blends. When comparing the stability results for the HC (severe hydrocracking process) and SR (hydrotreated atmospheric straight run gasoil) blends, it can be seen that in the majority of the cases the HC blends came up with better results.

RSSOT is a rapid method providing good discrimination and it could be more suitable for measuring directly the oxidation stability of fuels/biofuels compared to the Rancimat method. The main advantage of RSSOT over Rancimat method lies in the fact that the former is capable of

determining the stability of pure conventional diesel as well. Based on this, the effect of biodiesel on base diesel fuel's oxidation stability can be evaluated.

Rancimat and RSSOT seem to provide comparable oxidation stability determinations. Under the testing conditions employed, the induction periods produced by the RSSOT method gave very good agreement with the results from the Rancimat unit. Regression analysis was performed on the oxidation stability data by employing both a simple linear and a power-law model. A perfect correlation was found in the case of pure FAMEs ($R^2 > 0.98$) and a very satisfactory correlation was demonstrated when the whole data sets (FAME and B7 Blends) were evaluated ($R^2 > 0.92$). Both models fit well to the measured data, though it appears that the power law regression described better the aggregate results and the linear model was slightly better when analyzing separately the data sets of FAME and B7 Blends.

According to the correlation equations for the linear and nonlinear regression models, the 8 h lower limit in the Rancimat method was found to correspond approximately to 24 min or 27 min in the RSSOT test., whereas a 20-h minimum Rancimat value was associated approximately to 52 or 55 min under the RSSOT method. Further work is being conducted so as to verify and/or extend those preliminary results, however the existing differences in the test conditions and parameters of the two methods should not be disregarded.

Publication 31. Amara, A. B., et. al., "Experimental Study of the Impact of Diesel/Biodiesel Blends Oxidation on the Fuel Injection System," SAE No. 2014-01-2767.

Fuels were aged under accelerated conditions and tested on an injection test rig according to an operating cycle developed to promote injector needle blocking. The soaking duration was found to affect injector fouling. A relationship between the injector fouling tendency and the fuel stability was established. Under current test conditions, injector fouling increased with fuel oxidation measured with Total-Acid-Number. Needle fouling occurred at a TAN level of 0.25 mg KOH/g and needle blocking occurred at a total acid number (TAN) level of 0.5 and 1 mg KOH/g for B20-SME and B20-RME, respectively. The FAME composition and the fuel ageing procedure can have a significant impact on fuel injection system fouling tendency.

This study investigated the direct impact of fuel characteristics on fuel injection system. A procedure for a controlled ageing and a method to provoke Fuel Injection System (FIS) failure on an injection test bed have been developed. In our [publication authors] understanding, complementary to known stability measurements such as Rancimat (EN 15751) and delta TAN (NF EN ISO 12205) specified in diesel fuel specification (EN 590) or PetroOxy [RSSOT] (ASTM D7545) which indicate the fuel stability reserve, TAN measurement is well-adapted for fuel oxidation monitoring for high oxidation level. In the present work, using FAME/Diesel blends in a TAN range of 0.17 to 1.08 mg KOH/g, the build-up of internal deposits within the injectors, after 60h soaking, was correlated to TAN. FAME composition and the fuel ageing procedure can have a significant impact on FIS fouling tendency as well. The dilution of an oxidized fuel with a fresh B0 reduced the fouling rate oxidation but does not eliminate the risk of the injection system degradation or failure.

Publication 33. Christensen, E., et. al., "Impact of a Diesel High Pressure Common Rail Fuel System and Onboard Vehicle Storage on B20 Biodiesel Blend Stability," SAE No. 2016-01-0885.

Biodiesel blends were exposed to relatively high temperatures and high pressures in HPCR-equipped vehicles, and changes in the fuel related to oxidation stability were monitored. These experiments were conducted in a manner intended to simulate harsh, but realistic driving that could compromise fuel stability. Storage stability in the fuel tank was monitored after exposure of the entire vehicle to a hot and dry environment during a test cycle designed to create high fuel temperatures, pressures, and fuel return rates. The biodiesel (B100) utilized for the lower stability blend was out of specification for oxidation stability as the IP value of this blendstock was 1.5 h compared to the 3 h minimum requirement in D6751 (ASTM Standard Specification for B100.) Additionally, it was artificially aged prior to blending to achieve a low enough stability such that the B20 stability was only slightly above 6 hr. The use of highly unsaturated B100 ensured a high concentration of polyunsaturated esters, which are most susceptible to oxidation. This experiment was designed to introduce a potentially problematic, but on-specification B20 to harsh HPCR conditions.

Analysis of fuel from the HPCR return line showed no signs of fuel degradation as a result of the short-term exposure to these extreme conditions. Formation of peroxides is the first step in FAME oxidation, which was not observed in fuels collected in the HPCR return line. The acid numbers and Rancimat IPs were also not impacted by passing through the HPCR. These results indicate the HPCR conditions did not significantly induce fuel degradation via oxidation, at least for short-term, single-pass exposure. The oxidation of FAME to form acids and peroxides requires the presence of oxygen and time for the reaction to occur. The reaction can be accelerated by heat. Because no peroxides or acids formed during exposure to HPCR conditions, it appears that the level of dissolved oxygen present in the fuel, the temperature, and the residence time are such that the initiation of oxidation does not occur.

Subsequent storage stability of the fuel in the tank showed a small decrease in IP over time for the low-stability blend, but no significant change in the high-stability blend. Peroxide values of the B0 and B20s increased during storage; however, the final values measured would not indicate significant fuel degradation. Acid values did not change for any fuel, and the B20s did not differ from the B0; therefore, secondary oxidation products generated by peroxide degradation were not formed during storage. Storage of the low-stability B20 in the fuel tank for 26 weeks showed no change in acid number and an IP above 3 h at the end of this time frame. These results indicate that a B20 with a Rancimat IP of 6.5 h has adequate oxidation reserve to protect against acid and insoluble production when exposed to HPCR conditions and subsequently stored in a fuel tank under the conditions of this study.

The ambient conditions during the 26-week storage time were relatively moderate for the majority of this exposure. It is possible that hotter conditions could accelerate oxidation, leading to a different result. These ambient conditions did not impact the samples taken during the drive cycle (beyond their exposure history) as these were conducted in a running loss test cell with controlled temperature, but do impact conclusions regarding longer-term storage.

This study examined the impacts of HPCR exposure on fuel quality using only one vehicle design. These results may not apply to all light-duty diesel vehicle designs. Additionally, other engines and/or vehicles may generate more extreme conditions than experienced in these vehicles. However, these results provide some confidence that the ASTM D7467 stability requirement of 6 h minimum Rancimat IP provides adequate protection for modern fuel systems.

2.2 Task 2 Test Vehicles

For this task, two different, light-duty, diesel-powered vehicles were selected:

- 2013 Chevrolet Silverado 3/4-ton pickup truck with the 6.6L diesel engine (See Figure 1)
- 2012 Mercedes ML350 Blue Tec (See Figure 2)

These two vehicles were used in order to have a light duty truck and a passenger automobile. It was thought that these vehicle types would offer some differences in the fuel systems. Which would, in turn, have different effects on the fuel. SwRI initially proposed using a Volkswagen Jetta as the passenger automobile; but, it was replaced with the ML350 when the manufacturer offered the Blue Tec as a loan to the project. Appendices B and C contain information regarding the instrumentation of each vehicle for the testing that was conducted.



Figure 1. Chevrolet Silverado Test Vehicle



Figure 2. Mercedes ML350 BlueTec Test Vehicle

2.3 Task 3 Test Fuels

For this task, four potential blend components were obtained:

- Two hydrocarbon-only (petroleum) ULSD
- Two B100 biodiesel
 - o 1 soy derived
 - o 1 mixed fats derived

Table 1 contains a description of each component and the results of analysis of each are given in Tables 2 and 3. After consultation with AVFL panel members, it was decided to use diesel fuel CL14-6132 and biodiesel CL14-6152 to blend the various test fuels. The ULSD was thought to be more widely used than the TX-LED fuel and the soy biodiesel was chosen because it was more commonly used than mixed-fats biodiesel.

Sample ID	Description
CL14-6132	ULSD B-0, DF-8486.
CL14-6133	#2 TX-LED 15ppm ULSD
CL14-6152	Soy Methyl Ester Biodiesel
CL14-6173	Biodiesel-Mixed Fats

Table 1	Candidate	Test Fuel	Blend	Components
I able I.	Canuluate	I est I uei	Dienu	Components

Test	Method	Units	SwRI Sample ID	SwRI Sample ID
	Methou	Units	CL14-6132 Results	CL14-6133 Results
Cetane Number - CFR	D613			
Flash Point (Pensky Martin)	D93	°C	57.0	53.0
Water and Sediment	D2709	vol %	< 0.005	< 0.005
Distillation	D86			
IBP		°C	177.2	174.9
5%		°C	196.9	195.3
10%		°C	203.9	203.9
15%		°C	209.6	211.3
20%		°C	214.5	218.7
30%		°C	225.7	232.8
40%		°C	236.8	246.9
50%		°C	248.0	261.2
60%		°C	260.4	276.5
70%		°C	273.7	292.9
80%		°C	289.5	310.5
90%		°C	311.1	333.9
95%		°C	329.6	354.2
FBP		°C	338.0	360.2
Residue		%	1.5	1.4
Loss		%	1.1	1.1
		°C	44.10	57.30
Т90-Т10		°C	107.20	130.00
Kinematic Viscosity	D445			
40°C		cSt	2.15	2.4
Ash Content	D482	mass %	< 0.001	< 0.001
Sulfur - UV (Antek)	D5453	ppm	4	7
Copper Strip Corrosion	D130			
Test Duration		hrs	3.0	3.0
Test Temperature		°C	50	50
Rating		-	1A	1A
Aromatic Content	D1319			
Aromatics		vol %	14.6	40.9
Olefins		vol%	2.8	2.1
Saturates		vol%	82.6	57.0
Cloud Point	D2500	°C	-14	-11
Lubricity (HFRR)	D6079	μm	483	484
Electrical Conductivity	D2624			
Electrical Conductivity		pS/m	170	90
Temperature		°C	23.4	21.3
Density (15°C)	D4052	g/mL	0.8095	0.8457

 Table 2. Results of Analysis of Diesel Fuels

Test	Method	Unite	SwRI Sample ID	SwRI Sample ID
Test	Method	Onts	CL14-6152 Results	CL14-6173 Results
Total Sulfur	D5453	ppm	1.0	7.6
Cold Soak Filterability Test	D7501			
Time		sec	127	180
Volume		ml	300	300
Pass or Fail		-	PASS	PASS
Free and Total Glycerin	D6584			
Free Glycerin		wt %	0.010	0.010
Total Glycerin		wt %	0.104	0.078
Monoglyceride		wt %	0.240	0.230
Diglyceride		wt %	0.149	< 0.05
Triglyceride		wt %	0.093	<0.05
Flash Point (Pensky Martin)	D93	°C	99.5	145.5
Water and Sediment	D2709			
Sediment		vol%	< 0.005	< 0.005
Kinematic Viscosity	D445			
40°C		cSt	4.09	4.57
Sulfated Ash	D874		0.001	0.004
Sulfated Ash	D100	mass %	<0.001	<0.001
Copper Strip Corrosion	D130	1	2.0	20
Test Duration		hrs	3.0	3.0
lest lemperature		<u> </u>	50	50
Kaung	D(12	-	1A 49.10	1A
Cloud Doint	D015	-	48.10	00.0
Could Pollit	D2500		0.0066	0.0066
A sid Number by Potentiometric	D4550	111/111	0.0000	0.0000
Titration	D664			
Acid Number Inflection		mg KOH/g	0.28	0.33
Acid Number Buffer		mg KOH/g	0.24	0.29
Additives Elements in Lubricating	D 10 81			
Oil	D4951			
Barium		ppm	<5	<5
Boron		ppm	5	7
Calcium		ppm	<5	<5
Copper		ppm	<1	<1
Magnesium		ppm	<1	<1
Phosphorus		ppm	<5	<5
Zinc		ppm	<1	<1
Molybdenum		ppm	0	0
Distillation at Reduced Pressure	D1160			
IBP		°C	328	319
5 vol% AET °C		°C	345	339
10 vol% AET °C		°C	347	341
20 vol% AET °C		°C	348	343
<u>30 vol% AET °C</u>		°C	348	345
40 vol% AET °C		°C	349	346
50 vol% AET °C		°C	349	347
60 vol% AET °C		°C	350	349
70 V01% AEI °C		<u></u>	351	350
80 V01% AE1 °C		°C	351	351
90 V01% AET °C		°C	352	255
95 V01% AEI °C		°C	332 254	255
FBP Drosgrup		 mm⊔∝	10	555
Flomontol Analysic	D7111	mining	10	10
	0/111	nnh	214	180
Ma		nph	<100	<100
K K		npm	1.683	1 892
Na		ppm	<1	<1
Oxidation Stability of FAME				
Derivatives	EN15751	hrs	9.8	10.4

I abic 5. Itesuites of Divulesel Amaryse	Table 3.	Results	of Biodiesel	Analyses
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Table 3a.	Additional	Analysis	Results	for	Soy B100³
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Sample Name			B100 Biodiesel
Description			AVFL-17c Biodiesel
Additional Description			CL15-8893 Army Lab
Source			SWRI
ASR Number			20160327
AB Number			589903
Sample Receipt Date			~1/16/2016
Amount			1 qt
Last Revised			4/1/2016
Test	Method	AS Code	
Chemical Type			
Iodine Number in FAME by Rxn and Titration (g Iodine/100 g)	EN14111	Iodine Num in FAME by EN14111 - EXLB	110
FAME Profile by GC-MS	GC-MS	GC Mass Spectrometry	
methyl tetradecanoate (methyl myristate) C14:0 (wt%)			0.1
methyl hexadecanoate (methyl palmitate) C16:0 (wt%)			12.7
methyl heptadecanoate (methyl margarate) C17:0 (wt%) - internal standard			13.3 (assume none in sample)
methyl octadecanoate (methyl stearate) C18:0 (wt%)			3.4
methyl oleate C18:1 (wt%)			21.2
methyl linoleate C18:2 (wt%)			55.3
methyl linolenate C18:3 (wt%)			6.4
methyl eicosanoate (methyl arachidate) C20:0 (wt%)			0.3
methyl 11-eicosenoate C20:1 (wt%)			0
methyl eicosadienoate C20:2 (wt%)			0
methyl docosanoate (methyl behenate) C22:0 (wt%)			0.2
total (wt%)			99.6
Antioxidant Butylated Hydroxytoluene (BHT) in FAME by GC-MS (wt ppm)	GC-MS	GC Mass Spectrometry	<2

³ Conducted and Provided by Phillips 66.

Antioxidant t-Butyl Hydroquinone (TBHQ) in FAME by GC-MS (wt ppm)	GC-MS	GC Mass Spectrometry	NA
Antioxidant Pyrogallol (PG) in FAME by GC-MS (wt ppm)	GC-MS	GC Mass Spectrometry	NA
Glycerin (wt ppm)	GC-MS	GC Mass Spectrometry	<20
Water in Petroleum Products by Karl Fischer Titration (ppm)	D6304	H2O by MITSUBISHI (KF)	472
Metals by Inductively Coupled Plasma Mass Spectrometry (ppm)	ICP-MS	ICPMS Elemental Analysis	
V 51 (wtppm)			0.012
Cr 52 (wtppm)			0.046
Fe 56 (wtppm)			
Co 59 (wtppm)			< 0.005
Ni 60 (wtppm)			0.01
Cu 63 (wtppm)			0.026
Zn 66 (wtppm)			0.131
As 75 (wtppm)			< 0.005
Se 78 (wtppm)			0.007
Ag 107 (wtppm)			< 0.005
Cd 111 (wtppm)			< 0.005
Sn 118 (wtppm)			0.594
Sb 121 (wtppm)			< 0.005
Ba 138 (wtppm)			0.006
Pb 208 (wtppm)			0.039
Metals by Inductively Coupled Plasma Atomic Emission Spect (ppm)	ICP-AES	ICP-AES Elemental Analysis	
Al (wtppm)			<2.5
Ba (wtppm)			
Ca (wtppm)			<1.0
Cd (wtppm)			<0.36
Cr (wtppm)			<0.34
Cu (wtppm)			<0.91
Fe (wtppm)			< 0.52
K (wtppm)			

Table 3a. Additional Analysis Results for Soy B100³

Mg (wtppm)	<2.7
Mn (wtppm)	<0.57
Mo (wtppm)	<0.32
Na (wtppm)	
Ni (wtppm)	<0.75
P (wtppm)	<0.51
S (wtppm)	<99
Si (wtppm)	<0.57
Ti (wtppm)	<0.53
V (wtppm)	<1.1
Zn (wtppm)	<2.0

Table 3a. Additional Analysis Results for Soy B100³

2.4 Task 4 Vehicle Testing

The objectives of the vehicle testing were:

- 1. Mimic the degradation of specification-quality biodiesel blends seen by CRC AVFL members in other vehicle studies.
- 2. Identify analytical methods capable of detecting degradation of the test fuels during vehicle operation.
- 3. Determine the maximum temperatures and pressures that occur in the vehicle fuel systems. These parameters could then be used in designing non-vehicle, fuel-aging rigs.
- 4. Measure the conditions of fuel temperature and pressure in a light duty vehicle operating in summer.
- 5. Expose fuel(s) to these conditions and evaluate the effect on the fuel as measured by numerous candidate fuel stability test metrics.

2.4.1 On-Road Fuel Evaluation

An on-road "aging" of each test fuel was conducted in each vehicle. Approximately ½ tank of test fuel was put in the vehicle's tank. Mileage accumulation was conducted on the SwRI campus and the local public roads. The road course for the evaluation was the modified ASTM D5500 Intake Valve Deposit route used in CRC Project E-90-2b⁴, which includes both city and highway driving as well as a soak and extended idle. Each cycle is approximately 23.5 miles and is followed by a 20-min soak and a 15-min idle.

- 1. During the first day of operation of each vehicle, driving cycles were performed until the fuel gauge was reading approximately ¼ of a tank. The parameters were continuously measured and recorded at a data acquisition rate of 1 Hertz while the engine is running, during the 20-min soak, and for 30 min after the engine was shut off at the end of the 15-min idle.
- 2. Once the vehicle's engine was shut off after the 15-min idle at the end of the first day of driving, a one-liter fuel sample (#1) was taken from the tank sample tube.
- 3. On the next morning, a 0.5 liter sample (#2) was taken from the fuel tank.
- 4. During the second day the road course was again driven until approximately 1 gallon of fuel was left in the tank.
- 5. A 0.5-gallon sample (#3) was collected at the end of driving on the second day.
- 6. A sample (#4) of the remaining 0.5-gallon fuel in the tank was collected on the next morning.
- 7. After each fuel was completed, the fuel tank of the vehicle was rinsed with the next fuel, the rinse fuel was drained, and the next test fuel was added to the fuel tank.
- 8. The process was repeated with each test fuel.

⁴ Shoffner, B, et al., "Effects of Ethanol Blends on OBDII Systems of In-Use Vehicles," CRC Project E-90-2b, Coordinating Research Council, 2012.

2.4.2 Chassis Dynamometer Fuel Evaluation

The chassis dynamometer portion followed the same basic test procedure used in the on-road tests. Each vehicle utilized the same instrumentation, fuels, and drive cycle. However, for these tests, the ambient temperature was raised to 95 °F and a supplemental heat source (heating blankets) was used to directly heat to the underside of the vehicle. The supplemental heat source will simulate radiant heat emitted from the road surface during extreme temperature conditions. The goal of this portion of the vehicle testing was to allow comparison with the on-road tests and see how the fuel system and fuel stability respond to extreme heat.

The dynamometer drive cycle was a simulation of the on-road route. This cycle was also developed during CRC Project E 90 2b, "Effects of Ethanol Blends on OBDII Systems of In-Use Vehicles," and includes the 20-min soak and 15-min idle period. The data acquisition system collected the same parameters used during the on-road tests.

For each vehicle, the chassis dynamometer was set for the inertia and road load coefficients listed in the EPA's Test Car Database. The vehicle's cold tire pressure was set to the manufacturer's specification and a speed-proportional fan was directed at the vehicle's radiator. The following steps give a more detailed test sequence for each vehicle:

- 1. Setup vehicle for chassis dynamometer operation including coast down regressions.
- 2. Drain fuel and add the test fuel to tank until gauge reads ¹/₂ full.
- 3. Conduct repeat drive cycles, at 95 °F, (including soak and idle portions) until fuel gauge reads ¹/₄ full.
- 4. Take one-liter fuel sample directly after 15-min idle.
- 5. Soak vehicle overnight at standard ambient temperature.
- 6. Take one-liter fuel sample after overnight soak.
- 7. Repeat steps 3-6 with remaining ¹/₄ tank of fuel. (total of 4 samples)
- 8. Repeat steps 2-7 with each test fuel.

After completion of the vehicle portion of this program, the instrumentation was removed and the vehicles were returned.

For the vehicle testing each vehicle was tested with B0 and B5 fuels. Each of these fuel/vehicle combinations was tested on an on-road course and a heated dynamometer.

The two test vehicles were each evaluated on 8 different test days, as noted in Table 4. Representative temperature and pressure plots of the data collected during the vehicle testing are shown in Figures 3 and 4.

#	Vehicle	Fuel	Test Venue	Day
1	Silverado	B0	On-road	1
2	Silverado	B0	On-road	2
3	Silverado	B5	On-road	1
4	Silverado	B5	On-road	2
5	Silverado	B0	Chassis dynamometer	1
6	Silverado	B0	Chassis dynamometer	2
7	Silverado	B5	Chassis dynamometer	1
8	Silverado	B5	Chassis dynamometer	2
9	ML350	B0	On-road	1
10	ML350	B0	On-road	2
11	ML350	B5	On-road	1
12	ML350	B5	On-road	2
13	ML350	B0	Chassis dynamometer	1
14	ML350	B0	Chassis dynamometer	2
15	ML350	B5	Chassis dynamometer	1
16	ML350	B5	Chassis dynamometer	2

 Table 4. Vehicle Testing Summary



Figure 3. Plot of Data from Vehicle Testing with B0



Figure 4. Plot of Data from Vehicle Testing with B5

Table 5 is a summary of the highest temperatures recorded during the vehicle testing (both on-road and dynamometer). The maximum fuel rail pressures are also given in the table. There are some trends to the temperature and pressure data. Figure 5 is a plot of the temperature data and illustrates some of the trends:

- 1. The temperatures recorded during the on-road testing were consistently lower than the analogous temperatures during dyno-testing. Presumably, this was due to the lower ambient temperature, additional air flow cooling, and absence of heating mats.
- 2. In every instance, the highest temperature was either the Return Line Skin temperature or the Fuel Rail Skin temperature.
- 3. The temperatures recorded in the Silverado were consistently lower than the analogous temperatures recorded in the ML350 (with the exception of the fuel rail skin temperature on the dynamometer.
- 4. In general, there was very little difference in measured temperatures between B0 and B5 at any given measurement point under any given test condition.
- 5. The highest temperatures for both vehicles were recorded at the Fuel Rail Skin during dynotesting.
- 6. Although fuel tank temperatures varied, both the temperature change at any given point and the overall temperature increase followed a generally consistent pattern throughout the testing.
- 7. As the temperature of the fuel in the fuel tank went up, the temperatures at the other measurement points increased accordingly.

Regarding the maximum recorded fuel rail pressures, the pressures were higher during on-road testing compared to dyno-testing; and, the Silverado pressures were higher than the ML350 pressures.

Figure 6 is a compilation of the temperature plots from the B0 and B5 vehicle testing. The plots are presented in small size to facilitate visual comparisons between them. Larger, more legible, versions of these individual plots are found in Appendix D. Reviewing the plots leads to the following observations:

- 1. Overall, the temperatures were higher for the dyno-testing compared with the on-road testing. This can be seen by comparing the plots in Figure 6. All measured temperatures, not just the recorded maxima, were consistently lower during on-road testing.
- 2. The under-carriage heating used in the dyno-testing resulted in higher and more sustained heating of the fuel in the fuel tank, compared with the on-road testing.
- 3. Throughout the dyno-testing, the fuel temperature in the fuel tank had the longest time at temperature. The fuel rail skin temperature had the next-longest time. Throughout the onroad heating, the fuel rail skin temperature had the longest time at temperature. The supply line skin temperature was the next-longest time. The effects of increased vehicle cooling during on-road testing are confirmed by this.
- 4. The reduced vehicle cooling that occurred during dyno-testing is also seen in that the individual temperature plots are all generally closer to the higher temperatures. In contrast, the fuel rail temperatures during on-road testing are significantly higher compared to the other recorded temperatures in each case.

		Fuel Tank Bottom (FTB)	Supply Line Skin (SLS)	Return Line Skin (RLS) °C	Fuel in Line at Filter (FLF)	Fuel Rail Skin (FRS)	Fuel Rail Pressure psi
ML350							•
BO	Onroad	68	71	88	78	86	26341
	Dyno	82	87	96	92	98	23844
B5	Onroad	69	72	86	79	85	26409
	Dyno	82	87	93	92	99	25022
Silverado							
B0	Onroad	54	55	73	68	80	29407
	Dyno	82	83	91	89	104	27822
B5	Onroad	55	54	72	68	81	29799
	Dyno	79	82	89	87	103	26967

 Table 5. Summary of Data Maxima Recorded During Vehicle Testing



Figure 5. Maximum Recorded Fuel Temperatures During Vehicle Testing



Figure 6. Test Time in Seconds per Recorded Temperature Histogram Bin

In addition to the B0 and B5 blend testing reported above, a B20 blend was tested in the Silverado in the heated dynamometer facility. This B20 testing was conducted in order to obtain additional data on the effects of vehicle operation on a more concentrated biodiesel blend. The B20 used in this testing was blended from the same B0 and B100 used above. The blend was analyzed to confirm the blend concentration and the measured oxidation stability of the blend. Table 6 gives the results of this initial testing of the B20 blend. Two separate vehicle tests were conducted with the B20. In the first, the vehicle went through the same dynamometer testing as described above but without air sparging of the fuel during the test. In the second, the fuel in the vehicle fuel tank was sparged with air 4 times during the test cycle. The sparging was conducted to evaluate the possible effects of increased air/fuel mixing that seemed to occur with the on-road testing. The fuel was sparged for a total of 1 min each time, through a fuel sampling line that went to the bottom of the fuel tank. The timing for the sparging and sampling was as follows:

- 1. Setup vehicle for chassis dynamometer operation.
- 2. Add B20 test fuel to tank until gauge reads ¹/₂ full.
- 3. Conduct repeat drive cycles at 95°F (including soak and idle portions) until fuel gauge reads ¹/₄ full.
- 4. Take one-liter fuel sample directly after 15-minute idle.
- 5. Soak vehicle overnight at standard ambient temperature.
- 6. Take one-liter fuel sample after overnight soak.
- 7. Repeat Step 3 until approximately one gallon remains in tank.
- 8. Repeat Steps 4-6. (total of 4 samples collected)

Test	ASTM Method	Units	SwRI Sample ID CL15-7591 Results
RSSOT	D7545 (AL)	minutes	50.65
FAME Content	Biodiesel concentration by ERASPEC Instrument	%	20.1
Oxidation Stability of FAME Derivatives	EN15751		
Run 1		hrs	12.6
Run 2		hrs	12.7
Average		hrs	12.7

Table 6. Oxidation Stability and Blend Concentration Test Results for B20 Blend

2.4.3 Vehicle-Aged Fuel Analysis

The fuel samples taken from the vehicles during operation were analyzed for thermal stability, Rancimat, RSSOT, and total acid number. These analyses were selected as they are the fuel properties commonly believed to be indicators of degrading fuel quality. The results of the analysis of B0 and B5 fuel samples taken during vehicle testing are given in Tables 7-10. Table 11 contains the results of analysis of the fuel samples taken during B20 testing in the Silverado.

			On-Road Testing								
Fuel T	уре		ВО					B5			
Lab No.	CL14-		6355	6356	6357	6358		6375	6376	6377	6378
			Silverado, Sample #1 (1L) Fuel B0	Silverado, Sample #2 (500mL) Fuel B0	Silverado, Sample #3 (2.5L) Fuel B0	Silverado, Sample #4 (2.5L) Fuel B0		Silverado, Sample #1, Fuel B5	Silverado, Sample #2, Fuel B5	Silverado, Sample #3, Fuel B5	Silverado, Sample #4, Fuel B5
D6468											
90 Minutes	Repl 1	%	99	99	99	99		98.1	98.7	99	98.4
	Repl 2	%	99	99	99	99		98.7	98.9	99.1	98.4
	Avg	%	99	99	99	99		98	99	99	98
180 Minutes	Repl 1	%	97.5	97.8	98	97.9		95.5	95.2	96	95
	Repl 2	%	96.9	97	97.6	97.2		95.7	95.4	95.5	95.7
	Avg	%	97	97	98	98		96	95	96	95
EN15751	Run1	hours	>24	>24	>24	>24		13.1	14	12.6	12.2
	Run2	hours	>24	>24	>24	>24		13.2	14	11.7	12.3
	Average	hours	>24	>24	>24	>24		13.2	14	12.2	12.2
D7545	Results	minutes	71.5	71.16	71.5	70.88		69.43	70.68	65.31	61.4
D664											
Total Acid No	Buffer	mg KOH/g	<0.05	<0.05	<0.05	< 0.05		<0.05	<0.05	<0.05	<0.05

 Table 7. Results of Analysis of Vehicle Testing Fuel Samples – Silverado/On-Road

			Dynamo					er Testing			
Fuel T	уре			В	0			В5			
Lab No.	CL14-		6439	6440	6441	6442		6435	6436	6437	6438
			Silverado, Sample #1, Fuel B0, Day 1- 1/4 Tank-1 Liter	Silverado, Sample #2, Fuel B0, Day 2- 1/4 Tank5 Liter	Silverado, Sample #3, Fuel B0, Day 2- "E" Tank- 1/2 Gallon	Silverado, Sample #4, Fuel B0, Day 3- "E" Tank- 1/2 Gallon		Silverado, Sample #1, Fuel B5, Day 1- 1/4 Tank-1 Liter	Silverado, Sample #2, Fuel B5, Day 2- 1/4 Tank5 Liter	Silverado, Sample #3, Fuel B5, Day 2- "E" Tank- 1/2 Gallon	Silverado, Sample #4, Fuel B5, Day 3- ''E'' Tank- 1/2 Gallon
D6468											
90 Minutes	Repl 1	%	87.4	87.8	87.8	87.5		87.3	87.4	86.7	87.5
	Repl 2	%	87.7	87.6	87.1	87.7		87.5	87.4	87.5	87.5
	Avg	%	88	88	87	88		87	87	87	88
180 Minutes	Repl 1	%	86.2	86.5	86.6	86.8		86.6	86.7	86	86.4
	Repl 2	%	86	86.5	86.6	86.3		86.6	86.8	86	86.4
	Avg	%	86	86	87	87		87	87	86	86
EN15751	Run1	hours	>24	>24	>24	>24		17.3	16.4	14.6	16
	Run2	hours	>24	>24	>24	>24		15.7	16.9	16.1	16.1
	Average	hours	>24	>24	>24	>24		16.5	16.7	15.4	16
D7545	Results	minutes	65.33	67.5	66.93	66.98		84.05	73.55	68.43	70.18
D664											
Total Acid No	Buffer	mg KOH/g	<0.05	<0.05	<0.05	<0.05		<0.05	<0.05	<0.05	<0.05

 Table 8. Results of Analysis of Vehicle Testing Fuel Samples – Silverado/Dynamometer
Fue	I Туре			B	0		B5				
Lab N	o. CL14-		6518	6519	6520	6521		6514	6515	6516	6517
			ML350	ML350	ML350	ML350		ML350	ML350	ML350	ML350
			Sample #1	Sample #2	Sample #3	Sample #4		Sample #1	Sample #2	Sample #3	Sample #4
			Fuel BO	Fuel B0	Fuel B0	Fuel B0		Fuel B5	Fuel B5	Fuel B5	Fuel B5
D6468											
90 Minutes	Repl 1	%	92.4	92	92.4	92.4		91.7	90.5	91.3	91.6
	Repl 2	%	92.4	92	92.4	92.4		91.7	90.4	91.6	91.4
	Avg	%	92	92	92	92		92	90	91	92
180 Minutes	Repl 1	%	92.6	92.5	93.2	93.2		92.6	92.5	93.2	92.4
	Repl 2	%	93	93	93	93.2		92.1	92.7	93.2	92.8
	Avg	%	93	93	93	93		92	93	93	93
EN15751	Run1	hours	>24	>24	>24	>24		14.8	11.5	16.8	15.2
	Run2	hours	>24	>24	>24	>24		15.6	11.2	16	15.2
	Average	hours	>24	>24	>24	>24		15.2	11.4	16.4	15.2
D7545	Results	minutes	69.75	66.95	73.2	63.5		63.91	52.85	60.51	60.25
D664											
Total Acid No	Buffer	mg KOH/g	<0.05	<0.05	<0.05	<0.05		< 0.05	<0.05	<0.05	<0.05

Table 9. Results of Analysis of Vehicle Testing Fuel Samples – ML350/On-Road

			Dynamometer Testing										
Fue	el Type			B	0		B5						
Lab No. CL14-			6658 6659 6660		6660	6661		6657	6662	6663	6664		
			ML350	ML350	ML350	ML350		ML350	ML350	ML350	ML350		
			Sample #1	Sample #2	Sample #3	Sample #4		Sample #1	Sample #2	Sample #3	Sample #4		
			Fuel B0	Fuel B0	Fuel B0	Fuel B0		Fuel B5	Fuel B5	Fuel B5	Fuel B5		
D6468													
90 Minutes	Repl 1	%	92.1	92	92.1	92		92.1	92.1	92.3	92.2		
	Repl 2	%	92	92	92	92.2		92.7	92.5	92	92.5		
	Avg	%	92	92	92	92		92	92	92	92		
180 Minutes	Repl 1	%	90.8	90.7	90.5	91.8		91.3	91	91	90		
	Repl 2	%	91	90.7	91.1	91.9		91.2	91	91.3	90.9		
	Avg	%	91	91	91	92		91	91	91	90		
EN15751	Run1	hours	>24	>24	>24	>24		14.3	12.9	12.6	12.4		
	Run2	hours	>24	>24	>24	>24		13.6	14.6	12.7	12.8		
	Average	hours	>24	>24	>24	>24		14.2	13.7	12.6	12.6		
D7545	Results	minutes	68.81	66.8	69.43	65.7		63.08	58.53	51.91	49.33		
D664													
Total Acid No	Buffer	mg KOH/g	<0.05	<0.05	<0.05	<0.05		<0.05	<0.05	<0.05	<0.05		

Table 10. Results of Analysis of Vehicle Testing Fuel Samples – ML350/Dynamometer

	Dynamometer Testing, Silverad							, B20, with and without sparging						
Fuel T	уре			B20 with No	Air Sparging			B20 with Air Sparging						
Lab N	No.		7835	7836	7837	7838		7839	7840	7841	7842			
			Silverado, Sample #1 Fuel B20	Silverado, Sample #2 Fuel B20	Silverado, Sample #3 Fuel B20	Silverado, Sample #4 Fuel B20		Silverado, Sample #1 Fuel B20, w/sparge	Silverado, Sample #2 Fuel B20, w/sparge	Silverado, Sample #3 Fuel B20, w/sparge	Silverado, Sample #4 Fuel B20, w/sparge			
D6468														
90 Minutes	Repl 1	%	92.6	92.4	92.4	90		92.4	92.6	92.2	92.7			
	Repl 2	%	92.5	92.8	92.3	90.6		92.4	92.7	92.4	92.7			
	Avg	%	93	93	92	90		92	93	92	93			
180 Minutes	Repl 1	%	90.5	90.3	89.7	84.4		91.6	91	91	91.5			
	Repl 2	%	90.7	90.2	89.8	84.8		91.8	91.1	91	91.2			
	Avg	%	91	90	90	85		92	91	91	91			
EN15751	Run1	hours	6.1	6.1	6.1	5.1		8.1	7.4	6.7	6			
	Run2	hours	6.1	6.3	6.1	5		8	7.5	6.5	6			
	Average	hours	6.1	6.2	6.1	5.1		8.1	7.5	6.6	6			
D7545	Results	minutes	47	36	36	31		41	40	36	36			
D664 Total Acid No.	Inflect	mg KOH/g	0.17	0.21	0.17	0.17		0.18	0.14	0.15	0.14			
D3703	Peroxide	mg/kg	11.64	8.92	10.44	14.96		11.68	4.92	5.84	7.16			
D6304	Water	mg/kg	132	118	128	123		123	128	128	127			

 Table 11. Results of Analysis of B20 Fuel Samples from Vehicle (Silverado) Testing

Examination of the vehicle-aged fuel test results leads to the following observations:

- 1. The fuels experienced very little change in thermal stability as measured by D6468; however, the additional heating that the fuels experienced in the dynamometer testing seems to have resulted in slightly more degraded thermal stability compared to on-road testing in the Silverado.
- 2. The B0 samples showed no significant degradation in oxidation stability as measured by the Rancimat test (EN15751). This is to be expected since the Rancimat is not a reliable test of hydrocarbon fuel oxidation stability.
- 3. The B5 on-road samples from the Silverado had slightly poorer oxidation stability (by Rancimat) than did the dynamometer samples. We assume this is because of the fuel sloshing/air mixing that occurs during on-road testing. The B5 results from the ML350 were somewhat mixed.
- 4. The results also indicate that a strictly thermal stability test, such as D6468, will likely not be useful to measure changes to the stability characteristics of biodiesel blends during vehicle use and onboard storage.
- 5. For the B20 samples, the RSSOT and Rancimat results were worse than for the B0 and B5. Presumably this is due to the higher amount of biodiesel in the B20. The total acid number results were higher for the B20, compared with the other fuels. Again, it is assumed this is due primarily to the higher biodiesel content in the B20. Taken together, these results could indicate that higher biodiesel content blends are more susceptible to oxidation/degradation in vehicle operation. Additional testing with other fuels and longer vehicle test times is needed.
- 6. Based on the fuel sample analyses, the extent of fuel degradation during vehicle operation was comparatively slight. [Anecdotal reports from CRC AVFL members have described seeing significantly greater fuel degradation, in the field, with biodiesel blends that were specification quality when introduced to the vehicle.]

Considering all the information collected during the vehicle testing leads to the following points regarding a fuel-stressing apparatus.

- 1. The two scenarios utilized for the vehicle testing (on-road and heated dyno) resulted in measureable differences in the fuel temperatures throughout the vehicles. As such, a decision regarding fuel-stressing temperatures and/or fuel test method temperatures should be related to the vehicle-operation scenario that one hopes to replicate. Temperatures around 100 °C to 110 °C represent the highest temperatures encountered by the fuel in the current testing.
- 2. Heating of any fuel sump during processing or testing should be considered as this is similar to actual driving conditions. The maximum fuel tank temperature observed during vehicle testing was 82 °C (180 °F).
- 3. It is assumed that increasing the amount of oxygen available to the fuel during on-road operation (caused by sloshing) should lead to increased oxidation of the fuel. This assumption, however, was not consistently substantiated by the fuel testing results. It is worth noting that the test fuels had relatively short residence times in the vehicles prior to sampling and laboratory testing. Had the fuels been stored in the vehicles for longer periods, the effect of the increased oxygen availability might have been more clearly demonstrated.
- 4. The fuels tended to undergo relatively little measurable degradation during the vehicle testing. Factors that influenced this include the use of specification quality fuel and the fact that most of the fuel spent little time in the hottest parts of the vehicle. As the fuel was exposed to higher temperatures and more oxygen, there were measurable changes in the stability of the fuel. Using lower-quality test fuel in the vehicles tests would likely have resulted in larger measureable changes in the fuel.
- 5. Since adding heat and oxygen accelerates the degradation of the fuel, selection of conditions for stressing/testing will require decisions about the type of environment (vehicle conditions) one wishes to replicate.
- 6. Accelerating the conditions above/beyond those encountered in the vehicles is possible and would accelerate the degradation of the fuel. But, some decision is required regarding the degree to which acceleration is representative of vehicle operation/storage. A single fuel stressing/testing regime to represent all scenarios is not very likely. Perhaps using a small number of stressing/testing regimes, similar to vehicle test cycles, is most appropriate.
- 7. Conducting some bench-scale testing with fuels of poorer initial stability would help answer some of these questions.
- 8. It seems that a combination of Rancimat, RSSOT, and acid number testing were the most reliable method of assessing the stability change of a fuel during stressing. However, these test methods do not adequately assess the tendency of a fuel to form deposits on metal surfaces. A test method, such as a modified ASTM D3241 provides a more robust assessment of the change in fuel stability and deposit-forming characteristics.
- 9. It should again be noted that these vehicle tests were very short term; less than 7 total hours in the vehicle. Therefore, this testing did not accurately represent the effects of on-board vehicle storage for longer periods of time. Recall that the primary goals of the vehicle testing were to collect accurate temperature and pressure data to assist with the design of a fuel-aging apparatus.

2.5 Task 5 Develop bench-scale, fuel-stressing methodology (mimic the conditions that fuel experiences in HPCR fuel systems)

The emphasis of Task 5 was to develop bench-scale fuel-stressing capability. The fuel-stressing capability was designed to provide a means to realistically stress test fuels in quantities up to about 50 gallons. The stressed fuels would then be available for other testing in the laboratory or in vehicles.

The fuel aging apparatus known as the SwHiReTS is a newly-developed (by SwRI) test technique based on the High Reynolds Number Thermal Stability (HiReTS) tester (See Figure 7). The HiReTS is the equipment used in ASTM D6811, Standard Test Method for Measurement of Thermal Stability of Aviation Turbine Fuels under Turbulent Flow Conditions. In the current configuration of the SwHiReTS, fuel is pumped through stainless steel tubing at up to 100 milliliters per minute. Test temperature can be set as high as 540 °C with an internal pressure of up to 6.9 megapascals (1000 psi). The fuel can be run under either laminar or turbulent flow conditions. The test tubing can be analyzed for deposits as a whole or sectioned for a per-length basis.

The fuel aging and analysis for this task were conducted according to the protocol given in Appendix E. One slight deviation from this protocol was approved by the project technical monitors (Gunter and Woebkenberg), namely that when the fuel was not in the aging apparatus it was stored in an oven at 95-100 $^{\circ}$ F (not 90 $^{\circ}$ F).



Figure 7. Fuel Stressing Apparatus

Two test fuels were used in this task. Both were B20 blends made from the B0 and B100 used for all the test fuels in this project. Test fuel 1 was the B20, as prepared. Test fuel 2 was the same B20 with added water (deionized water, 200 ppm, total) and added vegetable oil (food grade canola oil, 3 wt%). The Day 0 measured water levels for the Test 1 and Test 2 fuels were 147 and 155 ppm, respectively. Table 12 contains a description of the two test fuel blends used for this task. Each of the fuel samples taken during the fuel stressing process was analyzed by the tests listed in Table 13. Of note in this list is the inclusion of ASTM D3241, "Standard Test Method for Thermal Oxidation of Aviation Turbine Fuels D3241." This analysis was added to the list because the test has shown some ability to evaluate the deposit forming tendencies of diesel fuels.⁵ According to the method:

"This test method for measuring the high temperature stability of gas turbine fuels uses an instrument 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. 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, and the rate of plugging of a 17 μ m nominal porosity precision filter located just downstream of the heater tube."

For this project, the D3241 test temperature was set at 240 °C, because that is the temperature most often reported in the literature when the D3241 apparatus is used to test diesel fuel. The 240 °C set temperature results in a temperature profile across the heater tube. The temperature profile has been recorded and is shown in Figure 8. The deposits on each D3241 heater tube were analyzed using an ellipsometer. The following information, from Appendix A3 of ASTM D3241, describes ellipsometry and various terms related to D3241 heater tube deposits and ellipsometry:

A3.2.1.1 deposit profile—three-dimensional representation in terms of deposit thickness along and around the length of the heater tube test section.

A3.2.1.2 deposit thickness—the thickness of deposit present on the heater tube substrate surface expressed in nanometers (nm).

A3.2.1.3 ellipsometry—a technique used for measuring the optical properties of surfaces (refractive index and absorption coefficient) based on changes in the polarized state of light upon reflection from the surface.

A3.2.1.3.1 *Discussion*—In the presence of a thin transparent layer, with a known refractive index and absorption coefficient, ellipsometry can also be used to provide film thickness information.

A3.2.1.4 maximum deposit thickness—the maximum thickness of an average 2.5 mm² deposit present on the D3241 heater tube surface, expressed in nanometers, nm.

The fuel sample test results are given in Table 14. We also ran D3241 on the two components of the B20 and the results are in Table 15. The diesel fuel failed. The failure mode in this case is that the total volume of deposit on the tube exceeded the ability of the ellipsometer to measure. Note that the instrument is able to measure a total volume of $3.99 \times 10-5 \text{ cm}^3$. Since the deposit

⁵ Reid, J., et al., "Internal Injector Deposits From Sodium Sources," SAE No. 2014-01-1388.

volume from the B0 is above this volume it can be seen that the amount of deposit from the B0 is at least one order of magnitude more than the deposits left by the test fuels. The B100 did run completely and we got a much higher deposit volume than the B20 tests. Additional testing is needed with other fuels to explore this further.

Figure 9 presents the ellipsometer plots for the D3241 tests listed in Table 14. The red areas are places where the deposit depth has exceed 85 nanometer deposit depth (this is the maximum deposit depth that the instrument is able to measure). Figure 10 is a plot of the RSSOT results for the samples from the fuel-stressing apparatus. Figure 11 is a plot of the Rancimat results for the samples from the fuel-stressing apparatus. Figure 12 is the plot of the D3241 total deposit volume for the samples from the fuel-stressing apparatus. Figure 13 is the plot of D3241 maximum deposit depth for the samples from the fuel-stressing apparatus. This number is an average of the highest values in a 2.5 mm² area. The RSSOT and Rancimat results tend to follow a similar pattern of decreasing induction period with increased aging, as would be expected. The Rancimat results demonstrated slightly more variation of induction period at the beginning of the aging; and, slightly more spread in the Fuel 1 vs. Fuel 2 results throughout the aging. This may be an indication of tighter precision for the RSSOT. Both the total deposit volume and the maximum deposit depth data show a trend of decreasing volume with Fuel 1 and increasing volume with Fuel 2, as the fuel is aged. The primary difference between these two test fuels is the 3% vegetable oil in Fuel 2. The decreasing volume with Fuel 1 may be an indication of deposits forming in the heating tubing of the fuel-stressing apparatus. Material deposited in the heating tubing would not be available for deposition on the D3241 heater tube. The increasing volumes with Fuel 2 may indicate the tendency of vegetable oil to form deposits on heated metal surfaces. In this case, the vegetable oil is in sufficiently high concentration to leave deposits in the heating tube and on the D3241 heater tube as well. Additional work with other fuels and blends is needed to investigate this finding further.

Number	Blend	Total Glycerin	Total Water			
1	B20 Soy	On-Spec	Low (~100 ppm)			
2	B20 Soy	High (3.0 wt%)	High (200 ppm)			

 Table 12. Fuel Stressing Apparatus Test Fuels and Target Contaminants Levels

Test Method	Description
D664	Total Acid Number (TAN) by Potentiometric Titration
D3241	Jet Fuel Thermal Oxidation Test
D3703	Hydroperoxide Number by Reaction with KI and Titration
D6304	Water by Karl Fischer Titration
D6468	High Temperature Stability of Middle Distillate
D2887	Simulated Distillation by High Temperature Method
D7545	Oxidation Stability by Induction Period, a.k.a. Rapid Small Scale Oxidation Test (RSSOT)

 Table 13. Fuel Stressing Apparatus Fuel Sample Analyses



Figure 8. D3241 Heater Tube Temperature Profile for 240 °C Set Temperature



Figure 9. Plots of D3241 Heater Tube Deposits as Measured by Ellipsometry (Fuel samples from stressing-apparatus fuel aging. See Table 14 for additional sample information.)

(Figure Continued on Next Page)



Figure 9 (Cont'd). Plots of D3241 Heater Tube Deposits as Measured by Ellipsometry (Fuel samples from stressing-apparatus fuel aging. See Table 14 for additional sample information.)



Figure 10. Stressing-Apparatus Fuel Samples RSSOT Test Results



Figure 11. Stressing-Apparatus Fuel Samples Rancimat Results



Figure 12. Stressing-Apparatus Fuel Samples D3241 Total Deposit Volume Results



Figure 13. Stressing-Apparatus Fuel Samples D3241 Maximum Deposit Depth Results

Review of the data in Table 14 leads to the following observations and conclusions from the bench scale fuel stressing apparatus testing:

- The total water test results indicate that essentially none of the added water in Test Fuel 2 was dissolved by the fuel. The Day 0 water levels for the Test 1 and Test 2 fuels were 147 and 155 pm, respectively. The variability of the results is likely due to small amounts of water dropping out of solution during the period between sampling and analysis.
- The RSSOT still seems to be a reliable indicator of change in the oxidative stability of the aged fuel. This was the case for both test fuels.
- The Rancimat also provides a reliable indication of changes in oxidative stability so long as there is biodiesel in the fuel. The test method is not applicable to B0 fuels.
- For Fuel 1 there seems to be a general trend of decreasing D3241 deposit volume with aging time. For Test Fuel 2, there is a trend of increasing deposit volume with aging time.
- The max deposit depth seemed to be generally higher for fuel 2. Additional testing is needed to further investigate D3241 testing.
- The RSSOT and Rancimat results from the fuel aging tests correlated well with the analogous results from the B20 vehicle testing.
- The simulated distillation final boiling point for sample 9313 (Test Fuel 2, Day 29) is significantly higher than the final boiling point of the other samples. The chromatogram for this sample was closely examined for evidence of material in that boiling range. A very

slight peak is visible but there is no way to determine if it is from contamination in the sample or the formation of material during aging of the fuel. It should be noted that the added vegetable oil would not typically be detected by D2887; however, if the vegetable oil degraded during aging, some of the breakdown byproducts might account for the higher boiling point material.

T 4	ASTM	T T •/	8892	9048	9057	9116	9147	9184	9200	9203	9245	9271	9291	9313
Test	Method	Units	Test Fuel No. 1 (normal glycerin, low water)							Test Fue	el No. 2 (higl	<mark>h glycerin, h</mark>	igh water)	
			Day 0	Day 1	Day 8	Day 15	Day 22	Day 29	Day 0	Day 1	Day 8	Day 15	Day 22	Day 29
Thermal Oxidation Test	D3241													
Test Temperature		°C	240	240	240	240	240	240	240	240	240	240	240	240
ASTM Code		rating	1A	<2	<2	1	1	1	1	<2	1	1	1	1
Maximum Pressure Drop		mmHg	1	0	0	0	0	0	0	0	0	0	0	0
Maximum Deposit Depth, (2.5 mm ² spot)		nm	21.94	20.736	30.349	18.975	8.655	14.633	18.244	108.667	13.171	23.9	113.941	131.212
Total Volume		cm ³	4.00E-06	4.92E-06	3.45E-06	3.32E-06	2.04E-06	2.31E-06	3.79E-06	1.19E-06	1.73E-06	2.82E-06	4.05E-06	4.3726E-06
								•						
Oxidation Stability-RSSOT	D7545	min	29	31	28	26	25	22	31	31	28	25	23	22
Acid Number	D664	KOH / g	0.05	0.06	0.06	0.07	< 0.05	< 0.05	0.06	< 0.05	0.07	0.06	0.05	< 0.05
Karl Fischer Water Content	D6304	mg/kg	147	116	97	100	95	127	155	131	132	151	84	160
High Temp Stability of Distillate Fuels	D6468													
90 min		% Reflectance	90	92	92	92	92	93	91	93	93	92	93	93
180 min		% Reflectance	85	92	92	92	92	93	90	92	92	92	92	92
Simulated Distillation	D2887													
IBP		°C	118.1	115.8	116.7	117.1	118.0	118.8	117.1	117.7	117.7	117.9	118.5	118.4
5%		°C	160.0	159.8	160.2	160.6	161.4	161.2	159.4	160.1	160.5	160.7	161.1	161.9
10%		°C	174.4	174.5	174.6	174.7	174.9	174.7	174.4	174.5	174.7	174.8	174.8	175.3
15%		°C	186.9	187.4	187.5	187.6	187.8	187.5	186.7	187.3	187.6	187.7	187.7	188.1
20%		°C	195.9	196.2	196.2	196.3	196.3	196.1	196.0	196.1	196.2	196.3	196.3	196.4
25%		°C	203.4	204.8	205.0	205.2	205.5	204.2	203.4	204.2	205	205.1	204.9	206.3
30%		°C	213.9	215.0	215.1	215.2	215.3	214.9	213.9	214.9	215.5	215.6	215.5	215.8

Table 14. Results of Analysis of Stressing Apparatus-Aged Fuel Samples

Test	ASTM	In:to	8892	9048	9057	9116	9147	9184		9200	9203	9245	9271	9291	9313
Test	Method	Units	Test Fuel No. 1 (normal glycerin, low water)							Test Fuel No. 2 (high glycerin, high water)					
			Day 0	Day 1	Day 8	Day 15	Day 22	Day 29		Day 0	Day 1	Day 8	Day 15	Day 22	Day 29
35%		°C	220.5	222.1	222.3	222.4	222.6	221.3		220.6	221.4	222.5	222.6	222.3	223.8
40%		°C	230.8	232.1	232.3	232.4	232.7	231.4		230.9	231.6	232.7	232.8	232.4	234.3
45%		°C	239.0	240.6	240.8	240.9	241.2	239.6		239.2	239.9	241.2	241.3	240.8	243.1
50%		°C	251.5	252.3	252.4	252.5	252.6	252.4		251.8	252.8	253.2	253.4	253.2	253.8
55%		°C	262.5	263.3	263.4	263.5	263.6	263.1		262.8	263.5	264.3	264.4	264.1	265.6
60%		°C	273.9	275.5	275.6	275.7	275.9	274.9		274.5	275.7	277	277.2	276.5	279.3
65%		°C	287.8	288.3	288.4	288.4	288.5	288.2		288.2	288.7	289.7	289.9	289.2	292.9
70%		°C	303.0	303.3	303.4	303.4	303.3	303.5		303.6	304.1	305.1	305.4	304.5	309.1
75%		°C	324.1	322.6	322.7	322.7	322.4	325.0		325.4	326.3	326.9	327.4	326.4	329.4
80%		°C	342.8	338.4	338.5	338.4	338.1	343.0		343.6	343.9	343.5	343.9	343.4	346.5
85%		°C	352.4	351.3	351.0	350.8	351.2	352.3		352.5	352.5	352.2	352.4	352.3	352.3
90%		°C	353.2	353.5	353.5	353.5	353.4	353.2		353.3	353.2	353.2	353.3	353.2	353.2
95%		°C	354.3	354.7	354.7	354.7	354.6	354.3		354.4	354.4	354.4	354.5	354.4	355.1
FBP		°C	387.0	395.1	395.2	394.8	389.6	389.6		390.4	390.4	396.9	399.9	392.9	555*
Oxidation Stability of FAME Derivatives	EN15751	hrs	8.5	11.7	11.0	9.8	10.8	9.3		10.7	11.2	11.1	10.8	9.4	8.9
								Γ			Γ		Γ		
Peroxide Number	D3703	mg/kg	6.4	35.16	6.44	7.56	16.80	8.9		8.6	8.9	7.16	6.24	9.32	9.16
										*This app if this is aging of t slight pea given add	barently higher some slight he fuel. Clos k that could litional inform	er FBP result contamination e examination be either one nation.	was re-exan on or someth n of the chron . Additional	nined and it is ing formed of natogram sho aging time n	s not clear during the bws a very hight have

Table 14. Results of Analysis of Stressing Apparatus-Aged Fuel Samples

Fuel		BO	B100
Test Temperature	°C	240	240
ASTM Code	rating	3P*	1
Max Pressure Drop	mmHg	0+	0
Max Deposit Depth	nm	208.075	227.203
Total Volume	cm ³	>3.99 E-5	9.65E-06

Table 15. Results of D3241 Testing of Base Blend Components

* peacock—A multicolor, rainbow-like tube deposit

+ 0 pressure drop indicates no filterable formed during testing

Figure 14 is a plot of RSSOT and Rancimat induction periods for both the vehicle (Silverado) and aging apparatus (Test Fuel 1) B20 samples. All the B20 Silverado results (both with and without sparging) were used. This plot shows that both the Silverado and the aging apparatus caused some oxidative degradation of the test fuel as indicated by changes in the measured induction periods. The results further indicate that the aging apparatus has the potential to age fuel similarly to aging in a vehicle. Additional work is needed to refine the aging apparatus conditions.



Figure 14. Plots of Induction Period Test Results for B20 Fuel

2.5.1 Task 6 Recommendations for Phase II (fuel effects testing) to CRC

Tasks 1-5 were aimed at collecting data from vehicle-aging of test fuels and use those data to evaluate a fuel-aging apparatus for its' ability to age fuel to a degree that is similar to the vehicle-aged fuel. As described above, these goals were successfully met. However, a more detailed study of the effects of various fuels, blend components, vehicle environments (such as metals, elastomers, and available oxygen) and additives is needed. Emphasis should be placed on testing a variety of fuels and fuel blend components. The aged fuels should be tested using the RSSOT, Rancimat, and D3241/ellipsometer as indicators of change in the fuel. The ellipsometer also provides a reliable indication of relative deposit forming characteristics.

It is recommended that efforts be made to improve the usefulness of the ellipsometric analysis of heater tubes when testing diesel fuel. These could include investigation of using a different temperature profile, to possibly cause deposits elsewhere on the tube, or a new ellipsometer designed to measure more of the heater tube surface. It is noted that the major D3241 deposit peaks on the D3241 tubes were near the end of measured region which may mean that the peaks were only partially captured by the ellipsometer method, resulting in possible inaccuracy.

Use of a D3241-type analysis for the study of diesel and biodiesel blends could provide very valuable information about fuel, additive, and contaminant effects. A breakpoint approach, currently applied to aviation fuel, would give researchers a tool to quantify some of these effects.

3.0 SUMMARY AND CONCLUSIONS

Two fuel blends, B0 and B5, were aged in two different vehicles (Chevrolet Silverado and Mercedes Blue Tec). The vehicle testing was conducted on a road course and in a heated dynamometer chamber. A third blend, B20, was aged in one vehicle in the heated dynamometer chamber.

Temperatures recorded from several fuel-system locations during the vehicle testing confirmed that the fuels got hotter as they moved through the system. The highest temperatures recorded in this study were in the range of 100-110 $^{\circ}$ C.

All three blends were made from the same B0 (commercially available ULSD, hydrocarbon only) and B100 (soy-derived biodiesel) to allow for property comparisons. The B20 and B20 with added vegetable oil and water were also aged in a fuel stressing apparatus. Fuel samples were collected throughout each aging regime and analyzed for indications of fuel aging.

Conclusions from the vehicle testing include:

- 1. The temperatures recorded during the on-road testing were consistently lower than the analogous temperatures during dyno-testing. Presumably, this was due to the lower ambient temperature, additional air flow cooling, and absence of heating mats.
- 2. In every instance, the highest temperature was either the Return Line Skin temperature or the Fuel Rail Skin temperature.
- 3. The temperatures recorded in the Silverado were consistently lower than the analogous temperatures recorded in the ML350 (with the exception of the fuel rail skin temperature on the dynamometer.
- 4. In general, there was very little difference in measured temperatures between B0 and B5 at any given measurement point under any given test condition.
- 5. The highest temperatures for both vehicles were recorded at the Fuel Rail Skin during dyno-testing.
- 6. Although fuel tank temperatures varied, both the temperature change at any given point and the overall temperature increase followed a generally consistent pattern throughout the testing.
- 7. As the temperature of the fuel in the fuel tank went up, the temperatures at the other measurement points increased accordingly.
- 8. Regarding the maximum recorded fuel rail pressures, the pressures were higher during onroad testing compared to dyno-testing; and, the Silverado pressures were higher than the ML350 pressures.
- 9. Overall, the temperatures were higher for the dyno-testing compared with the on-road testing. All measured temperatures, not just the recorded maxima, were consistently lower during on-road testing.
- 10. The under-carriage heating used in the dyno-testing resulted in higher and more sustained heating of the fuel in the fuel tank, compared with the on-road testing.

- 11. Throughout the dyno-testing, the fuel temperature in the fuel tank had the longest time at temperature. The fuel rail skin temperature had the next-longest time. Throughout the on-road heating, the fuel rail skin temperature had the longest time at temperature. The supply line skin temperature was the next-longest time. The effects of increased vehicle cooling during on-road testing are confirmed by this.
- 12. The reduced vehicle cooling that occurred during dyno-testing is also seen in that the individual temperature plots are all generally closer to the higher temperatures. In contrast, the fuel rail temperatures during on-road testing are significantly higher compared to the other recorded temperatures in each case.

Examination of the vehicle-aged fuel test results leads to the following observations:

- 1. The fuels experienced very little change in thermal stability as measured by D6468; however, the additional heating that the fuels experienced in the dynamometer testing seems to have resulted in slightly more degraded thermal stability compared to on-road testing in the Silverado.
- 2. The B0 samples showed no significant degradation in oxidation stability as measured by the Rancimat test (EN15751). This is to be expected since the Rancimat is not a reliable test of hydrocarbon fuel oxidation stability.
- 3. The B5 on-road samples from the Silverado had slightly poorer oxidation stability (by Rancimat) than did the dynamometer samples. We assume this is because of the fuel sloshing/air mixing that occurs during on-road testing. The B5 results from the ML350 were somewhat mixed.
- 4. The results also indicate that a strictly thermal stability test, such as D6468, will likely not be useful to measure changes to the stability characteristics of biodiesel blends during vehicle use and onboard storage.
- 5. For the B20 samples, the RSSOT and Rancimat results were worse than for the B0 and B5. Presumably this is due to the higher amount of biodiesel in the B20. The total acid number results were higher for the B20, compared with the other fuels. Again, it is assumed this is due primarily to the higher biodiesel content in the B20. Taken together, these results could indicate that higher biodiesel content blends are more susceptible to oxidation/degradation in vehicle operation. Additional testing with other fuels and longer vehicle test times is needed.
- 6. Based on the fuel sample analyses, the extent of fuel degradation during vehicle operation was comparatively slight. [Anecdotal reports from CRC AVFL members have described seeing significantly greater fuel degradation, in the field, with biodiesel blends that were specification quality when introduced to the vehicle.]

Considering all the information collected during the vehicle testing leads to the following points regarding a fuel-stressing apparatus.

- The two scenarios utilized for the vehicle testing (on-road and heated dyno) resulted in measureable differences in the fuel temperatures throughout the vehicles. As such, a decision regarding fuel-stressing temperatures and/or fuel test method temperatures should be related to the vehicle-operation scenario that one hopes to replicate. Temperatures around 100 °C to 110 °C represent the highest temperatures encountered by the fuel in the current testing. The maximum fuel tank temperature observed during vehicle testing was about 82 °C (180 °F).
- 2. Heating of any fuel sump during processing or testing should be considered as this is similar to actual driving conditions.
- 3. It is assumed that increasing the amount of oxygen available to the fuel during on-road operation (caused by sloshing) should lead to increased oxidation of the fuel. This assumption, however, was not consistently substantiated by the fuel testing results. It is worth noting that the test fuels had relatively short residence times in the vehicles prior to sampling and laboratory testing. Had the fuels been stored in the vehicles for longer periods, the effect of the increased oxygen availability might have been more clearly demonstrated.
- 4. The fuels tended to undergo relatively little measurable degradation during the vehicle testing. Factors that influenced this include the use of specification quality fuel and the fact that most of the fuel spent little time in the hottest parts of the vehicle. As the fuel was exposed to higher temperatures and more oxygen, there were measurable changes in the stability of the fuel. Using lower-quality test fuel in the vehicles tests would likely have resulted in larger measureable changes in the fuel.
- 5. Since adding heat and oxygen accelerates the degradation of the fuel, selection of conditions for stressing/testing will require decisions about the type of environment (vehicle conditions) one wishes to replicate.
- 6. Accelerating the conditions above/beyond those encountered in the vehicles is possible and would accelerate the degradation of the fuel. But, some decision is required regarding the degree to which acceleration is representative of vehicle operation/storage. A single fuel stressing/testing regime to represent all scenarios is not very likely. Perhaps using a small number of stressing/testing regimes, similar to vehicle test cycles, is most appropriate.
- 7. Conducting some bench-scale testing with fuels of poorer initial stability would help answer some of these questions.
- 8. It seems that a combination of Rancimat, RSSOT, and acid number testing were the most reliable method of assessing the stability change of a fuel during stressing. However, these test methods do not adequately assess the tendency of a fuel to form deposits on metal surfaces. A test method, such as a modified ASTM D3241 provides a more robust assessment of the change in fuel stability and deposit-forming characteristics.
- 9. It should again be noted that these vehicle tests were very short term; less than 7 total hours in the vehicle. Therefore, this testing did not accurately represent the effects of on-board vehicle storage for longer periods of time. Recall that the primary goals of the vehicle testing were to collect accurate temperature and pressure data to assist with the design of a fuel-aging apparatus.

Review of the stressing apparatus-aged fuel data leads to the following observations and conclusions from the bench scale fuel stressing apparatus testing:

- The total water test results indicate that essentially none of the added water in Test Fuel 2 was dissolved by the fuel. The variability of the results is likely due to small amounts of water dropping out of solution during the period between sampling and analysis.
- The RSSOT still seems to be a reliable indicator of change in the oxidative stability of the aged fuel. This was the case for both test fuels.
- The Rancimat also provides a reliable indication of changes in oxidative stability so long as there is biodiesel in the fuel. The test method is not applicable to B0 fuels.
- For Fuel 1 there seems to be a general trend of decreasing D3241 deposit volume with aging time. For Test Fuel 2, there is a trend of increasing deposit volume with aging time.
- The max deposit depth seemed to be generally higher for fuel 2. Additional testing is needed to further investigate D3241 testing.
- The RSSOT and Rancimat results from the fuel aging tests and B20 vehicle testing demonstrated that both aging techniques caused some degradation of oxidation stability. Further study would be needed to develop a correlation between the two methods of fuel aging.
- The simulated distillation final boiling point for sample 9313 (Test Fuel 2, Day 29) is significantly higher than the final boiling point of the other samples. The chromatogram for this sample was closely examined for evidence of material in that boiling range. A very slight peak is visible but there is no way to determine if it is from contamination in the sample or the formation of material during aging of the fuel. It should be noted that the added vegetable oil would not typically be detected by D2887; however, if the vegetable oil degraded during aging, some of the breakdown byproducts might account for the higher boiling point material.

APPENDIX A

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APPENDIX B

MERCEDES ML350 TEST INFORMATION

MERCEDES ML350 THERMOCOUPLE LOCATIONS

The ML-350 fuel tank is a "saddle" design.

Thermocouples

Fuel tank temperature is measured near the bottom of the saddle tank on the passenger side.

The connection of the fuel line to the high pressure fuel pump was modified to mount a thermocouple in the fuel stream at this location.

Two thermocouples were set to measure skin temperature at locations on the fuel lines under the vehicle in the proximity of engine.

A photograph of the tank after removal from the vehicle is shown below.



Figure B-1. Mercedes Saddle Tank after Removal

There is a fuel sending unit in each side of the saddle tank.

The fuel pump is on the passenger (right) side of the vehicle.

The fuel feed line crosses over from right to left on top of the tank as shown.

The return line directs fuel to the driver's side of the saddle tank.

The fuel tank thermocouple is located at the bottom of the passenger side of the fuel tank.

The fuel samples have been taken from a sample line that is located in proximity to the fuel tank thermocouple.



Figure B-2. Mercedes Tank Description



Figure B-3. Fuel Lines



Figure B-4. The Fuel Rail Skin Thermocouple is Set Under Rail at the Location Shown

The fuel line thermocouples were set on the driver's side of the engine. The photograph was taken from behind the underbody shielding in-board toward the engine.



Figure B-5. Mercedes Fuel Feed and Return Lines



Figure B-6. Liquid Fuel Thermocouple – Fuel Feed Line Upstream of the High Pressure Pump

OBD parameters

Mode	PID	Module	Description
Mode 1	****	****	Current powertrain diagnostic data
1	04	E8	Calculated load value
1	05	E8	Engine coolant temperature
1	0B	E8	Intake manifold absolute pressure
1	0C	E8	Engine speed
1	0D	E8	Vehicle speed
1	11	E8	Absolute throttle position
1	23	E8	Fuel rail pressure relative to atmosphere
1	24	E8	Equivalence ratio, Oxygen sensor voltage
1	2F	E8	Fuel level input
1	33	E8	Barometric pressure
1	46	E8	Ambient air temperature
1	49	E8	Accelerator pedal position
1	5C	E8	Engine oil temperature
1	5E	E8	Engine fuel rate
APPENDIX C

CHEVY SILVERADO TEST INFORMATION

CHEVROLET SILVERADO THERMOCOUPLE LOCATIONS



Figure C-1. In the Well of the Fuel Sending Unit



Figure C-2. In the Fuel Line Upstream of the High Pressure Fuel Pump



Figure C-3. Fuel Rail Skin Temperature



Figure C-4. Fuel Line Surface Temperature Near Exhaust System



Figure C-5. Photograph of the Underside of the Truck with the Fuel Tank Removed



Figure C-6. Diagram of Fuel System

APPENDIX D

SUMMARY DATA PLOTS FROM VEHICLE TESTING

























































APPENDIX E

FUEL STRESSING APPARATUS TEST PROTOCOL

AVFL-17c Biodiesel Oxidation Testing and Characterization in LD Diesel Vehicles Project Completion Test Plan

Garry Gunter August 21, 2015

This is a test plan for completion of the current ongoing project at Southwest Research Institute (SWRI). The objective of this phase of testing is to develop a bench fuel stressing apparatus and fuel stressing protocol to stress fuels in a manner similar to that experienced in the light duty (LD) vehicle testing portion of the project.

Test Fuels

Two fuels were tested to determine the effect of total glycerin (as triglycerides), water, and fuel aging for fuels subjected to stress similar to conditions measured in LD vehicle testing. The test fuel matrix is shown in Table I and test levels in Table II below.

#	Fuel	Total Glycerin	Water
1	B20 Soy	Normal	Low
2	B20 Soy	High	High

Table I. Test Fuel Matrix

Table II. Test Levels

Test Metric	Test Levels		
Total Glycerin Content	Normal	High	
(in B100 blend stock)	Total glycerin 0.10 ± 0.05 wt%	Total glycerin 0.30 wt% as Triglycerides 3.0 wt%	
	as mylycenues 1.0 wt/o		
Water Content	Low B20 70 ppm	High B20 200 ppm	

Total Glycerin Content

Total bonded and free glycerin content in B100 blend stock (ASTM D6751) is limited to 0.24 wt% as measured by ASTM D6584 (Glycerides and Glycerin in B100 by GC). Since bonded glycerin is defined as the glycerin portion of mono-, di-, and triglyceride molecules, and bonded glycerin comprises approximately 10.4 wt% of mass in triglycerides (according to the equation in the test method), this specification limit allows up to 2.3 wt% triglycerides in B100 blend stock. Total bonded glycerin content was measured for hundreds of market biodiesel samples in a series of fuel surveys performed by National Renewable Energy Laboratory (NREL) ^{i,ii,iii,iv}. Total bonded glycerin averaged 0.16 wt% with 90% of samples below 0.23 wt% and 95% of samples below 0.28 wt% as shown in Table III. Total bonded glycerin levels selected for testing were 0.10 wt% for normal level and 0.30 wt% for high level (off-specification) because these represent typical and 95th percentile levels in market biodiesel. These target levels correspond to triglyceride content of 1.0 and 3.0 wt% for normal and high levels, respectively. Biodiesel with high triglyceride level were prepared by spiking baseline B100 soy biodiesel with triglycerides (raw soybean oil) before blending to B20.

Total Glycerin by ASTM D6584 (wt%)				
Minimum	0.01			
Average	0.16			
Maximum	1.23			
P10%	0.04			
P20%	0.08			
P50% (Median)	0.14			
P80%	0.20			
P90%	0.23			
P95%	0.28			

Table III. Total Glycerin Content of B100 Biodiesel from NREL Fuel Surveys

Water Content

Water has potential to adversely affect fuel stability by participating in fuel degradation reactions, particularly by promoting microbial growth and by reacting with FAME to form free fatty acids and metal carboxylate soaps, which may contribute to corrosion, wear, suspended solids, deposits, and elastomer swelling in fuel systems ^{i,v}. ASTM D975 diesel specification limits water and sediment to less than 0.05 vol% by test method ASTM D2709 (water and sediment by centrifuge) and European EN 590 diesel specification limits water to less than 200 mg/kg by test method EN ISO 12937 (water by Karl Fischer). Fuel surveys found that water rarely approaches the ASTM specification limit ^{ii,iii,iv,vi}. In B100 biodiesel samples, water content ranged from about 50 to 1000 ppm with average of 265 ppm, as shown in Table IV. In petroleum diesel samples, water content ranged from about 50 to 120 ppm with average of about 90 ppm. For this study, water content of ULSD is targeted at 60 ppm for low level and 120 ppm for high level and biodiesel blend stock is targeted at 110 ppm for low level and 500 ppm for high level. These correspond approximately to 10th and 90th percentile water levels. Blending to B20 produces targets of 70 ppm for low level and 200 ppm for high level. Water content were adjusted by addition of deionized water to fuel.

ASTM D6304 Water by Karl Fischer Titration (ppm)						
	B100 Biodiesel	B8-B21 Biodiesel Blend	B0-B5 ULSD			
Minimum	54	47	52			
P10%	111	62	54			
Average	265	109	87			
P90%	494	162	120			
Maximum	979	208	121			

Table IV. Water Levels in Fuel Based on NREL and CRC Fuel Surveys

Fuel Stressing Apparatus

Fuel were stressed in a bench-scale fuel stressing apparatus designed to subject fuel to stress similar to conditions measured in LD vehicle testing. Maximum severity conditions identified in the vehicle testing portion of the project are listed in Table V below. Target test conditions are 110°C (230°F) at 35 bar (500 psi) for a residence time of 2 minutes. Target temperature and residence time are based on maximum conditions in the fuel rail. Target pressure is based on the maximum pressure thought feasible in a bench-scale fuel stressing apparatus and is not representative of fuel rail conditions.

	Running	Hot Soak	Target
Rail Temperature	100-110°C (212-230°F)	110°C (230°F)	110°C (230°F)
Rail Pressure	300-1,800 bar	-	35 bar (500 psi)
	(5,000-26,000 psi)		
Rail Residence Time	4 sec to 2 min	1 hr	2 min
Fuel Return Flow Rate	500-700 ml/min	-	500 ml/min
Tank Temperature	80°C (176°F)	80°C (176°F)	80°C (176°F)

Table V. Fuel Stressing Conditions Identified in Vehicle Testing

The fuel stressing apparatus is expected to be a tubular flow reactor or heat exchanger capable of subjecting fuel to the target conditions identified above. The fuel stressing apparatus must be designed with the ability to scale it up to a size capable of producing drumscale quantities of fuel for testing within an operating time of a few days.

Fuel Stressing Protocol

The fuel stressing protocol is intended to approximate conditions experienced by fuel in a LD vehicle operated daily in hot, humid summer conditions over a period of four weeks. It is intended to expose fuel to factors suspected to affect fuel stability including high temperature and pressure from fuel rail recirculation, storage temperature, air and humidity exposure during storage, storage time, and repeated fuel stress.

Store fuel in sealed container in climate-controlled storage until ready to begin testing.

Week 1, Day 1, Start of Testing:

- Fill test fuel container with about 16 liters of test fuel.
- Thoroughly stir fuel in test fuel container. Withdraw sample aliquot (1 liter) for full initial test matrix (all test methods in Table VI).
- To prevent cross-contamination of test fuels, the fuel stressing apparatus must be rinsed with clean fuel each time the fuel stressing apparatus is changed from one test fuel to another. Rinse fuel stressing apparatus by circulating clean, fresh baseline ULSD at room temperature conditions for about 10 minutes, then drain rinse fuel from the apparatus so it does not contaminate or dilute the next test fuel.
- Connect the test fuel container to the fuel stressing apparatus. Circulate test fuel from test fuel container through fuel stressing apparatus and back into the test fuel container for 7 hours. Operate fuel stressing apparatus at target test conditions listed in Table V. Adjust fuel recirculation flow rate (or cool returning fuel) so fuel in test container does not exceed the target of 80°C listed in the Table. Record test conditions including the fuel temperature in the test fuel container.
- Thoroughly stir fuel in test fuel container. Withdraw sample aliquot (1 liter) for fuel stability test matrix (all test methods in Table VI except Total Glycerin and FAME content). Note appearance of fuel in test fuel container and sample (color, clarity (haze), extra phases, particulate, floaters, deposits, etc.).
- Place breather cap on test fuel container and place it in warm storage overnight. Warm storage is a temperature-controlled location at approximately 90°F, out of direct sunlight. Record daily storage temperature and relative humidity.

Week 1, Day 2, Morning:

Repeat procedure from Day 1, except circulate fuel for only 1 hr, as outlined below.

- If the fuel stressing apparatus is switched from one test fuel to another, rinse and drain fuel stressing apparatus as described previously. If the fuel stressing apparatus is being used for the same test fuel as yesterday, rinsing is not required.
- Connect the test fuel container to the fuel stressing apparatus. Circulate test fuel from test fuel container through fuel stressing apparatus and back into the test fuel container for 1 hour. Operate fuel stressing apparatus at target test conditions as described previously.
- Place breather cap on test fuel container and place it in warm storage as described previously.

Week 1, Day 2, Afternoon:

Repeat procedure from Day 2 Morning. (i.e. Rinse apparatus (if necessary), circulate 1 hr, place test fuel in warm storage.)

Week 1, Day 3-5:

Repeat procedure from Day 2. (i.e. Rinse apparatus (if necessary), circulate 1 hr, place test fuel in warm storage, twice per day.)

Week 1, Day 6 and 7:

Leave test fuel container in warm storage over the weekend.

Week 2, Day 8:

• Thoroughly stir the fuel in the test fuel container. Withdraw sample aliquot (1 liter) for fuel stability test matrix (all test methods in Table VI except Total Glycerin and FAME content). Note appearance of fuel in test fuel container and sample (color, clarity (haze), extra phases, particulate, floaters, deposits, etc.).

Repeat procedure from Day 2. (i.e. Rinse apparatus (if necessary), circulate 1 hr, place test fuel in warm storage, twice per day.)

Week 2, Day 9-12:

Repeat procedure from Day 2. (i.e. Rinse apparatus (if necessary), circulate 1 hr, place test fuel in warm storage, twice per day.)

Week 2, Day 13 and 14:

Leave test fuel container in warm storage over the weekend.

Week 3, Day 15:

• Thoroughly stir the fuel in the test fuel container. Withdraw sample aliquot (1 liter) for fuel stability test matrix (all test methods in Table VI except Total Glycerin and FAME content). Note appearance of fuel in test fuel container and sample (color, clarity (haze), extra phases, particulate, floaters, deposits, etc.).

Repeat procedure from Day 2. (i.e. Rinse apparatus (if necessary), circulate 1 hr, place test fuel in warm storage, twice per day.)

Week 3, Day 16-19:

Repeat procedure from Day 2. (i.e. Rinse apparatus (if necessary), circulate 1 hr, place test fuel in warm storage, twice per day.)

Week 3, Day 20 and 21:

Leave test fuel container in warm storage over the weekend.

Week 4, Day 22:

• Thoroughly stir the fuel in the test fuel container. Withdraw sample aliquot (1 liter) for fuel stability test matrix (all test methods in Table VI except Total Glycerin and FAME content). Note appearance of fuel in test fuel container and sample (color, clarity (haze), extra phases, particulate, floaters, deposits, etc.).

Repeat procedure from Day 2. (i.e. Rinse apparatus (if necessary), circulate 1 hr, place test fuel in warm storage, twice per day.)

Week 4, Day 23-26:

Repeat procedure from Day 2. (i.e. Rinse apparatus (if necessary), circulate 1 hr, place test fuel in warm storage, twice per day.)

Week 4, Day 27 and 28:

Leave test fuel container in warm storage over the weekend.

Week 5, Day 29, End of Testing:

- Thoroughly stir fuel in test fuel container. Withdraw sample aliquot (1 liter) for fuel stability test matrix (all test methods in Table VI except Total Glycerin and FAME content). Note appearance of fuel in test fuel container and sample (color, clarity (haze), extra phases, particulate, floaters, deposits, etc.).
- If there is solid residue remaining in the fuel or test fuel container, attempt to obtain a sample for testing by direct probe mass spectrometry and/or FTIR-ATR. Collect residue sample in a glass container so sample is not contaminated with plasticizer from plastic container. (Phillips 66 in-kind analysis of solids and semi-solids). This is the end of testing for this fuel.

Fuel Analytical Test Methods

Fuel test methods of interest include all test methods evaluated in the vehicle testing portion of the project plus D3241, water, total glycerin, and simulated distillation. The difference between FAME and total glycerin may indicate other impurities including some types of heavy ends ^{vii}. Test methods of interest are shown in Table VI.
Test	Description	Sample	Initial	Stability
Method		Volume	Test	Test
		(ml)	Matrix	Matrix
D664	Total Acid Number (TAN) by Potentiometric Titration	20	Х	Х
D3241	Thermal Oxidation Stability of Aviation Turbine Fuels	600	Х	X
D3703	Hydroperoxide Number by Reaction with KI and Titration	70	Х	X
D6304	Water by Karl Fischer Titration	30	Х	Х
D4928				
D6468	High Temperature Stability of Middle Distillate	100	Х	X
D6584	Total Glycerin by GC (for B100 blend stock)	15	Х	
D7169	Simulated Distillation by High Temperature Method	10	Х	X
D7371	FAME in Diesel by FTIR-ATR-PLS or	50	Х	
EN14078	Transmission FTIR or GC			
EN14103				
D7545	Oxidation Stability by Induction Period,	5	Х	Х
	a.k.a Rapid Small Scale Oxidation Test (RSSOT)			
EN15751	Stability by Rancimat	50	Х	X
	Total sample volume	950		

Table VI. Analytical Test Methods

ⁱ R. McCormick, T. Alleman, M. Ratcliff, L. Moens, R. Lawrence, Survey of the Quality and Stability of Biodiesel and Biodiesel Blends in the United States in 2004, NREL/TP-540-38836, Oct. 2005

ⁱⁱ T. Alleman, R. McCormick, S. Deutch , 2006 B100 Quality Survey Results, NREL/TP-540-41549, May 2007

ⁱⁱⁱ T. Alleman, R. McCormick, Results of the 2007 B100 Quality Survey, NREL/TP-540-42787, Mar. 2008

^{iv} T. Alleman, L. Fouts, G. Chupka, Quality Parameters and Chemical Analysis for Biodiesel Produced in the United States in 2011, NREL/TP-5400-57662, Mar. 2013

^v S. Hoekman, A. Gertler, A. Broch, C. Robbins, Investigation of Biodistillates as Potential Blendstocks for Transportation Fuels, Coordinating Research Council (CRC) Report No. AVFL-17, Jun. 2009

^{vi} R. Legg, M. Legg, Survey of Biodiesel Content at Retail Diesel Fuel Outlets in Illinois and Minnesota, CRC Project E-112, May 2015

^{vii} S. Fernando, P. Karra, R. Hernandez, S. Jha, Effect of Incompletely Converted Soybean Oil on Biodiesel Quality, Energy 32 (2007) 844-851