



**COORDINATING RESEARCH COUNCIL, INC.**

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**September 22, 2016**

In reply, refer to:

CRC Project No. AVFL-17d

Dear Prospective Bidder:

The Coordinating Research Council (CRC) invites you to submit a written proposal to provide services for “Effect of Fuel Contamination on Biodiesel Blend Oxidation Stability in Laboratory Fuel Stressing Apparatus” (CRC Project No. AVFL-17d). A description of the project is presented in Exhibit A, “Statement of Work.”

Please indicate by letter, fax, or email by **October 10, 2016** if you or your organization intends to submit a written proposal for this research program. CRC will answer technical questions regarding the Request for Proposal if they are submitted in writing. CRC will then return written answers to all of the bidders, along with a copy of the original questions.

A CRC technical group composed of industry representatives will evaluate your proposal. CRC reserves the right to accept or reject any or all proposals.

The reporting requirements will be monthly progress reports and a summary technical report at the end of the contractual period. The reporting requirements are described in more detail in the attachment entitled “Reports” (Exhibit B).

The proposal must be submitted as two separate documents. The technical approach to the problem will be described in part one, and a cost breakdown that is priced by task will be described in part two. The cost proposal document should include all costs associated with conducting the proposed program. The technical proposal shall not be longer than 10 pages in length.

CRC expects to negotiate a cost-plus fixed fee or cost reimbursement contract for the research program.

Contract language for intellectual property and liability clauses is presented in Exhibit C and in Exhibit D, respectively.

Important selection factors to be taken into account are listed in Exhibit E. CRC evaluation procedures require the technical group to complete a thorough technical evaluation before considering costs. After developing a recommendation based on technical considerations, the costs are revealed and the recommendation is modified as needed.

Electronic copies of the technical and cost proposals should be submitted to:

Brent K. Bailey  
Coordinating Research Council  
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The deadline for receipt of your proposal is **October 29, 2016**.

Yours truly,

A handwritten signature in blue ink that reads "Brent K. Bailey". The signature is written in a cursive style with a large, stylized initial "B".

Brent K. Bailey  
Executive Director

## EXHIBIT A

### Statement of Work

# Effect of Fuel Contamination on Biodiesel Blend Oxidation Stability in Laboratory Fuel Stressing Apparatus

## Background

### Fuel Factors with Potential to Influence Oxidation Stability and Deposit Formation

Seven factors were identified having potential to affect fuel stability and tendency to form deposits for fuel subjected to stress similar to conditions measured in LD vehicle testing. These factors are biodiesel degree of unsaturation, triglycerides, heavy ends, antioxidant, cetane improver, water, and metals content. Additional factors such as microbial growth may impact fuel stability, but we currently have no plans to evaluate additional factors. Recommended test levels are shown in Table I.

Test levels in Table 1 were chosen to be representative of market fuels in the United States based on fuel survey results. Details of how test levels were selected for each test factor are discussed in Appendix A.

Table I. Test Levels

Test Factors	Test Levels	
Biodiesel Unsaturation	Beef tallow biodiesel	Soy biodiesel
Double Bond Equivalent (DBE)	Low 0.59	Moderate 1.50
EN 14111 Iodine Number (g Iodine/100 g sample)	50-82	120-131
Bis-Allylic Position Equivalent (BAPE)	0.05	0.73
Triglyceride Content (in B100 blend stock)	Normal Total glycerin 0.10 ± 0.05 wt% as Triglycerides 1.0 wt%	High Total glycerin 0.30 wt% as Triglycerides 3.0 wt%
Heavy Ends Content	Normal ULSD ~1 wt% Normal biodiesel 2-3 wt%	High ULSD > 2 wt% High biodiesel > 4 wt%
Antioxidant Level (in B100 blend stock)	Low - None	Normal TBHQ or PG 500 ppm
Cetane Improver Level (2EHN) (in final blended fuel)	None	Normal 2EHN 1000 ppm
Water Content (in final blended fuel)	Low ULSD 60 ppm Low B20 70 ppm	High ULSD 120 ppm High B20 200 ppm
Metals Content (in B100 blend stock)	Normal Ca+Mg <2 ppm Normal Na+K <3 ppm Normal P <3 ppm Normal Cu <1 ppm Normal Fe <1 ppm Normal Zn <1 ppm	High Ca+Mg 30 ppm High Na+K 80 ppm High P 20 ppm High Cu 5 ppm High Fe 10 ppm High Zn 10 ppm

### **Experimental Phase 1: Development of Modified JFTOT Fuel Oxidation Stability Test Method and Accelerated Fuel Stressing Protocol**

## Objective

This is a test plan for follow-on to the CRC AVFL-17c project.<sup>1</sup> The main objective of Phase 1 is to modify fuel stability test methods to make them capable of distinguishing between contaminated and clean biodiesel blend fuel in terms of their tendency to form deposits. Three test methods for fuel oxidation stability (RSSOT, Rancimat, and modified JFTOT) were identified by AVFL-17c project as capable of distinguishing between fresh and aged fuel. But only modified JFTOT showed promise of distinguishing between fuel contaminated with water and triglycerides compared to clean fuel. However, AVFL-17c results were not definitive, with clean fuel sometimes having higher deposits compared to aged fuel. Several known problems with the modified JFTOT method may have adversely affected the test results. This project attempts to address these problems by further development of the modified JFTOT method to improve its accuracy.

A second objective of Phase 1 is to test the feasibility of an “accelerated” fuel stressing protocol to speed up the preparation of fuels using the lab fuel stressing apparatus. If testing shows the “4-week” and “accelerated” fuel stressing protocols produce similar fuel oxidation stability as a function of total fuel stressing time online (hours in the fuel stressing apparatus), the accelerated fuel stressing protocol may replace the 4-week protocol in subsequent test phases.

If the main objective of Phase 1 is successful, a follow-on test phase (Phase 2) may be considered. The objective of the follow-on phase is to test the effect of various fuel factors on fuel stability and the tendency of fuel to form deposits.

All test fuels in both Phase 1 and Phase 2 will be 20 volume % biodiesel blended with ultra low sulfur diesel (ULSD).

## Approach

### Development of Modified JFTOT Fuel Oxidation Stability Test Method

The modified JFTOT method circulates biodiesel blend test fuel over a heated metal tube at a controlled flow rate causing solids to deposit onto the tube surface. The deposits on the tube are measured using an ellipsometer to determine the depth profile and total volume of deposits. Typically, the deposits are non-uniform, with the maximum deposit depth occurring near the effluent end of the tube (~50 mm tube length position). Therefore, in many cases the ellipsometer method was unable to accurately measure the maximum deposit depth (and total deposit volume) because of its position near the end of the tube. We plan to experiment with various modifications of the modified JFTOT method to move the maximum deposit depth earlier on the tube and thus improve the accuracy of deposit characterization. Some ideas for how to achieve this are as follows.

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<sup>1</sup> S. Westbrook, B. Shoffner, M. Blanks, Sr., K. Brunner, G. Wilson, III, G. Hansen, Sr., Thermal and Oxidative Instability in Biodiesel Blends During Vehicle Use and Onboard Fuel Storage, Coordinating Research Council Report No. AVFL-17c, Aug., 2016

- 1) Reduce JFTOT fuel flow rate - If deposits result from kinetically-controlled decomposition reactions, decreasing fuel flow rate should increase fuel residence time allowing longer deposit formation time and causing deposits earlier on the tube.
- 2) Increase JFTOT tube temperature – If deposits result from kinetically-controlled decomposition reactions, increasing tube temperature should make deposits occur faster, thus causing deposits earlier on the tube.
- 3) Decrease JFTOT tube temperature – If deposits result from solubility-controlled deposition as fuel cools near the end of the JFTOT tube, decreasing tube temperature should make deposits occur earlier on the tube.
- 4) Active cooling of the effluent end of the JFTOT tube - If deposits result from solubility-controlled deposition as fuel cools near the end of the JFTOT tube, actively cooling the effluent end of the tube should make deposits occur earlier on the tube.
- 5) Increased or reduced fuel test volume – If insufficient or excessive fuel deposit thickness is found to adversely affect the accuracy of deposit measurement, increasing or reducing the fuel test volume may be used to adjust the deposit thickness.

Many of these ideas are consistent with recommendations made for follow-on to the AVFL-2b project. A summary of AVFL-2b project results and recommendations is provided in Appendix B.

#### Preparation of Test Fuels for Modified JFTOT Test Development

Five fuels will be prepared for use in development of the modified JFTOT test. All base fuels are B20 soy biodiesel blend in ULSD. The fuel blend components must meet applicable ASTM fuel specifications (ASTM D6751 for B100 and ASTM D975 for ULSD) and the B20 blend must meet ASTM D7467 before dosing with contaminants.

Fuels will be prepared with indicated levels of triglycerides, water, heavy ends, cetane improver, and metals. Fuel parameter levels of normal, low, moderate, and high are defined in Table I. Triglycerides will be adjusted by doping with raw vegetable oil such as food-grade soybean oil. Water will be adjusted by doping with deionized water. Heavy ends will be adjusted by acquiring soy biodiesel with normal and high heavy ends content. Cetane improver will be adjusted by dosing with 2EHN. Metals (Cu+Fe+Zn) will be adjusted by dosing with compounds yet to be determined. Solubility of metals and water in fuel must be confirmed analytically before start of fuel stressing experiments in order to reduce the risk of insolubility or precipitation of fuel contaminants. Test fuels are listed below and tabulated in Table II.

- 1) B20 Baseline – B20 soy biodiesel blended into ultra low sulfur diesel (ULSD), low levels of contaminants, fuel has not been stressed in laboratory fuel stressing apparatus.
- 2) B20 Clean 4-Week – B20 soy biodiesel blended into ultra low sulfur diesel (ULSD), low levels of contaminants, fuel is stressed in the laboratory fuel stressing apparatus using the 4-week fuel stressing protocol same as used in the AVFL-17c project as described in detail in the sections below.
- 3) B20 Worst-Case 4-Week – B20 soy biodiesel blended into ULSD, high levels of water, triglycerides, heavy ends, cetane improver, and metals, fuel is stressed in the laboratory fuel stressing apparatus using the 4-week fuel stressing protocol.

- 4) B20 Clean Accelerated – B20 soy biodiesel blended into ULSD, low levels of contaminants, fuel is stressed in the laboratory fuel stressing apparatus using the accelerated fuel stressing protocol.
- 5) B20 Worst-Case Accelerated – B20 soy biodiesel blended into ULSD, high levels of water, triglycerides, heavy ends, cetane improver, and metals, fuel is stressed in the laboratory fuel stressing apparatus using the accelerated fuel stressing protocol.

Table II. Phase 1 Test Fuels for Modified JFTOT Test Development

Fuel #	Fuel Short Name	Base Fuel	Water	Triglycerides	Heavy Ends	Cetane Improver	Metals Cu+Fe+Zn	Fuel Stressing
1	B20 Clean Fresh	B20 Soy	Low	Normal	Normal	None	Normal	Fresh
2	B20 Clean 4-Week	B20 Soy	Low	Normal	Normal	None	Normal	4-Week
3	B20 Worst-Case 4-Week	B20 Soy	High	High	High	Normal	High	4-Week
4	B20 Clean Accelerated	B20 Soy	Low	Normal	Normal	None	Normal	Accelerated
5	B20 Worst-Case Accelerated	B20 Soy	High	High	High	Normal	High	Accelerated

#### Fuel Analytical Test Methods for Modified JFTOT Test Development

Three test methods for fuel oxidation stability (RSSOT, Rancimat, and modified JFTOT) were identified by AVFL-17c project as capable of distinguishing between fresh and aged fuel. These three test methods will also be used during further development of the modified JFTOT test. Additional fuel analytical tests with potential to affect fuel stability are tabulated in Appendix C.

#### Fuel Stressing Apparatus

Fuel will be 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 III 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.

Table III. Fuel Stressing Conditions Identified in Vehicle Testing

	Vehicle Running	Vehicle Hot Soak	Experimental Target
Rail Temperature	100-110°C (212-230°F)	110°C (230°F)	110°C (230°F)
Rail Pressure	300-1,800 bar (5,000-26,000 psi)	0	35 bar (500 psi)
Rail Residence Time	4 sec to 2 min	1 hr	2 min
Fuel Return Flow Rate	500-700 ml/min	0	500-700 ml/min
Tank Temperature	80°C (176°F)	80°C (176°F)	80°C (176°F)

The fuel stressing apparatus is expected to be a tubular flow reactor or heat exchanger capable of subjecting fuel to the experimental target conditions identified above. The fuel stressing apparatus must be designed with the ability to scale it up to a size capable of producing drum-scale quantities

of fuel for testing within an operating time of a few days. Fuel will be pumped from a test fuel container, through the fuel stressing apparatus, and back into the test fuel container. The test fuel container must be vented to the atmosphere, but not open to the atmosphere to avoid contamination. The fuel return line must return the fuel above the fuel liquid level, allowing some splashing and air exposure of returning fuel. This is intended to simulate a vehicle fuel tank system.

#### Four-Week 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 20 liters of test fuel. The test fuel container should be vented, but not directly open to the atmosphere to avoid excessive oxygen exposure and fuel light ends evaporation. The test fuel container should be capped at all times except when taking samples.
- Thoroughly stir fuel in test fuel container to ensure fuel uniformity, but do not entrain air into the fuel. Withdraw sample aliquot (1.8 liter) for oxidation stability testing (RSSOT, Rancimat, and modified JFTOT).
- 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 the “experimental target” test conditions listed in Table III. Heat or cool fuel in the fuel tank or fuel returning to the tank in order to maintain tank temperature near the target of 80°C listed in Table III. Record test conditions including the fuel temperature in the test fuel container (tank).
- Thoroughly stir fuel in test fuel container to ensure fuel uniformity, but do not entrain air into the fuel. Withdraw sample aliquot (1.7 liter) for oxidation stability testing (RSSOT, Rancimat, and modified JFTOT). Note appearance of fuel in test fuel container and sample (color, clarity (haze), extra phases, particulate, floaters, deposits, etc.).
- Place vented cap on test fuel container and place it in warm storage overnight. Warm storage is a temperature-controlled location at approximately 90°F (32°C), 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 vented 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 fuel in test fuel container to ensure fuel uniformity, but do not entrain air into the fuel. Withdraw sample aliquot (1.7 liter) for oxidation stability testing (RSSOT, Rancimat, and modified JFTOT). 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 fuel in test fuel container to ensure fuel uniformity, but do not entrain air into the fuel. Withdraw sample aliquot (1.7 liter) for oxidation stability testing (RSSOT, Rancimat, and modified JFTOT). 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 fuel in test fuel container to ensure fuel uniformity, but do not entrain air into the fuel. Withdraw sample aliquot (1.7 liter) for oxidation stability testing (RSSOT, Rancimat, and modified JFTOT). 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 to ensure fuel uniformity, but do not entrain air into the fuel. Withdraw sample aliquot (1.7 liter) for oxidation stability testing (RSSOT, Rancimat, and modified JFTOT). 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.

#### Accelerated Fuel Stressing Protocol

The purpose of the accelerated fuel stressing protocol is to reduce the time required to stress fuel from four weeks to a few days. The four-week fuel stressing protocol used to stress fuel in the laboratory fuel stressing apparatus for the AVFL-17c project stressed fuel daily for four weeks. The protocol stressed fuel 7 hours on day 1, 2 hours per day (1 hour morning and 1 hour afternoon) on day 2-5 (the first week), and 2 hours per day for weeks 2, 3 and 4. Fuel was stored in warm storage over the two-day weekends. The final fuel sample was collected the morning of the first day of week 5. The number of hours “online” in the fuel stressing apparatus was 7 hours on day 1, 2 hours per day on day 2-5 during the first week, and 2 hours per day for weeks 2, 3 and 4, for a total of  $7+(4*2)+(5*2)+(5*2)+(5*2) = 7+8+10+10+10 = 45$  hours.

The accelerated fuel stressing protocol stresses fuel for 45 hours straight in the fuel stressing apparatus with samples taken at start of testing and at hours 7, 15, 25, 35, and 45. If it is infeasible or inconvenient to operate the fuel stressing apparatus overnight, stressing time may be divided into periods of daily operation for convenience with the fuel stored in warm storage during periods of inactivity. We request that all fuels be stressed using the same schedule of fuel stressing periods so all “accelerated” samples are comparable. The accelerated fuel stressing protocol uses the same

starting fuel volume, sample volumes, analytical tests, and operating conditions for the fuel stressing apparatus as the 4-week fuel stressing protocol. Operating conditions for the fuel stressing apparatus are listed in the “Experimental Target” column in Table III.

### Experimental Phase 2 – Effect of Fuel Factors on Oxidation Stability and Deposit-Forming Tendency

This follow-on test phase will be considered after successful completion of the Phase 1 main objective of developing a modified JFTOT test method capable of discriminating between clean and contaminated fuel.

#### Effect of Fuel Factors on Oxidation Stability and Deposit-Forming Tendency

Fuels will be prepared with indicated levels of degree of unsaturation, triglycerides, water, heavy ends, cetane improver (2EHN), and metals. The test fuel matrix for Phase 2 is presented in Table IV. In Table IV, the “+” and “-” indicates high and low levels in Design of Experiments (DOE) notation. Fuel parameter levels of normal, low, moderate, and high are defined in Table I. Base fuels are ULSD or B20 soy biodiesel or B20 beef tallow biodiesel blend in ULSD. Fuel blend components must meet applicable ASTM fuel specifications (ASTM D6751 for B100 and ASTM D975 for ULSD), and the B20 blend must meet ASTM D7467 before dosing with contaminants.

Degree of unsaturation will be adjusted by using either soy or beef tallow biodiesel. Triglycerides will be adjusted by doping with raw vegetable oil such as food-grade soybean oil. Water will be adjusted by doping with deionized water. Heavy ends will be adjusted by acquiring soy and tallow biodiesel with normal and high heavy ends content. Cetane improver will be adjusted by dosing with 2EHN. Metals will be adjusted by dosing with compounds yet to be determined. Solubility of metals and water in fuel must be confirmed analytically before start of fuel stressing experiments in order to reduce the risk of insolubility or precipitation of fuel contaminants.

Table IV. Phase 2 Test Fuel Matrix

#	Fuel	Double Bond Equivalent	Triglyceride	Water	Heavy Ends	Cetane Improver	Metals Cu+Fe+Zn
1	B20 Soy	+ Moderate	- Normal	+ High	- Normal	- None	- Normal
2	B20 Soy	+ Moderate	+ High	- Low	+ High	- None	- Normal
3	B20 Tallow	- Low	+ High	+ High	- Normal	+ Normal	- Normal
4	B20 Soy	+ Moderate	- Normal	+ High	+ High	- None	+ High
5	B20 Soy	+ Moderate	+ High	- Low	+ High	+ Normal	- Normal
6	B20 Soy	+ Moderate	+ High	+ High	- Normal	+ Normal	+ High
7	B20 Tallow	- Low	+ High	+ High	+ High	- None	+ High
8	B20 Tallow	- Low	- Normal	+ High	+ High	+ Normal	- Normal
9	B20 Tallow	- Low	- Normal	- Low	+ High	+ Normal	+ High
10	B20 Soy	+ Moderate	- Normal	- Low	- Normal	+ Normal	+ High
11	B20 Tallow	- Low	+ High	- Low	- Normal	- None	+ High
12	B20 Tallow	- Low	- Normal	- Low	- Normal	- None	- Normal

Fuels will be stressed in the fuel stressing apparatus using either the “4-week” or the “accelerated” fuel stressing protocol. The accelerated protocol will be used if it is determined to be equivalent to the 4-week protocol based on Phase 1 results.

Fuels will be evaluated using RSSOT, Rancimat, and Modified JFTOT using methods developed in projects AVFL-17c and AVFL-17d Phase 1. These methods were found effective in discriminating for both fuel stressing time and fuel contaminant level.

## Appendix A: Background Information – Test Level Selection for Each Test Factor

### Biodiesel Unsaturation

Molecules containing double bonds are generally more prone to oxidation and have lower stability than saturated molecules. This is because the C-H bond of the allyl group (methylene group adjacent to the double bond) has about 15% lower bond strength than the C-H bond of a methylene group in a saturated hydrocarbon. This makes the allyl hydrogen easier to abstract, which is the first step of oxidation reactions to form peroxides. In addition, the C-H bond of a bis-allyl group (methylene group between two double bonds) has even lower bond strength and is even more prone to oxidation than the allyl C-H bond. For this reason, fatty acid methyl ester (FAME) with higher concentration of molecules with two and three double bonds (methyl linoleate, methyl linolate) has lower stability. The number of bis-allylic groups in biodiesel may be quantified by a measure called Bis-Allylic Position Equivalents (BAPE), which correlates well with fuel stability as measured by Oil Stability Index (OSI).<sup>2,3</sup> Biodiesel degree of unsaturation is 0.59 (average number of double bonds per molecule) for beef tallow-based biodiesel and 1.50 for soy-based biodiesel. These levels were chosen because these biodiesel feed stocks are the most commonly available in the United States. Since the range of biodiesel unsaturation levels ranges from about 0.1 for coconut biodiesel to 2.2 for linseed biodiesel, beef tallow and soy biodiesel represent low and moderate degree of unsaturation, respectively. Degree of unsaturation may be quantified using test method EN 14111 Iodine Number of Fatty Acid Methyl Ester (FAME) by Reaction and Titration. The iodine number of beef tallow and soy biodiesel is about 66 and 126 g iodine/100 g sample, respectively, based on a literature survey.<sup>4</sup> The FAME Profile (a.k.a. Fatty Acid Profile) of typical soy and beef tallow biodiesels is presented in Table V.

Table V. FAME Profile of Typical Biodiesels

Biodiesel Type	C16:0	C18:0	C18:1	C18:2	C18:3	Total	Double Bond Equiv. (DBE)	Allylic Position Equiv. (APE)	Bis-Allylic Position Equiv. (BAPE)
Beef	28.0	24.2	43.8	3.3	0.7	100.0	0.525	0.956	0.047
Soy	9.4	4.4	22.0	55.3	8.9	100.0	1.593	1.724	0.731

### 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

<sup>2</sup> G. Knothe, R. Dunn, Dependence of Oil Stability Index of Fatty Compounds on Their Structure and Concentration and Presence of Metals, *J. Am. Oil Chem. Soc.*, vol. 80, no. 10, 2003, p. 1021-1026

<sup>3</sup> G. Litwinienko, A. Daniluk, T. Kasprzycka-Guttman, A Differential Scanning Calorimetry Study on the Oxidation of C<sub>12</sub>-C<sub>18</sub> Saturated Fatty Acids and Their Esters, *J. Am. Oil Chem. Soc.*, 76:655-657, 1999

<sup>4</sup> S. Hoekman, A. Broch, C. Robbins, E. Cenicerros, Investigation of Biodiesel Chemistry, Carbon Footprint and Regional Fuel Quality, CRC report AVFL-17a, Jan. 2011

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).<sup>5,6,7,8</sup> 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 VI. 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 95<sup>th</sup> 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 will be prepared by spiking baseline B100 soy biodiesel with triglycerides (raw soybean oil) before blending to B20.

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

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

### Heavy Ends Content

For purposes of this study, heavy ends content is defined as the fraction of fuel boiling above 755°F (402°C) as measured by ASTM D7169 High Temperature Simulated Distillation test method. This corresponds to the 99% boiling point (T99) for a typical #2 ULSD. Heavy ends of biodiesel include free and bonded glycerin, insolubles, and unsaponifiable matter.<sup>9</sup> Heavy ends of diesel are simply high-boiling hydrocarbons. Since it is difficult to artificially reproduce the complex mixture of heavy ends materials, we plan to find market samples of both biodiesel and ULSD containing normal and high heavy ends levels instead of artificially spiking heavy ends into a normal sample. Normal levels of heavy ends content of ULSD and B100 biodiesel is about 1 wt% and 2-4 wt%, respectively, based on limited fuel surveys performed on Phillips 66 refineries and biodiesel suppliers. These represent typical #2 diesel and B100 biodiesel levels. To put this in perspective, the D2887 (Simulated Distillation at normal conditions) final boiling point (FBP) of summer ULSD ranged from 695 to 821°F with an average of 760°F. For purposes of this study, normal level of heavy ends is targeted at 1 wt% for ULSD and 2-3 wt% for B00. High level of heavy ends content is targeted at > 2 wt% for ULSD and > 4 wt% for B100.

### Antioxidant Level

<sup>5</sup> R. McCormick, T. Alleman, M. Tatcliff, 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

<sup>6</sup> T. Alleman, R. McCormick, S. Deutch, 2006 B100 Quality Survey Results, NREL/TP-540-41549, May 2007

<sup>7</sup> T. Alleman, R. McCormick, Results of the 2007 B100 Quality Survey, NREL/TP-540-42787, Mar. 2008

<sup>8</sup> 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

<sup>9</sup> S. Sanford, J. White, P. Shah, C. Wee, M. Valverde, G. Meier, Feedstock and Biodiesel Characteristics Report, Renewable Energy Group Inc., www.regfuel.org, Nov. 2009

### Antioxidant Level

Antioxidants may be used to improve oxidation stability of biodiesel. The most effective antioxidants include t-butyl hydroquinone (TBHQ) and pyrogallol (1,2,3-tri-hydroxy benzene, PG) at dosage rates of 200-1000 ppm.<sup>10,11</sup> Butylated hydroxytoluene (BHT) is not a preferred antioxidant because of reduced effectiveness for biodiesel. Treat rates greater than 1000 ppm offer little benefit. For this study, either TBHQ or PG antioxidant will be studied at levels of none and normal (500 ppm). We need test methods to quantify antioxidant levels.

### Cetane Improver Level

2-ethylhexylnitrate (2EHN) and diisobutylperoxide (DIBP) are the two most common cetane improvers used in market diesel with 2EHN being most widely used. Cetane improvers have potential to affect fuel stability, especially if they decompose to form reactive species upon exposure to heat in the vehicle fuel system.<sup>12</sup> The dosing rate of 2EHN ranges from 500 to 4000 ppm, with modest rates of 500-1000 ppm being most common.<sup>13</sup> For this study, 2EHN cetane improver will be dosed in both ULSD and B20 at a normal level of 1000 ppm.

### 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.<sup>5,10</sup> ASTM D975 diesel specification limits water and sediment to a 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.<sup>6,7,8,14</sup> In B100 biodiesel samples, water content ranged from about 50 to 1000 ppm with average of 265 ppm, as shown in Table VII. 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 10<sup>th</sup> and 90<sup>th</sup> percentile water levels. Blending to B20 produces targets of 70 ppm for low level and 200 ppm for high level. Water content will be adjusted by addition of deionized water to fuel.

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<sup>10</sup> 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

<sup>11</sup> S. Jain, M. Sharma, Stability of Biodiesel and Its Blends: A Review, Renewable and Sustainable Energy Reviews 14 (2010) 667-678

<sup>12</sup> Diesel Fuels Technical Review, Chevron Corp., 2007

<sup>13</sup> P. Richards, Automotive Fuels Reference Book, 3<sup>rd</sup> edition, SAE, 2014

<sup>14</sup> R. Legg, M. Legg, Survey of Biodiesel Content at Retail Diesel Fuel Outlets in Illinois and Minnesota, CRC Project E-112, May 2015

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

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

### Metals Content

Metals may contribute to fuel system and engine wear, engine deposits, filter plugging, and may act as catalysts to promote fuel degradation reactions.<sup>5,15</sup> Acting as a catalyst, metals may exacerbate fuel degradation caused by other impurities. Therefore, it is important to examine the effect of metals in combination with other fuel impurities. Metals of interest include calcium (Ca), copper (Cu), iron (Fe), magnesium (Mg), phosphorus (P), potassium (K), sodium (Na), and zinc (Zn). Cu and Fe are thought to promote fuel oxidation more actively and at lower concentrations than other metals of interest.<sup>15</sup> Several studies show that above a threshold concentration, the effect of metals on stability is nearly independent of the metals concentration in the fuel.<sup>11</sup> Ca and Mg are absorbents for purifying biodiesel, Na and K are catalysts for biodiesel production, P occurs naturally in triglyceride feed stocks used to produce biodiesel, and Cu, Fe, and Zn may originate from contact with fuel system components. In addition, Ca, Mg, K, and Zn are components of lube oil, and Ca and Na may originate from water contamination, especially hard water and sea water. Based on limited fuel survey data, metals content of biodiesel-containing fuels are presented in Table VIII. Metals will be added to biodiesel at levels of interest before blending to B20.

<sup>15</sup> J. Waynick, Characterization of Biodiesel Oxidation and Oxidation Products – Task 1 Results Technical Literature Review, CRC Project No. AVFL-2b Task 1, Aug. 2005

Table VIII. Metals Content from Fuel Surveys

Metals	Typical Level (ppm)	High Level (ppm)	Fuel Type	Source
Ca	<2	35	B100	NREL 2004 (27 samples)
Mg	<1	7		
Na	<2	37		
K	ND	ND		
P	<10	30		
Cu	<2	5		
Fe	<2	12		
Zn	<2	38		
Ca+Mg	<2	17		
Na+K	<5	82		
P	<5	10		
Cu	<1	1		
Fe	<1	3		
Zn	<1	9		
Ca+Mg	<1	29	B100	NREL 2008 (105 samples)
Na+K	<2	83		
P	<5	21		
Ca	0.2 avg.	0.7		
Mg	<0.1	<0.1		
Na	0.6 avg.	2		
K	<0.1	<0.1		
Ca+Mg	<0.6	2.8	B100	NREL 2013 (67 samples)
Na+K	<3	18		

#### Appendix B: Summary of AVFL-2b Project Recommendations

##### **AVFL-2b Characterization of Biodiesel Oxidation and Oxidation Products – Experimental Investigation of Biodiesel Oxidation and Deposition Tendency**

SwRI Task 2 report, Aug. 2007

Three biodiesels with no added antioxidant (B100 soy, B100 soy, and B100 yellow grease) were evaluated by numerous stability and deposit indicator test methods including Rancimat, insoluble by modified D2274, TAN, peroxide value, polymer content, anisidine value, conjugated diene content, and JFTOT at 260 and 300°C. One of the two B100 soy fuels had typical stability by Rancimat induction period, while the other had unusually high stability. These two B100 soy fuels were further tested by quiescent aging (storage in sealed container with small headspace for 6 weeks at 50°C (122°F) and agitated aging (ASTM D2274 at 95°C (203°F) oxygen bubbling for 16 hrs). The two B100s were then blended with ULSD to make B20, which was then tested before and after quiescent and agitated aging.

The three B100s varied widely in stability which correlated with JFTOT deposit volume. A rough correlation was also found between Rancimat IP and other methods including D2274 total insolubles, TAN, delta TAN, polymer content, delta polymer, and peroxide value. A linear relationship was found between polymer content and TAN. Combination of delta TAN or delta polymer with Rancimat IP is proposed as a good stability indicator for biodiesel. Stability differences observed with B100 disappeared with blending to B20 except for the most severe

oxidation stressing. JFTOT results showed correlation of stability with deposit forming tendency on hot steel surfaces. JFTOT also showed correlation between deposit volume and extent of prior oxidation as well as stability of un-oxidized B100 and B20 samples.

Deposit values reached saturation levels using the standard JFTOT conditions and made the test less discriminating. It is proposed to optimize JFTOT by reducing test fuel volume from 600 to 200 ml as well as shorten residence time and reduce tube temperature to increase sensitivity to stability differences in biodiesel.

Although the high-stability B100 soy was claimed to have no added antioxidant, test results suggest that it very likely did contain synthetic antioxidant.

### Appendix C: Fuel Analytical Test Methods

Fuel test methods of interest are tabulated in Table IX. The difference between FAME and total glycerin may indicate other impurities including some types of heavy ends.<sup>16</sup> All Modified JFTOT tests include a quantitative measure of deposit thickness using an ellipsometer. Other test methods may be applicable, but are not included in this test plan including polymer content, anisidine value, and conjugated diene content.

Table IX. Analytical Test Methods

Test Method	Description	Sample Volume (ml)
<b>Fuel Characterization Tests</b>		
D7371	FAME in Diesel by FTIR-ATR-PLS or Transmission FTIR or GC	50
EN14078		
EN14103		
EN14111	Iodine Number of Fatty Acid Methyl Ester (FAME) by Reaction and Titration	5
AOCS Ce 1c-89 or GC-MS	FAME Component Profile by GC-FID (a.k.a. Fatty Acid Profile) or FAME Profile by GC-MS	1
Calculated	Bis-Allylic Position Equivalent (BAPE)	-
Calculated	Allylic Position Equivalent (APE)	-
Calculated	Iodine Value (IV)	-
D6584	Total Glycerin by GC (for B100 blend stock)	15
D7169	Simulated Distillation by High Temperature Method	10
GC-MS	Antioxidant Content (TBHQ, PG, BHT)	1
GC-MS	Cetane Improver (2-EHN)	1
D6304	Water by Karl Fischer Titration	30
D4928		
D5185	Metals by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) and/or ICP-Mass Spectrometry (ICP-MS) (Ca, Mg, Na, K, P, Cu, Fe, Zn)	5
<b>Fuel Stability Tests</b>		
D7545	Oxidation Stability by Induction Period, a.k.a. Rapid Small Scale Oxidation Test (RSSOT)	5
EN15751	Stability by Rancimat	50

<sup>16</sup> S. Fernando, P. Karra, R. Hernandez, S. Jha, Effect of Incompletely Converted Soybean Oil on Biodiesel Quality, Energy 32 (2007) 844-851

D3241 Modified	Modified Jet Fuel Thermal Oxidation Test (JFTOT) (Variable conditions to be determined, deposit thickness by ellipsometer)	500
<b>Additional Tests of Interest</b>		
D664	Total Acid Number (TAN) by Potentiometric Titration	20
D2274	Oxidation Stability by Accelerated Oxidation	500
D3241	Jet Fuel Thermal Oxidation Test (JFTOT) (300°C, 450 ml, 3.0 ml/min fuel flow rate, deposit rating by color, deposit thickness by ellipsometer)	500
D3703	Hydroperoxide Number by Reaction with KI and Titration	70
D6468	High Temperature Stability of Middle Distillate	100
?	Modified Oil Stability Index (OSI)	?
D6890	Derived Cetane Number by IQT	100
Total sample volume		1963

#### Appendix D: Statistical Design of Experiments (DOE)

A statistician was consulted regarding design of fuel matrices for Phase 1 and Phase 2. The Phase 1 fuel matrix in Table II did not lend itself to DOE analysis since it is a scoping study with multiple factors changing at once. (There is not much DOE can do to evaluate 8 factors with only 5 treatments.) But this is fine since the objectives of Phase 1 are 1) to generate test fuel for development of the modified JFTOT stability test method and 2) to test feasibility of the “accelerated” fuel stressing protocol.

DOE methodology was applied to the Phase 2 fuel matrix in Table IV to produce a 2-level, 6-factor, 1-replicate, 12-run, Plackett-Burman experimental design. Design features include orthogonality, balance, and no confounding between main effects<sup>17</sup>.

#### Appendix E: Acronyms

APE	Allylic Position Equivalent
B20	20 vol % biodiesel in ULSD
B100	100% biodiesel
BAPE	Bis-Allylic Position Equivalent
BHT	Butylated Hydroxytoluene
DBE	Double Bond Equivalent
DIPB	Diisobutylperoxide
DOE	Design of Experiments
2EHN	2-Ethylhexyl Nitrate
FAME	Fatty Acid Methyl Ester
FBP	Final Boiling Point
FTIR-ATR-PLS	Fourier Transform Infrared – Attenuated Total Reflectance – Partial Least Square
GC	Gas Chromatography
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
JFTOT	Jet Fuel Thermal Oxidation Test
LD	Light Duty

<sup>17</sup> R. Myers, D. Montgomery, C. Anderson-Cook, Response Surface Methodology - Process and Product Optimization Using Designed Experiments, 3<sup>rd</sup> Edition, Wiley, 2009, p. 165-167

NREL	National Renewable Energy Laboratory
OSI	Oil Stability Index
PG	Pyrogallol
RSSOT	Rapid Small Scale Oxidation Test
SwRI	Southwest Research Institute
T99	Temperature at which 99 vol% of sample distills off
TAN	Total Acid Number
TBHQ	t-Butyl Hydroquinone
ULSD	Ultra Low Sulfur Diesel

#### Appendix F: Project Timing

Phase 1 – 2016 Q3 – 2017 Q1

Phase 2 – 2017 2Q – 2017 Q4

## **EXHIBIT B**

### **REPORTS**

#### **MONTHLY TECHNICAL PROGRESS REPORTS**

The contractor shall submit a monthly technical progress report covering work accomplished during each calendar month of the contract performance. An electronic Microsoft® Word compatible file (<1 MB) of the monthly technical progress report shall be distributed by the contractor within ten (10) calendar days after the end of each reporting period. The report shall contain a description of overall progress, plus a separate description for each task or other logical segment of work on which effort was expended during the reporting period.

#### **FINAL REPORT**

The contractor shall submit to or distribute for CRC an electronic (Microsoft Word) copy transmittable via email) of a rough draft of a final report within thirty (30) days after completion of the technical effort specified in the contract. The report shall document, in detail, the test program and all of the work performed under the contract. The report shall include tables, graphs, diagrams, curves, sketches, photographs and drawings in sufficient detail to comprehensively explain the test program and results achieved under the contract. The report shall be complete in itself and contain no reference, directly or indirectly, to the monthly report(s).

The draft report must have appropriate editorial review corrections made by the contractor prior to submission to CRC to avoid obvious formatting, grammar, and spelling errors. The report should be written in a formal technical style employing a format that best communicates the work conducted, results observed, and conclusions derived. Standard practice typically calls for a CRC Title Page, Disclaimer Statement, Foreword/Preface, Table of Contents, List of Figures, List of Tables, List of Acronyms and Abbreviations, Executive Summary, Background, Approach (including a full description of all experimental materials and methods), Results, Conclusions, List of References, and Appendices as appropriate for the scope of the study. Reports submitted to CRC shall be written with a degree of skill and care customarily required by professionals engaged in the same trade and /or profession.

Within thirty (30) days after receipt of the approved draft copy of the final report, the contractor shall make the requested changes and deliver to CRC thirty (30) hardcopies including a reproducible master copy of the final report. The final report shall also be submitted as electronic copies in a pdf and Microsoft Word file format. The final report may be prepared using the contractor's standard format, acknowledging author and sponsors. An outside CRC cover page will be provided by CRC. The electronic copy will be made available for posting on the CRC website.

## **EXHIBIT C**

### **INTELLECTUAL PROPERTY RIGHTS**

Title to all inventions, improvements, and data, hereinafter, collectively referred to as (“Inventions”), whether or not patentable, resulting from the performance of work under this Agreement shall be assigned to CRC. Contractor X shall promptly disclose to CRC any Invention which is made or conceived by Contractor X, its employees, agents, or representatives, either alone or jointly with others, during the term of this agreement, which result from the performance of work under this agreement, or are a result of confidential information provided to Contractor X by CRC or its Participants. Contractor X agrees to assign to CRC the entire right, title, and interest in and to any and all such Inventions, and to execute and cause its employees or representatives to execute such documents as may be required to file applications and to obtain patents covering such Inventions in CRC’s name or in the name of CRC’s Participants or nominees. At CRC’s expense, Contractor X shall provide reasonable assistance to CRC or its designee in obtaining patents on such Inventions.

To the extent that a CRC member makes available any of its intellectual property (including but not limited to patents, patent applications, copyrighted material, trade secrets, or trademarks) to Contractor X, Contractor X shall have only a limited license to such intellectual property for the sole purpose of performing work pursuant to this Agreement and shall have no other right or license, express or implied, or by estoppel. To the extent a CRC member contributes materials, tangible items, or information for use in the project, Contractor X acknowledges that it obtains only the right to use the materials, items, or information supplied for the purposes of performing the work provided for in this Agreement, and obtains no rights to copy, distribute, disclose, make, use, sell or offer to sell such materials or items outside of the performance of this Agreement.

## **EXHIBIT D**

### **LIABILITY**

It is agreed and understood that \_\_\_\_\_ is acting as an independent contractor in the performance of any and all work hereunder and, as such, has control over the performance of such work. \_\_\_\_\_ agrees to indemnify and defend CRC from and against any and all liabilities, claims, and expenses incident thereto (including, for example, reasonable attorneys' fees) which CRC may hereafter incur, become responsible for or pay out as a result of death or bodily injury to any person or destruction or damage to any property, caused, in whole or in part, by \_\_\_\_\_'s performance of, or failure to perform, the work hereunder or any other act of omission in connection therewith.

## **EXHIBIT E**

### **PROPOSAL EVALUATION CRITERIA**

- 1) Merits of proposed technical approach.
- 2) Previous performance on related research studies.
- 3) Personnel available for proposed study – related experience.
- 4) Timeliness of study completion.
- 5) Cost.