Research to Address Technical Barriers to Expanded Markets for Biodiesel and Biodiesel Blends

Cooperative Research and Development Final Report

CRADA Number: CRD-15-00593

NREL Technical Contact: Robert McCormick

NREL is a national laboratory of the U.S. Department of Energy
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Contract No. DE-AC36-08GO28308

Technical Report
NREL/TP-5400-89192
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Cooperative Research and Development Agreement (CRADA) Final Report

Report Date: July 18, 2024

In accordance with requirements set forth in the terms of the CRADA, this document is the CRADA final report, including a list of subject inventions, to be forwarded to the U.S. Department of Energy (DOE) Office of Scientific and Technical Information as part of the commitment to the public to demonstrate results of federally funded research.

Parties to the Agreement: Clean Fuels Alliance America (CFAA) (formerly National Biodiesel Board)

CRADA Number: CRD-15-00593

CRADA Title: Research to Address Technical Barriers to Expanded Markets for Biodiesel and Biodiesel Blends

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Sponsoring DOE Program Offices:

Office of Energy Efficiency and Renewable Energy (EERE), Bioenergy Technologies Office (BETO); Office of Energy Efficiency and Renewable Energy (EERE), Vehicle Technologies Office (VTO)

Joint Work Statement Funding Table Showing DOE Commitment:

Estimated Costs	NREL Shared Resources a/k/a Government In-Kind
Year 1. Modification #1	$50,000.00
Year 2	$0.00
Year 3	$0.00
Year 4	$0.00
Year 5	$0.00
Year 6	$0.00
Year 7	$0.00
Year 8	$0.00
TOTALS	$50,000.00

Executive Summary of CRADA Work:

NREL and CFAA will work cooperatively to assess the effects of biodiesel blends into petroleum diesel on the performance of modern diesel engines. This work will include research to understand the impact of biodiesel blends on the operation and durability of particle filters and nitrogen oxides (NO_x) control sorbents/catalysts, to quantify the effect on emissions control systems performance, and to understand effects on engine component durability. This research was performed at NREL Renewable Fuels and Lubricants (ReFUEL) laboratory (an engine testing laboratory), as well as at third-party labs paid directly by CFAA with NREL as part of the project management team. Also, research to develop appropriate ASTM International (ASTM) standards for biodiesel quality and stability was conducted in NREL's bench-scale fuel chemistry laboratory. The cooperative project involved laboratory testing and research at NREL using biodiesel from a variety of sources and in collaboration with a broad range of other stakeholders. In addition, NREL will work with CFAA to set up an industrial steering committee to design the scope for the various tasks and to provide technical oversight to these projects. NREL and CFAA will cooperatively communicate the study results to as broad an audience as possible. This research benefits the public by expanding markets for a domestically produced, low-carbon-intensity (CI) fuel for use in diesel engines including on-highway, non-road, and railroad applications.

Over more than 8 years the joint work statement (JWS) was modified 18 times. The following table provides the modification history.

Original CRADA	Aug. 2015	Task 1: Oxidation stability and property loan (environmental chamber)
Mod 1	June 2016	Adds additional scope to Task 1, Task 2 retail B20 survey (co-funded by VTO), Task 3 Fourier-transform infrared spectroscopy (FTIR) method expansion to raw vegetable oil (RVO)
Mod 2	Feb. 2017	Adds funds in, no change in scope
Mod 3	July 2017	Add Task 4 Northeast oxidation stability quality support and extends POP
Mod 4	Sept. 2017	Adds Task 5 expansion of Task 2 B20 survey, Task 6 depletion of oxidation reserve in marketplace, Task 7 fuel analysis and troubleshooting
Mod 5	Oct. 2017	Adds Task 8 biodiesel metals effects on diesel aftertreatment engine aging study
Mod 6	Sept. 2018	New scope for Tasks 6 and 8, adds Task 9 off-highway engine emissions impacts of high-level blends and B100
Mod 7	Oct. 2018	Adds Task 10 analytical troubleshooting, additional work on FTIR method, microwave plasma atomic emission spectrometry (MP-AES) method, cold soak filter blocking tendency (CSFBT) for filter clogging
Mod 8	Dec. 2018	Adds loaned property, Seta CSFBT instrument for work under Task 10
Mod 9	April 2019	Corrects Mod 8 to add value of loaned property
Mod 10	Aug. 2019	Adds Task 11, which modified prior Tasks 8 and 9 for work on engine testing of high-level biodiesel blends and B100
Mod 11	Nov. 2019	Adds Task 12 cooperative efforts on engine performance on high-level blends: management of projects at University of Michigan, Southwest Research Institute (SwRI), and Purdue University
Mod 12	Dec. 2019	Task 10 is amended
Mod 13	Feb. 2020	Adds loan on off-highway diesel engine, Caterpillar C7.1; also fixes loaned equipment table
Mod 14	April 2020	Amends Tasks 8, 10, and 11 and extends POP
Mod 15	Sept. 2020	Amends Tasks 1, 8, and 10
Mod 16	Aug. 2021	Amends Tasks 1 and 10, adds Task 13 (incorrectly listed as Task 12 in JWS) to revise *Biodiesel Handling and Use Guide*, adds Task 14 (incorrectly listed as Task 13 in JWS) for techno-economic analysis study
Mod 17	Aug. 2022	Amends Tasks 1, 8, 10, and 13 and adds Task 15 (incorrectly listed as Task 14 in the JWS) to continue project management technical support; extends POP
Mod 18	July 2023	No-cost extension

Summary of Research Results:

Task 1: Oxidation Stability

This task was conducted in two phases, with the first occurring from 2015 to 2017 and the second from 2020 to 2023. The first phase focused on 20 vol % blends of biodiesel into petroleum diesel (B20), while the second focused on B50 and neat biodiesel (B100). Specific modifications to the JWS for Task 1 are listed below, along with a brief statement on task outcome. A detailed research summary is also presented below.

Task 1: Readditizing B20 With Antioxidant Additives After Loss of Induction Period (Original CRADA – August 2015)

- This task was successfully completed.

Task 1 Part 2: Impact of the Presence of Water and of Petroleum Diesel Chemistry on the Stability of Biodiesel Blends (Added as Mod 1 May 2016)

- This task was not completed, as the partner directed resources into the original Task 1 scope. Aspects of this task's scope were later included in Task 6.

Task 1: Long-Term Storage and Readditization of B100 and B50 With Antioxidant Additives After Simulated Aging (Added as Mod 15 September 2020)

- This large task was 50% completed during the period of performance for this CRADA, achieving several of the task objectives. Note that this work continues under a new agreement with CFAA.

Readditization of B20 Blends

In research conducted prior to this CRADA, NREL demonstrated that both B100 and B20 blends could be aged to fail the ASTM stability requirements, and then treated with additional antioxidant to pass these requirements, with no deleterious effect on stability. This "readditization" essentially reset the fuel stability back to an earlier point in time if stability was not allowed to get too low (Christensen and McCormick 2014). Under the CRADA initiated in 2015, NREL performed additional studies of readditization of B20 blends that were obtained from commercial outlets across the United States. This work was published as Christensen, Alleman, and McCormick (2018).

Commercial biodiesel blends were aged at 43°C while monitoring stability. The oxidation stability—or oxidation reserve expressed as Rancimat induction period (IP)—gradually decreased from its initial value (Figure 1a). At a predetermined IP, an antioxidant was used to restore IP to the ASTM D7467 specification minimum value of 6 h, referred to as readditization. At lower IP values, the amount of antioxidant required increased significantly, and effectiveness tended to reduce. Peroxide formation was monitored (Figure 1b) and showed that readditization arrested oxidation. Acid content was also monitored (Figure 1c). Once IP fell to essentially zero, the acid content increased to above the allowable limit, and insoluble material was also detected.

Storage life was increased relative to the as-received fuels as evidenced by longer time to produce acids. Experience in the field may vary based on storage conditions; however, these results indicate readditization can significantly increase storage life of biodiesel blends when used with regular monitoring of IP and acid number. An assessment of the storage stability of the as-received fuels showed that the initial IP did not predict storage behavior, although B20 fuels above the specification minimum remained stable for >12 weeks accelerated aging (simulating 1 year of real-world aging).

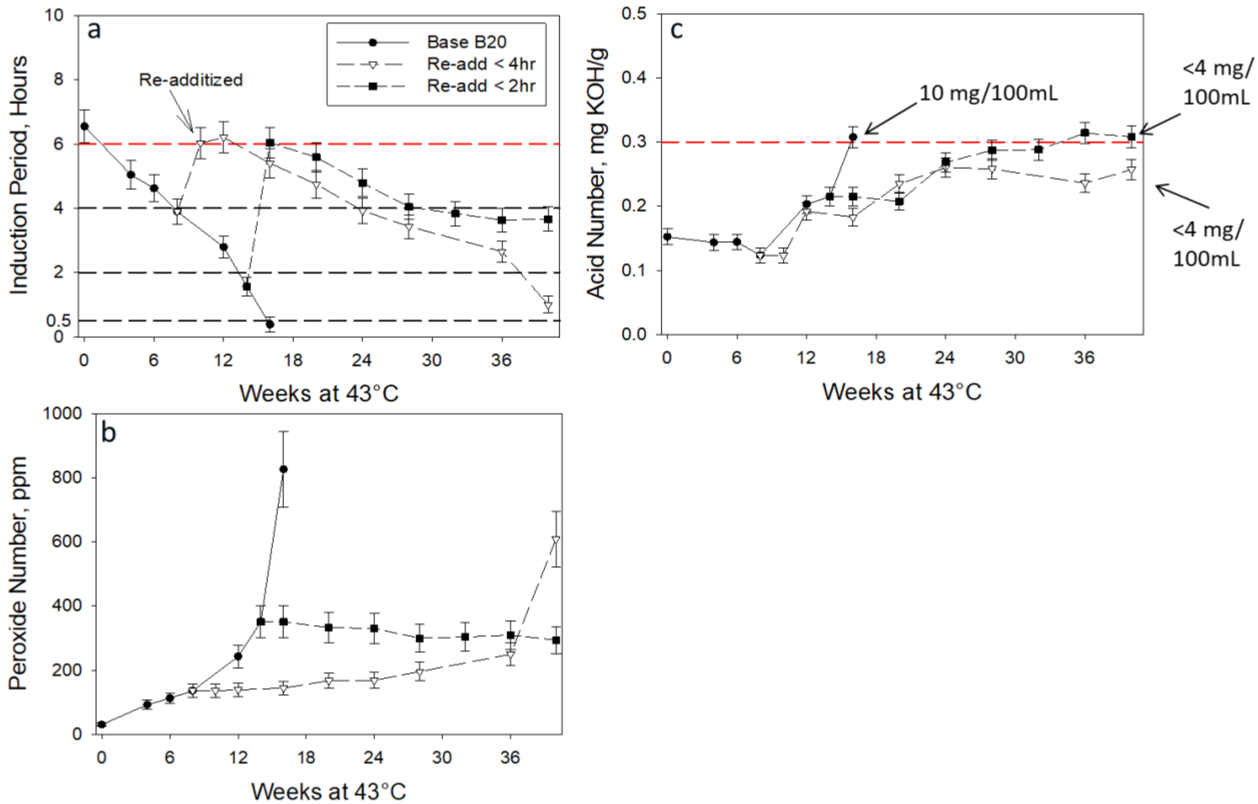

Figure 1. Results for aging and readditization of a commercial B20: (a) Rancimat induction time versus weeks of aging, (b) peroxide concentration versus weeks of aging, and (c) acid number versus weeks of aging with mg/100 mL of insoluble for final samples.

Long-Term Storage and Readditization of B50 and B100

In recent years, biodiesel users have begun to demand higher blend levels to achieve governmental or corporate decarbonization targets. While research has been done on the stability of B100, this work took place more than 15 years ago when biodiesel quality was nowhere near as high as it is today (McCormick and Westbrook 2010). There is essentially no prior research on the stability of biodiesel blends of 50% or higher. This ambitious study had two major objectives: (1) obtain foundational data using modern biodiesel and petroleum diesel on the stability of B50 and B100, and (2) investigate the readditization strategy for B50 and B100. The aging study of B50 and B100 was completed during this study.

Twelve biodiesel samples and six petroleum diesel samples were obtained from geographically diverse sources in the United States. All possible B50 blends were prepared for a total of 72 B50 samples (total of 90 samples including B100 and B0). These were aged at 43°C for 12 weeks using the ASTM D4625 protocol. IP was measured at 2-week intervals, while peroxide and acid number were measured for selected samples. Figure 2 shows results for the B100 samples. All samples could be aged for more than 6 weeks without forming failing levels of acids (>0.5 mg KOH/g)—consistent with results of earlier studies. Figure 3 shows IP versus time results for all B50 samples. Most B50 samples had initial IP >9 hours, similar to what would be expected for B20 samples. This result was in some ways unexpected but upon reflection makes sense. Antioxidant is added to the B100 to meet a minimum 3-hour IP. This is intended to be enough antioxidant to ensure the stability of B20 after blending. When blending B50, 2.5 times more biodiesel is blended, but at the same time 2.5 times more antioxidant is blended because it is present in the B100, accounting for the similar initial stability. The rate of aging for B50 is, on average, also very similar to rates observed for B20. Future work under a new agreement with CFAA is examining readditization of B50 and B100 samples.

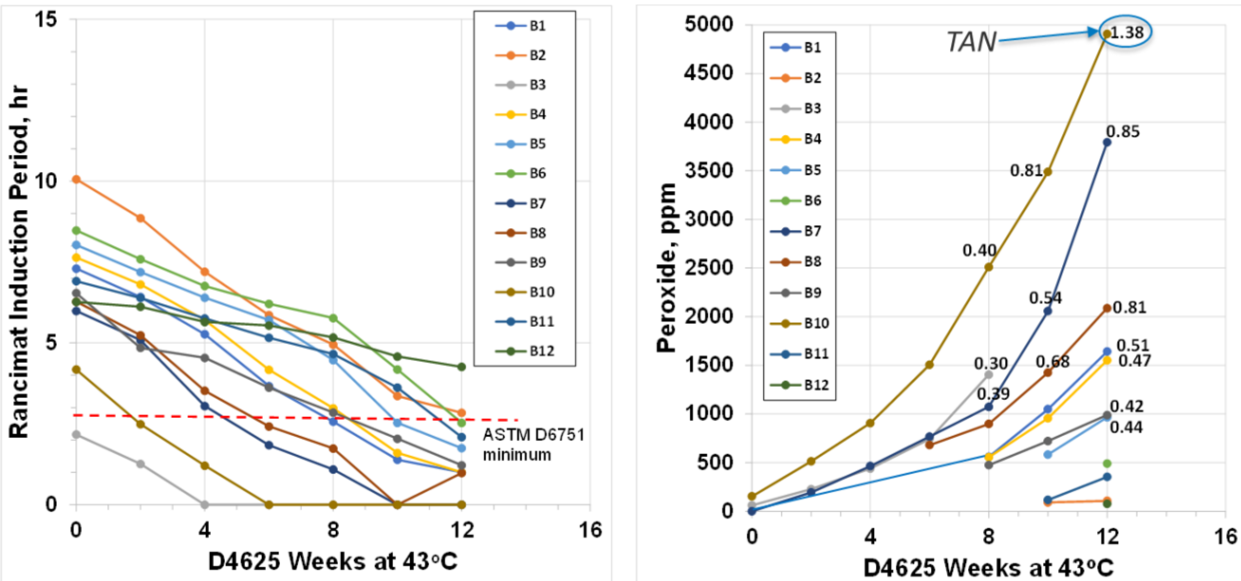

Figure 2. Results for aging of B100 at 43°C. Left panel shows IP versus weeks of aging. The right panel shows peroxide concentration versus weeks of aging; numbers on the chart are acid values.

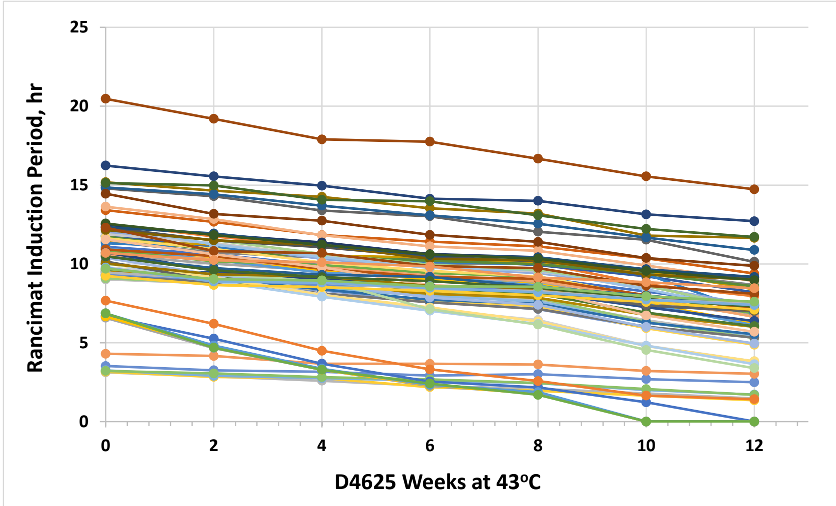

Figure 3. IP versus time of aging at 43°C for B50 samples.

Task 2 and Task 5: B20 Quality Survey

This task was conducted under two CRADA tasks, and results were combined to make one survey. This is the only CRADA task that applied DOE funds. The initial focus was on oxidation stability, but evolved to also focus on methods for analysis of metals that can impact diesel emissions control systems (Na, K, Ca, Mg, and P).

Task 2: B20 Retail Quality Survey (Added as Part of Mod 1)

- This task was successfully completed. The scope of this task was reduced by the partner from 50 to 35 samples.

Task 5: B20 Quality Survey (Added in Mod 4)

- This task was successfully completed.

<u>B20 Retail Quality Survey</u>

Between February and July 2016, 35 biodiesel blend samples were collected and tested for blend content, triglyceride (RVO) content, critical properties related to oxidation stability, and metals content (Na, Ca, Mg, K, and P). Nine of the samples were collected from captive fleets using B20, and 26 samples were from retail pumps selling B6–B20 blends.

Every sample was tested for biodiesel content and triglyceride content, oxidation stability, acid value, cloud point, water content, and peroxides. Only samples that failed to meet the oxidation stability limit in ASTM D7467—the standard for B6 to B20 blends—were tested for polymer content. A subset of the samples was tested for metals (Na, Ca, Mg, K, and P).

Samples were typically B20, with an average biodiesel content of 18 vol %. No triglyceride contamination was found in the samples by FTIR. As in previous surveys, there was a significant failure rate for oxidation stability of 18%. However, this represents a 25% improvement relative to the 24% failure rate in our most recent previous survey, and the average IP was more than 18 hours. Peroxides were low in all cases; however, samples with the highest levels of peroxides also failed oxidation stability. No failures were observed on acid value. Polymeric material can form from oxidation and was measured by gel permeation chromatography. Polymeric material was very low regardless of the oxidation stability of the samples. Cloud point varied by about 20°C across the samples, with no evident trends based on location and/or time of year the sample was collected. Metals analysis showed that every sample was below the limit of detection for the inductively coupled plasma (ICP) method employed—U.S. Environmental Protection Agency (EPA) 6010C (EPA 2007). For phosphorus, the EPA method provided a fivefold decrease in the limit of detection compared to current ASTM methods, indicating better detection limits are possible. Water content averaged 124 ppm and did not correlate with sample location, time of year, or biodiesel content, indicating station and/or tank housekeeping is likely the dominant factor impacting this property. Results were reported to DOE in an unpublished milestone report in Q4 2016.

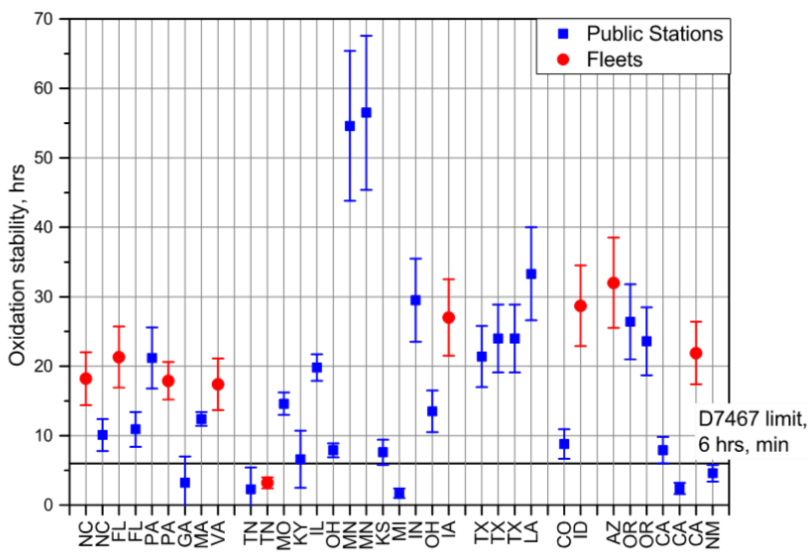

Figure 4. Oxidation stability for nominally B20 samples collected in 2016.

The study was expanded under Task 5 to investigate several methods for metals analysis. ASTM D6751 limits the concentrations of sodium + potassium to 5 ppm maximum, calcium + magnesium to 5 ppm maximum, and phosphorus to 10 ppm. Metals are controlled because of the potential for abrasive solids to contribute to engine component wear, for soluble soaps to cause filter clogging and injector deposits, and for additional diesel particle filter (DPF) ash loading from biodiesel metals to cause an issue.

The limits on metals are meant to be protective when biodiesel is used in blends. Current test methods have some significant limitations when trying to get to the lowest possible detection limits, as the limit of detection is 1 ppm. In total, 35 B20 samples collected from public stations and mandated fleets around the United States were tested for metal content using three different methods. Two of the methods were based on ICP, with one using ICP-AES after ashing and the other using direct analysis by ICP mass spectrometry. The third analytical method was MP-AES, an emerging alternative to ICP-AES. UOP-389, an ICP-AES wet ashing method, showed the best results of the ICP methods and was used to test all samples in this study, as shown in Figure 5. The study results were published as Alleman, Fouts, and Christensen (2019).

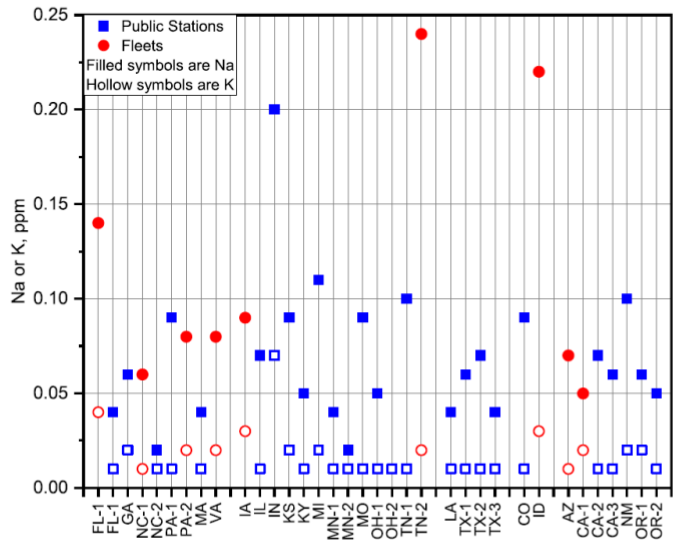

Figure 5. Results of analysis for Na and K for B20 samples collected in 2016.

Task 3: Expanding FTIR Method D7371 To Quantify RVO Contaminant in Biodiesel (Added in Mod 1)

This task was successfully completed. Previous research at NREL developed an FTIR method for quantifying the amount of biodiesel present in biodiesel blends. This method was formalized and standardized as *ASTM D7371: Standard Test Method for Determination of Biodiesel (Fatty Acid Methyl Esters) Content in Diesel Fuel Oil Using Mid Infrared Spectroscopy (FTIR-ATR-PLS Method)*. At the time this task was performed, there was a problem in the market of fuel sellers adding RVO to biodiesel to increase their profits (RVO costs less than biodiesel). However, because of its very high boiling point and viscosity, RVO can cause engine operational and durability problems. Hence, CFAA requested that NREL work to expand the scope of this method so it could also quantify low levels of RVO in biodiesel blends.

RVO consists of triglycerides (TAG). To determine whether TAG was present in the Bxx blends in this study, the ASTM D7371 method was modified to include additional discrimination in the carbonyl and fingerprint regions of the spectra (see Figure 6). The instrument parameters were the same as specified in ASTM D7371.

The modified method was developed only to examine possible low levels of TAG contamination in Bxx blends; the modification is not meant to quantify biodiesel content in TAG-containing blends, nor to measure TAG greater than 5 vol %. A factorial calibration was developed using commercial soybean oil in three different diesel fuels (low, mid, and high aromatic) and a typical biodiesel (B100). This method was applied to the 35 commercial B20 samples collected in Task 2, and no TAG contamination was observed.

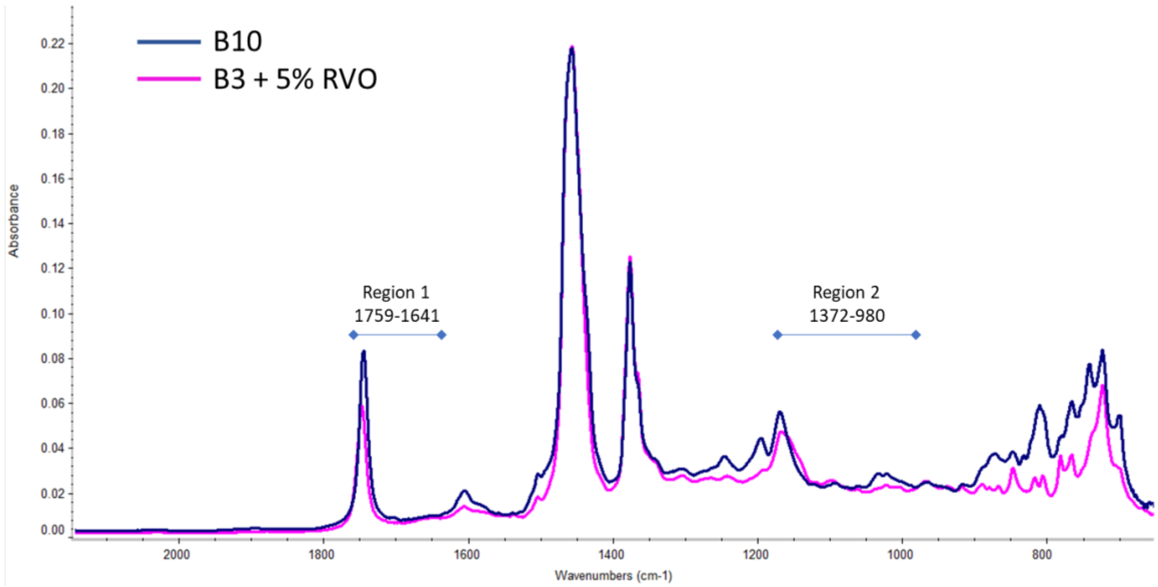

Figure 6. FTIR spectra for a B5 blend, and a B3 blend spiked with RVO at 5 vol %. Spectral regions used for RVO analysis are shown.

Task 4: Northeast Oxidation Stability Fuel Quality Support (Added in Mod 3)

This task was not completed, as resources were directed to other tasks. The original intent of this task was to support biodiesel distributers in the Northeast United States in understanding their fuel's oxidation stability and the cause of other field issues. We did not evaluate any samples from the Northeast, and resources were redirected by CFAA to other oxidation stability efforts (Tasks 1 and 6).

Task 6: Potential Causes and Solutions to Depletion of Oxidative Reserve in the Marketplace (Added in Mod 4 With Scope Updated in Mod 6)

This task was successfully completed. Recent surveys of biodiesel blend quality have shown a higher-than-expected percentage (roughly 15%) of samples falling below the as-delivered oxidation reserve requirement of 6 hours minimum for B6 to B20 blends. At the same time, surveys of biodiesel quality have shown high compliance with the B100 oxidation reserve requirement intended to ensure all B6 to B20 blends would meet 6 hours. Assuming the fuel initially met or exceeded the requirement at the point of blending, a plausible cause of lower-than-expected oxidation reserve would be contamination or incompatible storage conditions. This task's original scope was to examine three potential causes of depletion of IP in the field: tank water bottoms, dissolved iron, and cetane improver fuel additive. During the project, CFAA decided not to investigate the cetane improver additive and to devote all task resources to water and metals effects.

<u>Impact of a Water Layer on Long-Term Stability</u>

Diesel fuel tanks in fuel distribution and retail systems tend to have a water layer beneath the fuel. In this study, NREL showed that some antioxidant additives are soluble in water and can be extracted into the water layer, reducing stability below expected levels. This study was published as Christensen and McCormick (2023).

Antioxidant additives are used to increase biodiesel storage stability, and previous studies that evaluated the effectiveness of antioxidants demonstrated that more polar antioxidants tend to be the most effective (provide the largest improvement in stability per unit of antioxidant added). For example, results for a commercial B20 samples are shown in Figure 7. The very high initial IP of more than 20 hours strongly points to the use of a polar antioxidant. However, polar antioxidants have significant water solubility, and diesel fuel storage tanks are commonly contaminated with water (forming a layer of water under the fuel). This can lead to a dramatic reduction in stability during real-world storage, as shown for the sample aged with a water layer in Figure 7. This study investigated whether nonpolar antioxidants, which are less effective in dry environments, might be more effective under wet conditions simulating real-world storage. Biodiesel blends treated with polar and nonpolar antioxidants were subjected to accelerated aging using the ASTM D4625 protocol (storage at 43°C, open to air, for up to 24 weeks) both with and without added water. Fuels treated with polar/higher-effectiveness compounds and stored in contact with water (simulating water in a storage tank) or high humidity showed accelerated loss of stability compared to dry storage. The same fuel treated with a nonpolar antioxidant and stored in the same conditions did not exhibit accelerated stability loss and thus had higher storage stability over the long term despite treatment with an initially less effective additive. Analysis of the fuels during aging showed that this loss of stability was not due to oxidation but rather extraction of the polar antioxidant into the water layer. Antioxidant additives that are incompatible with wet or humid storage conditions were found to cause faster-than-anticipated loss of stability, which was preventable with the use of nonpolar additives.

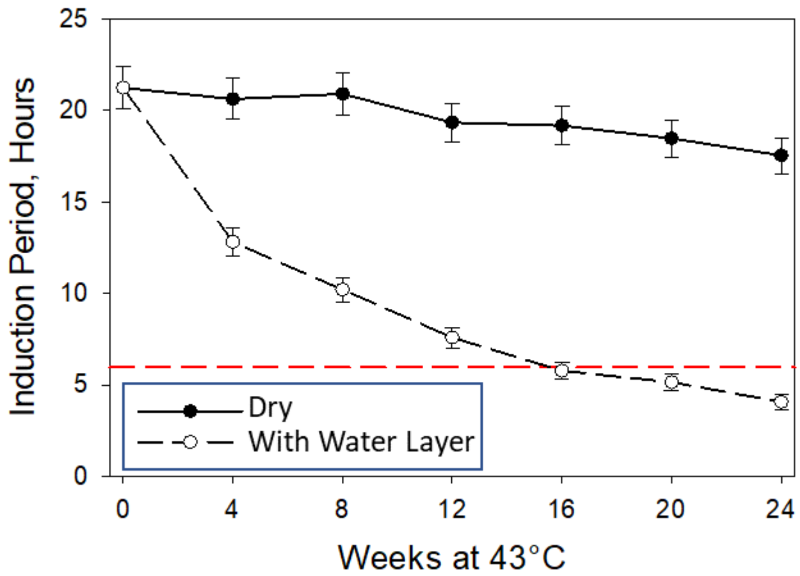

Figure 7. IP versus aging time for a commercial B20 sample. Dashed red line indicates minimum IP requirement.

Impacts of Dissolved Metals on Oxidation Stability

Underground storage tank corrosion has become widespread in the United States, with increased frequency reported since the introduction of ultra-low-sulfur diesel (ULSD) in 2006. The primary mode of corrosion is thought to be microbially induced corrosion, and investigations into causes and solutions are ongoing. In many of the cases investigated, corrosion was the result of microbes that produce carboxylic acids, particularly acetic acid and formic acid. The act of carboxylic acid corrosion of steel produces iron carboxylate salts, which have been shown to reduce oxidation reserve of biodiesel. It is therefore possible that steel corrosion could compromise the stability of biodiesel blends in the field. An experiment was conducted at NREL in which salts of iron were added to biodiesel blends for analysis of Rancimat IP. In this experiment iron salts were dissolved in solvents and added directly to the Rancimat reaction vessel prior to determination of IP. The results of these experiments, shown in Figure 8, verified that iron salts can reduce the IP of B20 at low concentrations, resulting in a value below the 6-hour minimum.

Biodiesel blends were stored using the ASTM D4625 aging protocol in contact with corroded steel, as well as with addition of iron salts. Although negative impacts on stability were shown with direct addition of iron salts to fuel during measurement of Rancimat IP (a highly accelerated test), the same degree of impact was not observed with fuel stored under more realistic conditions after addition of iron salts or in contact with corroded steel. Iron acetate formed from steel corrosion was found to have too low of solubility to remain in solution and negatively impact stability. Contact with corroded surfaces did not result in absorption of metal salts by the fuel. When soluble iron salts were added to B20, these were found to be removed over time, likely due to adhering to the glass containers used in storage stability studies.

When an additive was used to increase B20 IP to near 12 hours, negative impacts on IP values were observed both in contact with corroded steel and after addition of iron salts, even though dissolved iron was not measurable in the fuel. These negative impacts were not the result of the iron catalyzing oxidation but an indirect effect of the additive interacting with metal surfaces or metal complexes. It is possible for storage in contact with corroded surfaces to result in depletion of B20 oxidation reserve in a short period of time, not because of iron catalyzing oxidation, but due to reduced additive concentration or efficacy.

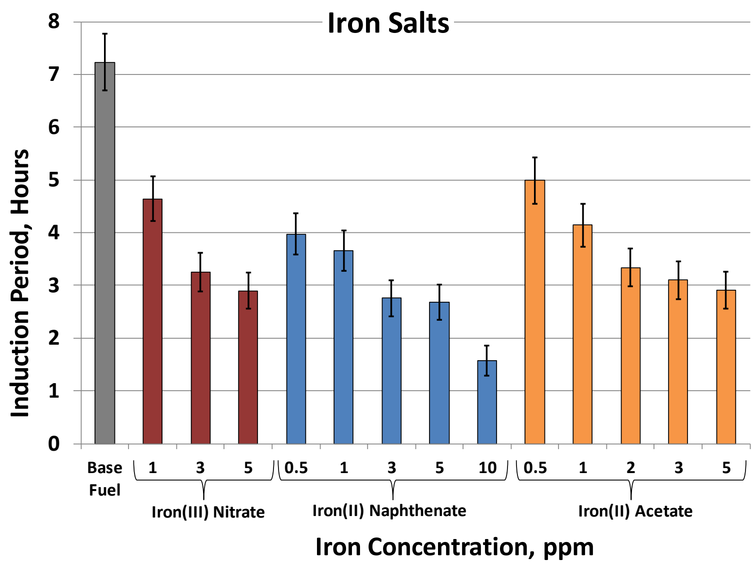

Figure 8. Impact of iron salts on Rancimat IP.

Task 7: Fuel Analysis (Added in Mod 4)

The purpose of this task was to analyze problematic field samples to determine the cause of observed issues. However, biodiesel quality had improved dramatically by this time, and no samples were received for analysis. Resources for this task were directed to other CRADA tasks at the direction of the sponsor.

Task 8: Original Equipment Manufacturers (OEMs): Approvals, Emissions, and Impacts for On and Off-Road—Biodiesel Metals Effects (Added in Mod 5, With Scope Changes in Mods 6, 14, 15, and 17)

This task was successfully completed. This task was to provide technical data on biodiesel metals' effects on emissions control catalysts for off-road engines. It investigated various phenomena regarding biodiesel metal impacts on diesel aftertreatment systems to facilitate off-road OEM support of B20 or higher blends in new diesel engines. Several different subtasks were conducted at NREL or managed by NREL for CFAA. The exact scope of these projects was significantly modified by CFAA during discussions with OEM partners and other stakeholders to obtain the most meaningful results within budgetary constraints.

Investigation of Fuel Metals Impact on Tier 4B Off-Road Engine Exhaust Aftertreatment Systems

Fiat Powertrain Technologies (FPT), a global manufacturer of engines for farming and construction equipment, was a partner in this project with NREL and CFAA. The study focused on metals impacts on diesel emissions controls for an off-road engine (Pidria et al. 2023).

An accelerated aging study was conducted to evaluate the long-term performance of a Tier 4 Final (T4F) engine and aftertreatment system (consisting of a diesel oxidation catalyst [DOC] and NOx selective catalytic reduction [SCR] system) with biodiesel containing doped metals. The fuel studied was B100 containing 2-ppm Na, 1-ppm Ca, and 1-ppm K to represent a 5-times acceleration compared to B20. A 2017 FPT 6.7-L, 205-kW, T4F non-road diesel engine with DOC/Fe-zeolite SCR (no DPF) was used for this research. Two identical aftertreatment systems were aged, one on conventional ULSD and the second on the B100 containing 4-ppm total metals. Aftertreatment systems were de-greened, and then initial performance was benchmarked in terms of non-road transient cycle emissions, ramped modal cycle (RMC) emissions, DOC efficiency, ammonia storage, and urea trade-off.

Each aftertreatment system was aged on the target fuel for 600 hours, with interim evaluations by the non-road transient cycle (NTRC) and ramped modal cycle (RMC) at 150, 300, and 450 hours. At the completion of system aging, all performance evaluations were then repeated. All NTRC and RMC evaluations were performed on EPA certification diesel, while other performance evaluations utilized a commercial ULSD. Comparing evaluations before and after aging for the systems aged on ULSD and B100 with 4-ppm metals (which simulated 3,000 hours of B20 aging) showed no difference in terms of deterioration factor for the aftertreatment systems aged on the two fuels (Figure 9). Post-mortem analysis of the DOC confirms the expected increase of alkali metals concentration in the B100 DOC but showed no impact on specific surface area. Furthermore, no surface area loss was observed for the Fe-zeolite SCR catalyst.

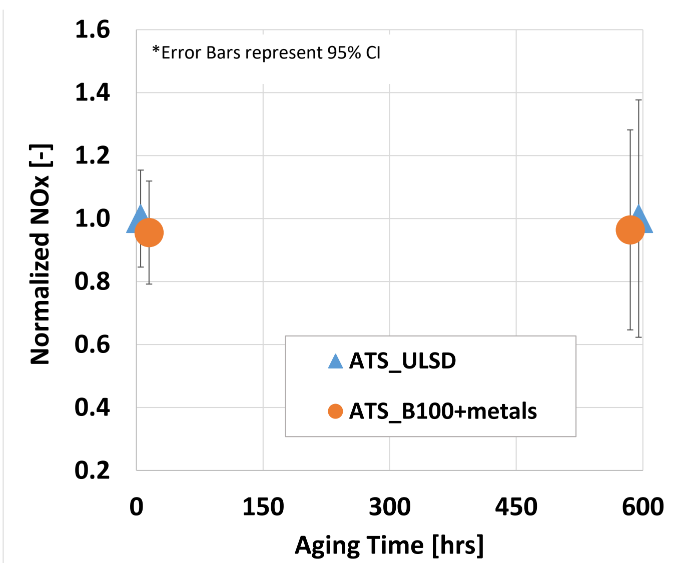

Figure 9. Normalized hot start non-road transient cycle NOx emissions for the T4F engine at the beginning and end of the 600-hour durability protocol.

DPF Durability Performance Comparison Using Metals-Doped B20

For this study NREL and CFAA partnered with SwRI. The project objective was to generate experimental data to evaluate the impact of metals-doped B20 on DPF ash loading and performance compared to that of conventional petrodiesel. DPFs capture soot, which is periodically burned off, but also capture ash that comes primarily from the lube oil but also the fuel. Ash must be removed by backflushing the filter with compressed air, an operation that requires removal of the DPF from the engine. There has been concern among OEMs that biodiesel fuel ash would more rapidly cause increased pressure drop, leading to much more frequent DPF maintenance.

Accelerated ash loading was conducted on two DPFs—one exposed to regular diesel fuel and the other to B20 containing metal dopants equivalent to 4-ppm B100 total metals (currently total metals are limited to 10 ppm in ASTM D6751, the standard for B100). Periodic performance evaluations were conducted on the DPFs at 10-g/L ash loading intervals. The DPFs were aged/loaded to 30 g/L of ash, which required more than 500 hours for B20 and more than 1,500 hours for ULSD. Ash loaded more quickly onto the DPF because of the higher levels of ash provided by the combination of lube oil ash and fuel ash (Figure 10). For ULSD fuel ash is minimal. Nevertheless, as shown in Figure 10 (right), pressure drop over the B20 DPF was significantly lower than for the ULSD DPF.

After the evaluations at 30 g/L, the DPF was cleaned with a commercial DPF cleaning machine and another round of DPF evaluations were conducted. A comparison of the effect of ash loading with the two fuels and DPF cleaning is presented. The metals-doped B20 fuel resulted in ash that was similar to that deposited when exposed to ULSD (lube oil ash) and exhibited similar ash cleaning removal efficiency. Metals-doped B20 resulted in faster ash accumulation within the DPF, as expected, but did not appear to have a negative effect on DPF pressure drop or regeneration rates (up to 30 g/L of ash) or exhibit deleterious physical effects on the DPF substrate (Lakkireddy et al. 2023a).

The DPFs were cleaned, and ash samples were taken from the cleaned material. X-ray fluorescence, X-ray photoelectron spectroscopy, and X-ray diffraction were conducted on the ash samples. Core samples were taken from the cleaned DPF and subjected to scanning electron microscope energy-dispersive X-ray spectroscopy and X-ray fluorescence analysis. The X-ray diffraction and X-ray photoelectron spectroscopy analysis showed that the compounds present in the ash from the two DPFs were nearly identical, though differing in concentration. $CaSO_4$ was the biggest component of the ash from both DPFs, as calcium detergents are common lube oil additives. The metals-doped B20 fuel resulted in ash with similar characteristics to that deposited by the lube oil and did not appear to have any deleterious physical effects on the DPF substrate (did not penetrate the substrate) (Lakkireddy et al. 2023b).

The results of this study were used to ballot a new low-metals grade of B100 into the D6751 ASTM standard. The low-metals grade is for B100 to be used in blending fuels to be used in new technology diesel engines equipped with DPFs and other emissions control components. This grade limits total metals (Na + K + Ca + Mg) to a maximum of 4 ppm and was published in May 2023 as ASTM D6751-23a.

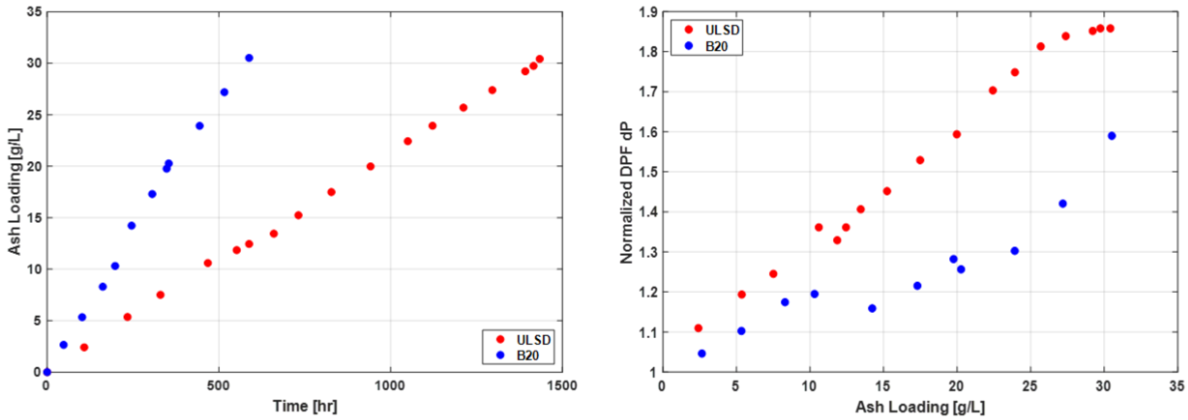

Figure 10. Ash loading and DPF pressure drop (dP) during DPF aging.

Task 9: Off-Highway Engine Emissions Impacts of Bxx and B100 (Added in Mod 6)

This task was successfully completed. Under this task, a Caterpillar off-road engine (C7.1 ACERT Tier 4B emissions level) was used for emissions testing of various blends of biodiesel, renewable diesel, and California Air Resources Board (CARB) emissions certification diesel. This engine was equipped with DPF and SCR NO_x reduction systems. The engine was installed and underwent the OEM-recommended break-in procedure. A total of 15 test campaigns were conducted, each consisting of one cold start plus five hot start non-road transient cycles, followed by two ramped modal cycles, with each campaign testing one fuel. The CARB diesel base fuel was tested five times over the course of the study to ensure consistency of results. Several other fuels were also tested multiple times. Soot emissions from this engine were almost undetectable and well below the Tier 4B limit due to the high efficiency of the DPF. While there were NO_x emissions differences between the fuels (see Figure 11), all fuels produced emissions well below the Tier 4B limit of 0.3 g/bhp-h.

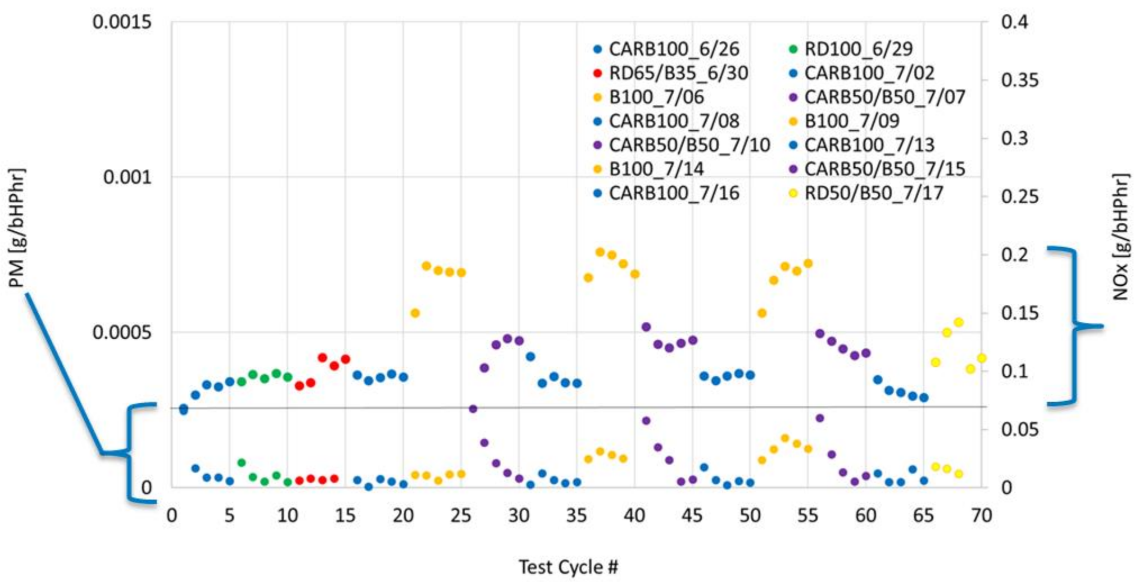

Figure 11. Complete non-road transient cycle NOx and particulate matter results for the Task 9 study.

Task 10: Analytical Method Development, Investigation, and Troubleshooting With Biodiesel and Market Diesel Fuels and Fuel Oils (Added in Mod 7 With Updates in Mods 12, 14, 15, 16, and 17)

This task was successfully completed. This multi-topic task continued from October 2018 until the end of the CRADA in 2023. Actions and results under each topic are summarized below.

Analytical Troubleshooting

This task was envisioned to involve evaluation via chemical analysis or property measurements of samples that caused problems in the field. No samples were presented for analysis, and resources were directed to other projects under this task.

Strategic Planning for Engine Testing

NREL collaborated with CFAA and an industry steering committee to produce research plans for the engine testing work executed under Tasks 8 and 9, as well as future work that will be completed under a new CRADA.

Modify D7371 FTIR Method To Measure RVO Contaminants

The technical work to develop modifications to the method was already completed under Task 3. This task was intended to support NREL in completing an ASTM interlaboratory study to quantify method precision and proposing modifications to the method via an ASTM ballot. CFAA decided not to go forward with this project at the present time, and resources were directed to other projects under this task.

Fully Develop the MP-AES Method for Biodiesel Metals Analysis

The CRADA modification creating this task occurred during the final stages of Task 2: B20 Retail Quality Survey, which included an assessment of methods for analysis of metals. The final report for Task 2 (Alleman, Fouts, and Christensen 2019) provides details on MP-AES analysis, which ultimately did not have superior detection limits to other methods.

Evaluation of CSFBT Test for Assessing Performance of Biodiesel Blends

There continued to be occasional reports of unexpected fuel filter clogging issues during wintertime for biodiesel blends. It was believed that this issue occurred when biodiesel was blended with more highly paraffinic fuels that could be made in a petroleum refinery, or in the extreme case could be 100% paraffin such as hydrocarbon renewable diesel. Under this task NREL was to evaluate the CSFBT method to evaluate samples of biodiesel blended into paraffinic fuels. This was a low-priority project for CFAA, and no samples were supplied. Resources were directed to other CRADA projects.

Reports and Analysis of BQ9000 Program Quality Data

The BQ-9000 program is a voluntary quality assurance program established by the biodiesel producers and CFAA (BQ-9000 Quality Management Program, 2023). BQ-9000 producers represent 90% of U.S. and Canadian biodiesel production. As part of this program, producers must supply monthly data on critical quality parameters. The data were shared with NREL for the calendar years 2017 to 2022—representing between 300 and 500 samples annually. Each year, a report providing a statistical analysis of the data was prepared and published by NREL (Alleman 2020a, 2020b, 2020c, 2021, 2022; McCormick 2023).

The results for all 6 years were summarized in a recent paper (McCormick, Alleman, and Nelson 2023). The results show very consistent and high-quality B100 produced in the 2017–2022 time frame. Additionally, the study reviewed results of earlier quality surveys conducted between 2004 and 2011, revealing how quality has changed over time in response to ASTM standard revisions, as well as the significant overall improvement in quality for modern biodiesel production. For example, Figure 12 shows results for Rancimat IP. The minimum IP required is 3 hours; however, since 2017 the mean value for BQ-9000 companies, representing more than 90% of the U.S. market, has been 9.5 hours, with a 5th percentile value of 5.4 hours.

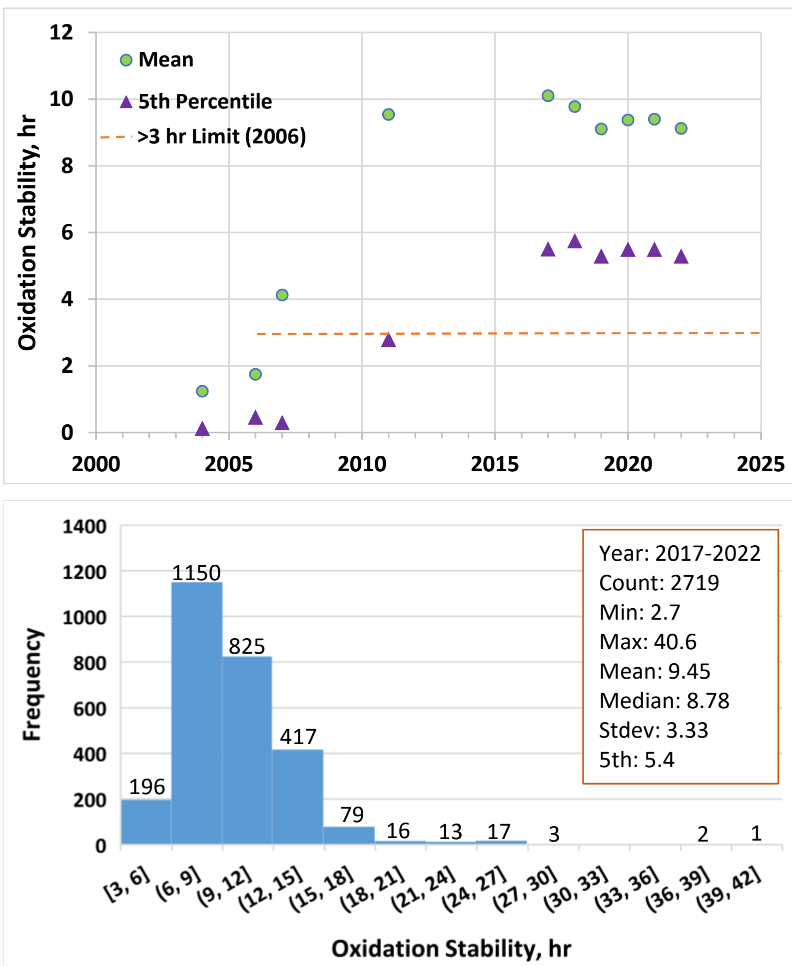

Figure 12. Quality survey and BQ-9000 producer results for Rancimat IP.

Task 11: Engine Performance and Emissions Impacts of Blends Over B20 (Added in Mod 10, Updated in Mod 14)

This task was successfully completed. This task provided funds for increasing the scope of Tasks 8 and Task 9, which were described above. It also directed NREL to undertake the role of technical project manager for three projects funded by CFAA at other institutions.

Task 12: Cooperative Efforts on Engine Performance and Emissions Impacts of Blends Over B20 (Added in Mod 11)

Several tasks mention NREL's project management role for CFAA-funded projects being performed at the University of Michigan, SwRI, and Purdue University. The project on DPF ash loading described under Task 8 was one of the SwRI projects managed by NREL. A second was not completed under this CRADA but is the subject of a new CRADA with CFAA. NREL ultimately did not manage the project at Purdue.

University of Michigan: Defining the CO_2 Reduction Opportunity via Calibration Tuning for Biodiesel Blends

The objective of this project was to leverage the lower CI of biodiesel compared to

conventional fossil diesel fuels and adjust the engine calibration to improve engine efficiency, lower NO_x, and decrease tailpipe CO_2 emissions for B100 relative to fossil diesel. This project was performed by Courtney Videchak and Andrè Boehman at the University of Michigan in collaboration with Ford. The research was conducted on a Ford 6.7-L Powerstroke engine. Baseline emissions and fuel economy were measured, and then a detailed parametric study was run to provide data for optimization. The optimized calibration showed B100 to be nearly NO_x neutral and to produce a 59% reduction in particulate matter and a life cycle greenhouse gas emission reduction of 65%–75%. These results are summarized in Figure 13, where some particulate reduction is sacrificed to reduce NO_x, while still retaining life cycle greenhouse gas emissions reductions.

Figure 13. Comparison of results for the original engine calibration with the B100 calibration for greenhouse gas emissions, NOx, and particulate matter.

Task 13 (Mislabeled as Task 12 in JWS): Cooperative Funding—Update Biodiesel Storage and Handling Guidelines (Added in Mod 16, Updated in Mod 17).

This guide has been published by NREL since the first edition in 2001. Prior to this update, the most recent version was the fifth edition published in 2016. With extensive new information available on biodiesel quality and how to maintain it in the distribution system—most of which was developed under this CRADA—CFAA sponsored a major review to create the sixth edition, published in 2023 (McCormick and Moriarty 2023).

Major updates included addition of the low-metals grade, extensive new information on oxidation stability, and information on applications beyond on-road diesel including home heating oil, rail, and marine.

Task 14 (Mislabeled as Task 13 in JWS): Cooperative Funding—Biodiesel Techno-Economic Analysis (Added in Mod 16)

Comparative Analysis on Pathways From Triglyceride Feedstocks to Biodiesel, Renewable Diesel, and Renewable Jet Products

The project focused on comparative analysis of conversion pathways from fats, oils, and greases (FOG) to finished products via transesterification and hydroprocessing. As primary comparative analysis metrics, the team used the minimum fuel selling price (MFSP) and marginal abatement cost (MAC) for CO_2, which combines both cost and CI into a single metric.

The original goal of this work was to determine the "best use" of FOG resources for the purpose of renewable fuel production on the bases of cost, process conversion efficiency, and CI of required process inputs. The conversion options considered are (1) biodiesel via transesterification, (2) diesel fuel via hydrotreating and isomerization, and (3) jet and diesel fuel mix by hydrotreating and hydrocracking, which is a higher-severity operation relative to isomerization. The team quickly found, however, that the "best use" solution depends on many factors including scale of operation, feedstock cost and CI, hydrogen source, and repurposing opportunities with existing refinery equipment.

The major findings from this work are that feedstock cost is the primary contributor to MFSP for all pathways from FOG feedstocks to finished fuels. Capital cost is the primary differentiator between biodiesel and hydroprocessing pathways, with biodiesel having the economic advantage based on the capital costs bases applied. Sensitivity analysis on plant scale and capital cost reductions/escalations prove that capital cost is the primary differentiating variable in MFSP and MAC. Therefore, it is important to continue investigating actual capital costs for both biodiesel and hydroprocessing technologies. In addition, capital cost reductions through existing unit conversions and/or coprocessing may improve the economics of the hydroprocessing pathways.

In addition to feedstock cost, CI of individual feedstocks can substantially impact MAC. Hydrogen consumption is a minor contributor to MAC, favoring biodiesel over renewable diesel and renewable jet.

Additional details of this analysis have not been publicly released by CFAA.

Task 15 (Mislabeled as Task 14 in JWS): Project Management and Technical Support

Additional funds have been provided to complete ongoing projects and prepare a final report.

This report serves to meet the requirement for the CRADA Final Report with preparation and submission in accordance with the agreement's Article X.

References

Alleman, T. 2020a. *Assessment of BQ-9000 Biodiesel Properties for 2017*. Golden, CO: National Renewable Energy Laboratory. NREL/TP-5400-75795. www.nrel.gov/docs/fy20osti/75795.pdf.

Alleman, T. 2020b. *Assessment of BQ-9000 Biodiesel Properties for 2018*. Golden, CO: National Renewable Energy Laboratory. NREL/TP-5400-75796. www.nrel.gov/docs/fy20osti/75796.pdf.

Alleman, T. 2020c. *Assessment of BQ-9000 Biodiesel Properties for 2019*. Golden, CO: National Renewable Energy Laboratory. NREL/TP-5400-76840. www.nrel.gov/docs/fy20osti/76840.pdf.

Alleman, T. 2021. *Assessment of BQ-9000 Biodiesel Properties for 2020*. Golden, CO: National Renewable Energy Laboratory. NREL/TP-5400-79815. www.nrel.gov/docs/fy21osti/79815.pdf.

Alleman, T. 2022. *Assessment of BQ-9000 Biodiesel Properties for 2021*. Golden, CO: National Renewable Energy Laboratory. NREL/TP-5400-83108. www.nrel.gov/docs/fy22osti/83108.pdf.

Alleman, Teresa L., Lisa Fouts, and Earl D. Christensen. 2019. *Metals Analysis of Biodiesel Blends*. Golden, CO: National Renewable Energy Laboratory. NREL/TP-5400-72341. www.nrel.gov/docs/fy19osti/72341.pdf.

Christensen, E., and R. L. McCormick. 2014. "Long-Term Storage Stability of Biodiesel and Biodiesel Blends." *Fuel Processing Technology* 128: 339–348. doi.org/10.1016/j.fuproc.2014.07.045.

Christensen, E., T.L. Alleman, and R.L. McCormick. 2018. "Re-additization of commercial biodiesel blends during long-term storage." *Fuel Processing Technology* 177: 56–65. www.osti.gov/servlets/purl/1461852.

Christensen, E.D., and R.L. McCormick. 2023. "Water Contamination Impacts on Biodiesel Antioxidants and Storage Stability." *Energy Fuels*. doi.org/10.1021/acs.energyfuels.2c03911.

Lakkireddy, V., R.L. McCormick, P. Weber, and S. Howell. 2023a. "Diesel Particulate Filter Durability Performance Comparison Using Metals Doped B20 vs. Conventional Diesel Part I: Accelerated Ash Loading and DPF Performance Evaluation." SAE Technical Paper 2023-01-0297. doi:10.4271/2023-01-0297.

Lakkireddy, V., R.L. McCormick, P. Weber, and S. Howell. 2023b. "Diesel Particulate Filter Durability Performance Comparison Using Metals Doped B20 vs. Conventional Diesel Part II: Chemical and Microscopic Characterization of Aged DPFs." SAE Technical Paper 2023-01-0296. doi:10.4271/2023-01-0296.

McCormick, R. 2023. *Assessment of BQ-9000 Biodiesel Properties for 2022*. Golden, CO: National Renewable Energy Laboratory. NREL/TP-5400-86227. www.nrel.gov/docs/fy23osti/86227.pdf.

McCormick, R., T. Alleman, and R. Nelson. 2023. "Statistical Treatise on Critical Biodiesel (B100) Quality Properties in the United States from 2004-2022." SAE Technical Paper 2023-24-0097. doi:10.4271/2023-24-0097.

McCormick, R.L., and K. Moriarty. 2023. *Biodiesel Handling and Use Guide, 6th Edition*. Golden, CO: National Renewable Energy Laboratory. www.nrel.gov/docs/fy23osti/86939.pdf.

McCormick, R.L., and S.R. Westbrook. 2010. "Storage Stability of Biodiesel and Biodiesel Blends." *Energy Fuels* 24: 690–698. doi.org/10.1021/ef900878u.

Pidria, M.F., C. Walters, R. Abel, J. Burton, P. Sindler, M. Thornton, and R.L. McCormick. 2023. "Investigation of Fuel Metals Impact on Tier 4B Off-Road Engine Exhaust Aftertreatment Systems." Presented at the 16th International Conference on Engines & Vehicles for Sustainable Transport 2023, Capri, Naples, Italy, Sept. 11, 2023.

U.S. Environmental Protection Agency (EPA). 2007. "Method 6010C (SW-846): Inductively Coupled Plasma-Atomic Emission Spectrometry." Revision 3.

Subject Inventions Listing:

None.

ROI #:

None.