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Locomotive Performance and Engine Durability Assessment of B5 to B20 Biodiesel Fuel Usage

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13. ABSTRACT (Maximum 200 words)

This report summarizes work performed by Southwest Research Institute (SwRI®) to investigate the durability of several locomotive engine components under various blends of biodiesel from 5 percent biodiesel (B5) of up to 20 percent biodiesel (B20). Due to changes in the U.S. diesel fuel regulations, mandates, and specifications, American railroads will be using fuel with B5, with the likelihood of using biodiesel blends of B20 in diesel locomotive engines. Although biodiesel blends have been in the automotive fuel market for several years, there is less experience with regular operation of locomotive engines operating on these fuels, although, locomotive manufacturers and railroad companies have raised concerns, especially when biodiesel concentrations are higher than B5.

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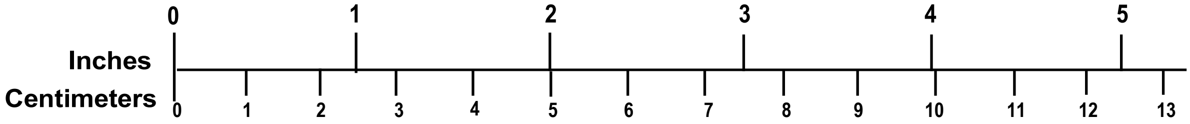
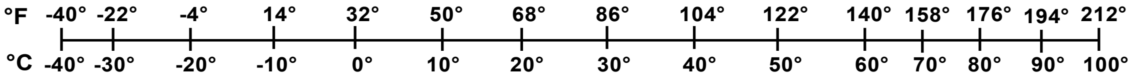
LENGTH (APPROXIMATE)			**LENGTH** (APPROXIMATE)		
1 inch (in)	=	2.5 centimeters (cm)	1 millimeter (mm)	=	0.04 inch (in)
1 foot (ft)	=	30 centimeters (cm)	1 centimeter (cm)	=	0.4 inch (in)
1 yard (yd)	=	0.9 meter (m)	1 meter (m)	=	3.3 feet (ft)
1 mile (mi)	=	1.6 kilometers (km)	1 meter (m)	=	1.1 yards (yd)
			1 kilometer (km)	=	0.6 mile (mi)
AREA (APPROXIMATE)			**AREA** (APPROXIMATE)		
1 square inch (sq in, in^2)	=	6.5 square centimeters (cm^2)	1 square centimeter (cm^2)	=	0.16 square inch (sq in, in^2)
1 square foot (sq ft, ft^2)	=	0.09 square meter (m^2)	1 square meter (m^2)	=	1.2 square yards (sq yd, yd^2)
1 square yard (sq yd, yd^2)	=	0.8 square meter (m^2)	1 square kilometer (km^2)	=	0.4 square mile (sq mi, mi^2)
1 square mile (sq mi, mi^2)	=	2.6 square kilometers (km^2)	10,000 square meters (m^2)	=	1 hectare (ha) = 2.5 acres
1 acre = 0.4 hectare (he)	=	4,000 square meters (m^2)			
MASS - WEIGHT (APPROXIMATE)			**MASS - WEIGHT** (APPROXIMATE)		
1 ounce (oz)	=	28 grams (gm)	1 gram (gm)	=	0.036 ounce (oz)
1 pound (lb)	=	0.45 kilogram (kg)	1 kilogram (kg)	=	2.2 pounds (lb)
1 short ton = 2,000 pounds (lb)	=	0.9 tonne (t)	1 tonne (t)	=	1,000 kilograms (kg)
				=	1.1 short tons
VOLUME (APPROXIMATE)			**VOLUME** (APPROXIMATE)		
1 teaspoon (tsp)	=	5 milliliters (ml)	1 milliliter (ml)	=	0.03 fluid ounce (fl oz)
1 tablespoon (tbsp)	=	15 milliliters (ml)	1 liter (l)	=	2.1 pints (pt)
1 fluid ounce (fl oz)	=	30 milliliters (ml)	1 liter (l)	=	1.06 quarts (qt)
1 cup (c)	=	0.24 liter (l)	1 liter (l)	=	0.26 gallon (gal)
1 pint (pt)	=	0.47 liter (l)			
1 quart (qt)	=	0.96 liter (l)			
1 gallon (gal)	=	3.8 liters (l)			
1 cubic foot (cu ft, ft^3)	=	0.03 cubic meter (m^3)	1 cubic meter (m^3)	=	36 cubic feet (cu ft, ft^3)
1 cubic yard (cu yd, yd^3)	=	0.76 cubic meter (m^3)	1 cubic meter (m^3)	=	1.3 cubic yards (cu yd, yd^3)
TEMPERATURE (EXACT)			**TEMPERATURE** (EXACT)		
[(x-32)(5/9)] °F	=	y °C	[(9/5) y + 32] °C	=	x °F

QUICK INCH - CENTIMETER LENGTH CONVERSION



QUICK FAHRENHEIT - CELSIUS TEMPERATURE CONVERSIO



For more exact and or other conversion factors, see NIST Miscellaneous Publication 286, Units of Weights and Measures. Price $2.50 SD Catalog No. C13 10286

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This project was performed by the Design & Development Department within the Engine, Emissions, and Vehicle Research Division, and the Fuels and Lubricants Technology Department within the Fuels and Lubricants Research Division of the Southwest Research Institute (SwRI®). SwRI® personnel who made significant contributions to the project were Steven G. Fritz, Project Manager, Steven R. Westbrook, Staff Scientist, Dr. Nigil S. Jeyashekar, Senior Research Engineer, and Doug Yost, Principal Engineer.

Addy Majewski of Ecopoint, Inc. performed the literature review and set up the Locomotive Biodiesel Forum, and independent consultant Dennis McAndrew provided input and guidance throughout the project, and led the effort to outline a future biodiesel field test protocol.

Project oversight was initially provided by the SAE TC7 Subcommittee Biodiesel in Railroad Applications, chaired by Manuch Nikanjam. During the project, oversight was transferred to the Fuel, Lubricants, & Environmental (FL&E) Committee of the Locomotive Maintenance Officers Association with Thomas E. Gallagher as the FL&E Committee Chairman. The guidance, support, and samples of fuel samples and locomotive engine parts (filters, seals, fuel injectors) for analysis from members of these committees were essential to the project.

Contents

Illustrations

Executive Summary

This report summarizes work performed by the Southwest Research Institute (SwRI®) and funded by the Federal Railroad Administration, to support the American railroad industry in assessing the durability of several locomotive engine components under various blends of biodiesel from 5 percent biodiesel (B5) of up to 20 percent biodiesel (B20). The research was conducted between August 2013 and April 2015.

Project oversight was initially provided by the Society of Automotive Engineers (now referred to as SAE International) within the SAE TC7 Subcommittee Biodiesel in Railroad Applications, which FRA is a member. During the period of performance for the project, oversight was transferred to the Fuel, Lubricants, and Environmental (FL&E) Committee of the Locomotive Maintenance Officers Association (LMOA).

The main work products are summarized in four topical reports provided by SwRI® and can be found in the appendices. These four reports are:

- Appendix A: Topical Report No. 1 – FTIR Characterization of Biodiesel Markers in Elastomer and Fuel Filter Components in Locomotive Engines
- Appendix B: Topical Report No. 2 – Locomotive Engine Fuel Injector Deposit Characterization Using FTIR
- Appendix C: Topical Report No. 3 – Analytical Characterization of Locomotive Injector Tip Deposits
- Appendix D: Topical Report No. 4 – Literature Review: Biodiesel as a Locomotive Fuel

Each of these topical reports were posted to the Locomotive Biodiesel Forum website that was established as part of this project to serve as an online repository for relevant information.

1. Introduction

The Federal Railroad Administration (FRA) provided support to the Southwest Research Institute (SwRI®) to research locomotive engine performance and durability for locomotives operating on 5 percent (B5) and up to 20 percent (B20) blends of biodiesel fuel. Five percent of pure biodiesel (100 percent [B100] biodiesel per ASTM International's [ASTM] D6751 specification) use in diesel fuel (ASTM D975) is now widespread in the U.S. due to the Renewal Fuel Standards-2 (RFS-2) regulations, which requires transportation fuel sold in the U.S. to contain a minimum volume of renewable fuel such as biodiesel as required by the Energy Independence and Security Act (EISA) of 2007. Railroads generally specify ASTM D975 diesel fuel in their fuel procurement for use in their locomotives, therefore use of B5 may be prevalent throughout the system. However, the potential adverse effects of blends of biodiesel higher than B5 on locomotive engine components were of concern to the rail industry. B20 biodiesel is the highest blend of biodiesel that can be used in a locomotive engine without requiring engine modification of its utilization. These are the reasons why B5 and B20 biodiesel fuels were the main focus of this research. FRA and SwRI®, participants in the SAE International (formerly the Society of Automotive Engineers) TC7 Subcommittee Biodiesel in Railroad Applications (referred to as the Subcommittee) identified several research areas that will develop knowledge about biodiesel use in locomotives. FRA implemented a multi-phase, multi-year program that assessed how biodiesel use in locomotives affect engine performance and durability, as well as emissions using the results and recommendations provided by SwRI®.

1.1 Background

As a result of changes in the U.S. diesel fuel regulations, mandates, and specifications, American railroads will be using fuel with 5 percent biodiesel (B5), and with the further likelihood of receiving biodiesel blends of up to 20 percent (B20) in diesel locomotive engines. Although biodiesel blends have been in the automotive fuel market for several years, there is less experience with regular operation of locomotive engines operating on these fuels, and locomotive manufacturers and railroad companies have expressed their concerns, especially when biodiesel concentrations higher than B5 are used.

1.2 Objectives

The objective of this research effort is to investigate the wear and durability of several locomotive engine components under various blends of biodiesel from B5 to B20.

1.3 Scope

The scope of this research is limited to the determination of exposure and absorption of biodiesel in the elastomers and other fuel filter components used in locomotive engines, as well as changes in fuel injector tip deposit. The study also looked at biodiesel as a locomotive fuel. Quantifying the physical, chemical and mechanical properties changes in elastomers and other fuel components that stem from biodiesel absorption was beyond the scope of this research study.

1.4 Overall Approach

The overall approach to the research was to conduct literature and technology research for biodiesel effects on locomotive operations and laboratory testing of various locomotive engine components to determine if there are any effects to the biodiesel. A literature review of biodiesel use in comparison to diesel fuel in locomotive engines was conducted to gain an understanding of the performance of engine components after prolonged exposure to biodiesel. Fourier Transform Infrared (FTIR) spectroscopy tests were used to identify whether fuel wetted elastomers in locomotive engine fuel systems had been exposed to biodiesel, and to determine the chemical composition of injector tip deposits on selected locomotive fuel injectors. Energy Dispersive Spectroscopy (EDS) and x-ray diffraction (XRD) were also used to analyze deposits on inject tips. The effort was to determine whether the formation of injector tip deposits was primarily due to the presence of biodiesel present in diesel fuel.

1.5 Organization of the Report

The report summarizes the four topical reports contained in Appendix A, Appendix B, Appendix C, and Appendix D, which detail the research undertaken to address possible durability issues with using biodiesel in locomotive engines.

2 Technical Approach

The technical approach taken to conduct the research is outlined in the proceeding sections below.

2.3 Locomotive Biodiesel Forum

A public Locomotive Biodiesel Forum was established as part of this project to serve as an online repository for relevant information. There are 24 Locomotive Maintenance Office Associates (LMOA) Fuel Lubricants & Environmental (FL&E) Committee members participating in this forum. The forum is accessible via this website at: http://www.fuelreport.net/forum/index.php.

Figure 1 is a screenshot of the General Forum topics. Figure 2 through Figure 8 shows screen shots of each topic within the forums.

FORUM

General Topics
General Topics + Announcements + Housekeeping

Fuel Related Issues
Cloud Point, Pour Point, Cold Filtering, Contamination, Crystal/Cloud Formation, etc.

Filter Related Issues
Plugging, Deterioration, Short Lifetime, etc.

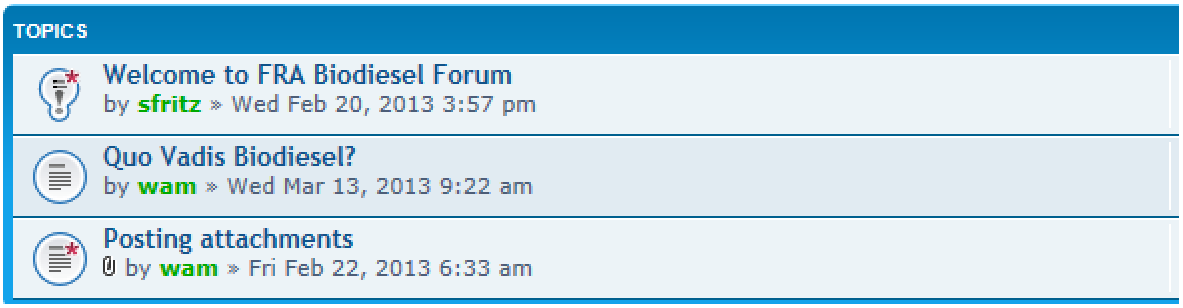
Wayside Equipment & Tank Issues
Rust, Corrosion, Sediment, etc.

Engine Related Issues
Fuel Pumps, Injectors, Seals, Gaskets, Hoses, Leaks, etc.

Field Test Protocols
There are several LMOA and AAR field tests protocols out there. This is intended to be a central location for them during this investigation period.

Literature Review Input to Addy
Topics, links, info, etc. for Addy to consider for the Literature Review Task of the FRA Project.

Figure 1. Locomotive Biodiesel Forum—General Forum



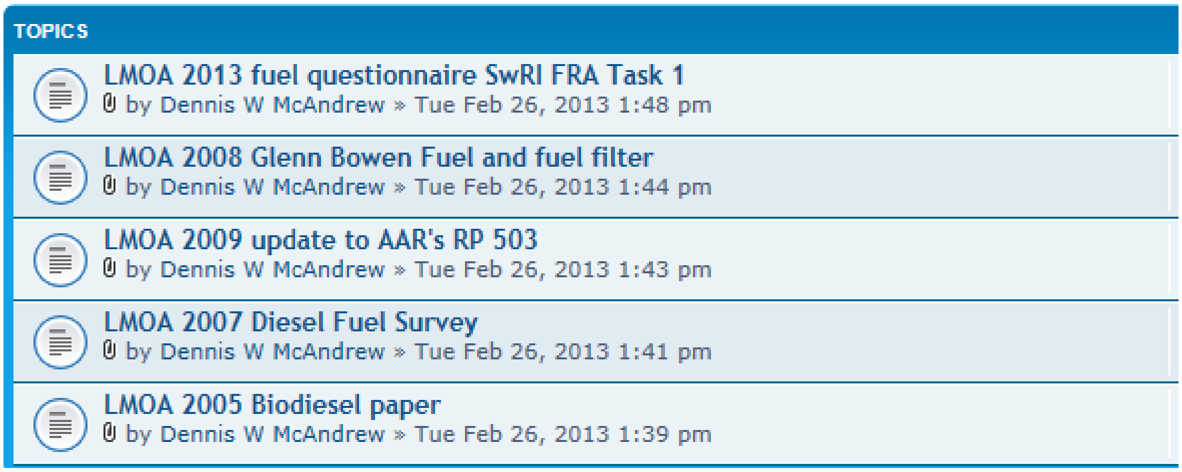
TOPICS

Welcome to FRA Biodiesel Forum
by sfritz » Wed Feb 20, 2013 3:57 pm

Quo Vadis Biodiesel?
by wam » Wed Mar 13, 2013 9:22 am

Posting attachments
by wam » Fri Feb 22, 2013 6:33 am

Figure 2. Locomotive Biodiesel Forum—General Topics



TOPICS

LMOA 2013 fuel questionnaire SwRI FRA Task 1
by Dennis W McAndrew » Tue Feb 26, 2013 1:48 pm

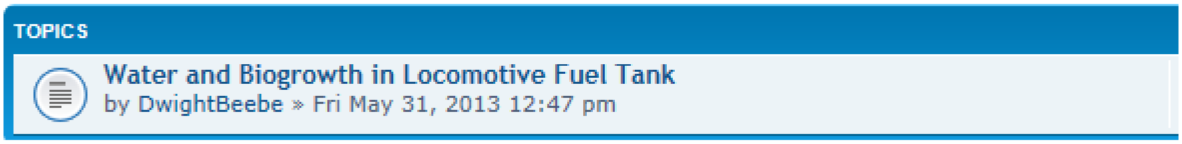
LMOA 2008 Glenn Bowen Fuel and fuel filter
by Dennis W McAndrew » Tue Feb 26, 2013 1:44 pm

LMOA 2009 update to AAR's RP 503
by Dennis W McAndrew » Tue Feb 26, 2013 1:43 pm

LMOA 2007 Diesel Fuel Survey
by Dennis W McAndrew » Tue Feb 26, 2013 1:41 pm

LMOA 2005 Biodiesel paper
by Dennis W McAndrew » Tue Feb 26, 2013 1:39 pm

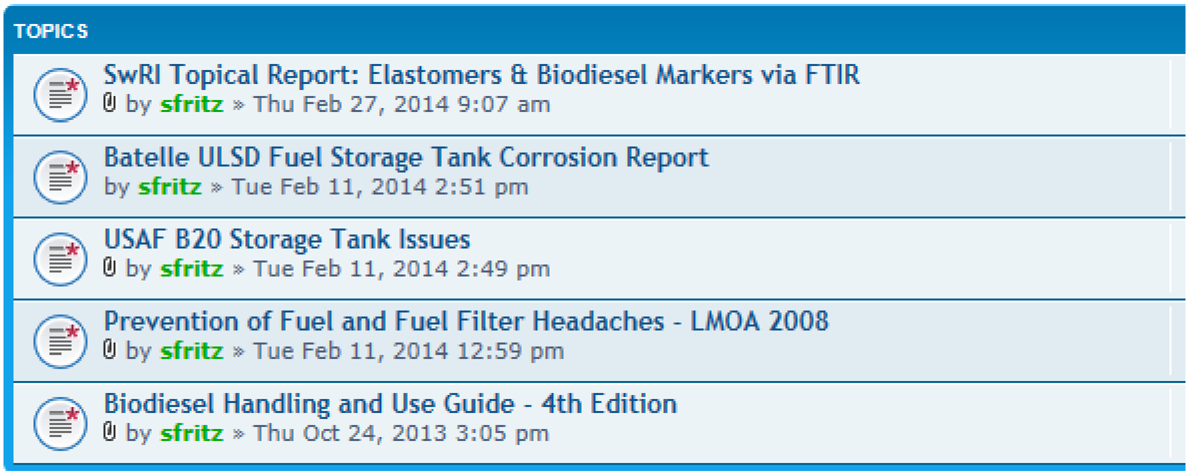
Figure 3. Locomotive Biodeisel Forum—Fuel Related Issues



TOPICS

Water and Biogrowth in Locomotive Fuel Tank
by DwightBeebe » Fri May 31, 2013 12:47 pm

Figure 4. Locomotive Biodiesel Forum—Filter Related Issues



TOPICS

SwRI Topical Report: Elastomers & Biodiesel Markers via FTIR
by sfritz » Thu Feb 27, 2014 9:07 am

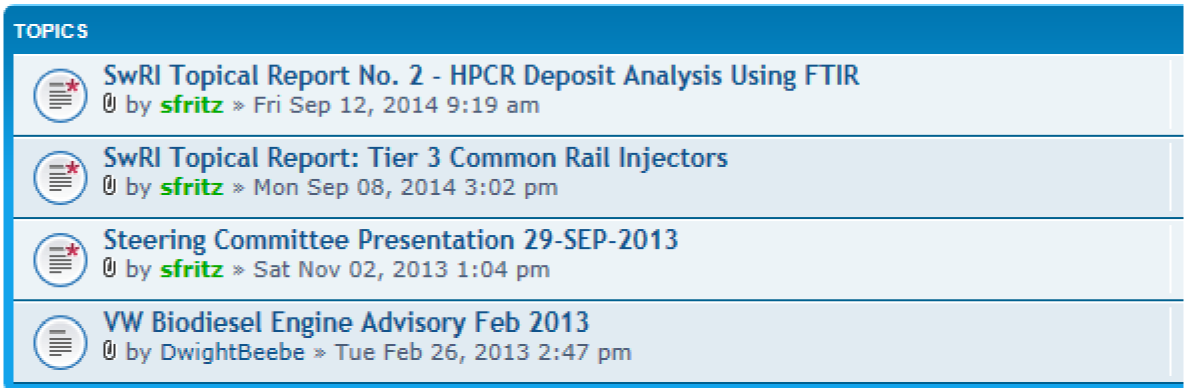
Batelle ULSD Fuel Storage Tank Corrosion Report
by sfritz » Tue Feb 11, 2014 2:51 pm

USAF B20 Storage Tank Issues
by sfritz » Tue Feb 11, 2014 2:49 pm

Prevention of Fuel and Fuel Filter Headaches - LMOA 2008
by sfritz » Tue Feb 11, 2014 12:59 pm

Biodiesel Handling and Use Guide - 4th Edition
by sfritz » Thu Oct 24, 2013 3:05 pm

Figure 5. Locomotive Biodiesel Forum—Wayside Equipment and Tank Issues



TOPICS

SwRI Topical Report No. 2 - HPCR Deposit Analysis Using FTIR
by sfritz » Fri Sep 12, 2014 9:19 am

SwRI Topical Report: Tier 3 Common Rail Injectors
by sfritz » Mon Sep 08, 2014 3:02 pm

Steering Committee Presentation 29-SEP-2013
by sfritz » Sat Nov 02, 2013 1:04 pm

VW Biodiesel Engine Advisory Feb 2013
by DwightBeebe » Tue Feb 26, 2013 2:47 pm

Figure 6. Locomotive Biodiesel Forum—Engine Related Issues

TOPICS

Fuel Additve AAR RP 503 LMOA updates
by Dennis W McAndrew » Fri Apr 12, 2013 11:32 am

LMOA 2013 and SAE SwRI FRA task 3
by Dennis W McAndrew » Tue Feb 26, 2013 1:49 pm

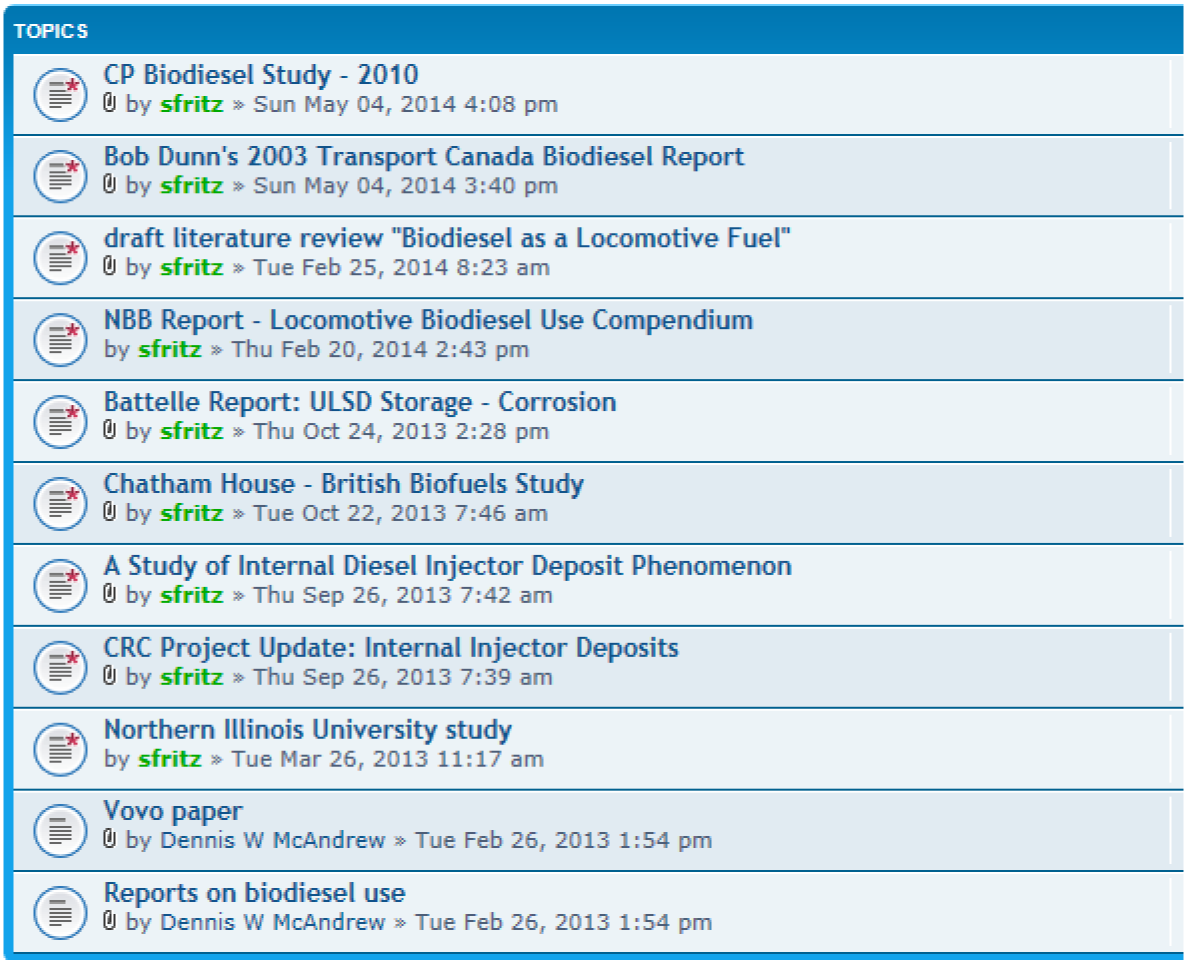
AAR 1983 fuel field testing second part
by Dennis W McAndrew » Tue Feb 26, 2013 1:38 pm

AAR 1983 fuel field testing
by Dennis W McAndrew » Tue Feb 26, 2013 1:36 pm

LMOA 2012 Biodiesel Alt Fuel Field Test Protocol
by Dennis W McAndrew » Tue Feb 26, 2013 1:34 pm

LMOA 2000 Crankcase Oil Field Protocol
by Dennis W McAndrew » Tue Feb 26, 2013 1:32 pm

Figure 7. Locomotive Biodiesel Forum—Field Test Protocols


TOPICS

CP Biodiesel Study - 2010
by **sfritz** » Sun May 04, 2014 4:08 pm

Bob Dunn's 2003 Transport Canada Biodiesel Report
by **sfritz** » Sun May 04, 2014 3:40 pm

draft literature review "Biodiesel as a Locomotive Fuel"
by **sfritz** » Tue Feb 25, 2014 8:23 am

NBB Report - Locomotive Biodiesel Use Compendium
by **sfritz** » Thu Feb 20, 2014 2:43 pm

Battelle Report: ULSD Storage - Corrosion
by **sfritz** » Thu Oct 24, 2013 2:28 pm

Chatham House - British Biofuels Study
by **sfritz** » Tue Oct 22, 2013 7:46 am

A Study of Internal Diesel Injector Deposit Phenomenon
by **sfritz** » Thu Sep 26, 2013 7:42 am

CRC Project Update: Internal Injector Deposits
by **sfritz** » Thu Sep 26, 2013 7:39 am

Northern Illinois University study
by **sfritz** » Tue Mar 26, 2013 11:17 am

Vovo paper
by Dennis W McAndrew » Tue Feb 26, 2013 1:54 pm

Reports on biodiesel use
by Dennis W McAndrew » Tue Feb 26, 2013 1:54 pm

Figure 8. Locomotive Biodiesel Forum

2.4 Topical Reports

This section summarizes the work performed as part of this project found in four topical reports. Copies of the topical reports are included as Appendices A through Appendix D.

2.4.1 Topical Report No. 1 – FTIR Characterization of Biodiesel Markers in Elastomer and Fuel Filter Components in Locomotive Engines

Found in Appendix A, the goal of this research was to develop a technique to identify if unknown fuel wetted elastomers in locomotive engine fuel systems had been exposed to biodiesel. This goal was accomplished by conducting FTIR tests on a selection of commercially available elastomers and comparing it to locomotive fuel system elastomers exposed to biodiesel. These tests were conducted under pre-soak conditions, where the elastomers were tested as received without being exposed to biodiesel and post-soak conditions, where the elastomers had exposure to biodiesel.

By comparing the FTIR spectra of locomotive fuel system elastomers to the spectra of commercially available elastomers, the general material type of the locomotive elastomers were determined. It was also concluded that the FTIR technique could confirm the absorption of biodiesel in the elastomer matrix by the presence of a carbonyl peak (C=O) ranging from 1737.62 cm^{-1} to 1743.49 cm^{-1}.

Six new elastomers used in locomotive engines were tested at pre-soak and post-soak conditions. The method was able to identify if these elastomers have absorbed biodiesel, irrespective of elastomer identity for all the six locomotive elastomers. Four sets of new locomotive engine fuel filters were subjected to pre-soak and 100 percent biodiesel post-soak FTIR analysis. It was concluded that the presence of biodiesel was identified in all filter elements and O-rings. Five in-service elastomers and O-rings that showed signs of wear and degradation were tested for identity and the presence of biodiesel using FTIR. It was concluded that most of the degraded in-service elastomers and O-rings have evidence of biodiesel diffusion into the seal material.

Overall, it can be concluded that FTIR can be used as a suitable tool to identify the presence of biodiesel in fuel wetted locomotive elastomer and fuel filter components. Future tests should focus on correlation between the percentage biodiesel content and the extent of degradation in physical property such as O-ring squeeze, hardness and tensile strength, for a statistically significant number of O-rings.

2.4.2 Topical Report No. 2 – Locomotive Engine Fuel Injector Deposit Characterization Using FTIR

The goal of this work was to determine the chemical composition of internal injector deposits on selected locomotive fuel injectors, found in Appendix B. The effort was to determine if the formation of internal injector deposits was primarily due to the presence of biodiesel present in diesel fuel. The internal deposits formed in locomotive engine fuel injectors were characterized by FTIR on deposits collected from the control valve area of a locomotive engine fuel injector. The scope of this study was limited to high-pressure common-rail (HPCR) fuel injectors from Cummins QSK19 non-road diesel engines used in genset switcher locomotives.

It was concluded that the highest concentration of internal injector deposits were metal carboxylate salts that resulted from trace metal contaminants. The second highest deposit concentration were polymeric amides that likely formed from succinimide-based additives that are used as dispersants in diesel fuel. The injectors that were exposed to biodiesel blends contained deposits that resulted from high temperature oxidation of biodiesel. However, based on FTIR, it was determined that these deposits were relatively lower in concentration compared to the deposits due to trace metal contaminants and additives in diesel fuel.

Elemental analysis was conducted on deposits from an injector needle. The deposits contained significant concentration of calcium, which correlated with FTIR results on metal (calcium) carboxylate salt deposits, further supporting the fact that the primary source of deposits were due to trace metals. The results from elemental analysis also had significant concentrations of chromium with low concentrations of iron, indicating that the source of chromium was not due to wear debris, rather, the source of chromium was the fuel. Overall, it was concluded that most of the internal injector deposits were caused due to trace metal contaminants, followed by varnish like deposits that coated on the injector surface formed from succinimide based additives (dispersants) in the fuel, followed by soft and sticky deposits from fatty acid methyl ester (FAME) in biodiesel.

2.4.3 Topical Report No. 3 – Analytical Characterization of Locomotive Injector Tip Deposits

This research was conducted to determine the chemical composition of injector tip deposits on selected locomotive fuel injectors, found in Appendix C. The effort was to determine if the formation of injector tip deposits was primarily due to the presence of biodiesel present in diesel fuel. The deposits formed in locomotive engine fuel injector tips were characterized by EDS, XRD and FTIR techniques. The scope of this study was limited to HPCR fuel injectors from a 4,500 HP, Tier 3, GE AC45CCTE locomotive.

The injector tip deposits from three locomotive fuel injectors were collected for chemical characterization. The residual fuel was collected and the biodiesel content was measured to be 2.2 percent. Analytical characterization of injector tip deposits by EDS and XRD indicated that the deposits were primarily carbon. EDS characterization indicated some silicon and sulfur content, while sulfur content could be related to fuel, the source of silicon cannot be conclusively related to diesel fuel. FTIR characterization indicated that the injector tip deposits could be the result of high temperature thermal oxidation of biodiesel present in the diesel fuel, and that the deposits also contained polymeric amide-based deposits that could have resulted from succinimide-based fuel additives. It can be stated that the deposit characterization from the injector tips was similar in nature to internal injector deposits found on these injectors. The only exception was that the internal injector deposits also indicated that deposits could have formed from metal carboxylate salts.

2.4.4 Topical Report No. 4 – Literature Review: Biodiesel as a Locomotive Fuel

The use of biodiesel in the United States has been increasing, driven by the Energy Policy Act of 2005 renewable fuel standard (RFS) programs and by mandatory requirements introduced by some States. Under the ASTM, International D975 standard, up to 5 percent biodiesel can be blended in No. 2 diesel without disclosing it to the customer. The railway industry must ensure that locomotives can be operated with at least B5 blends.

The informational search suggests that recent science and the US energy security situation provides little justification for the continued use or expansion of crop based biofuels. The future of biofuels seems to be a political issue that will depend, to a large degree, on the agricultural subsidy policy at the Federal and State levels. The outcomes of the political debate are difficult to predict–one possibility is that that future biodiesel mandates may increase. Blend levels up to B20 have been already considered by some States.

Testing biodiesel blends in medium speed diesel engines to date in North America has been limited. The data available suggests that biodiesel impacts on medium-speed engines may not necessarily mirror those in high-speed diesel engines. Additional work is needed to characterize the effects of biodiesel blends, especially blends above 5 percent, and up to 20 percent. FRA funded B5 and B20 performance and exhaust emissions testing on two line-haul locomotives in 2012 (Fritz, Hedrick, & Rutherford, 2013). The areas that require further research include:

- Effect on emissions and performance on the U.S. Environmental Protection Agency regulated Tier 0—Tier 4 locomotives. The effects on the oxides of nitrogen (NOx) emissions from existing locomotives is especially concerning even as a small increase in NOx from these engines may cause emissions to exceed the certification limits and/or the

NOx emission caps under the memorandum of understandings (MOU) with railroads that are in place in parts of California and in Canada.

- Effects on combustion and fuel injection system behavior. Impact on the long-term performance of the fuel injection system, with a focus on newer, Tier 3+ locomotives that utilize high pressure fuel injection systems believed to be more sensitive to injection deposit formation and blocking with biodiesel.
- Oil dilution in medium speed engines and the effect on engine durability.
- Low temperature operability issues.
- Effect on aftertreatment devices that may see use in Tier 4 locomotives, including Selective Catalytic Reduction (SCR) catalyst systems and diesel particulate filters.
- Compatibility with the current lubricating oil specifications.

Wayside storage of biodiesel blends is another area of concern. Existing experience seems to indicate that blends of up to B5 can be stored in wayside facilities—with good housekeeping—with no problems. Storage of higher blends may lead to such problems as precipitate formation in cold weather, at temperatures above those for diesel fuel, and microbial growth. Guidelines should be developed that would cover the feasibility and the relevant procedures for wayside storage of higher biodiesel blends. Considering the wayside storage concerns, direct-to-locomotive (DTL) fueling with B5 blends from commercial fuel terminals presents a less risky fueling option in terms of potential biodiesel related issues.

Still another source of uncertainty with biodiesel fuels is related to the feedstock, while most of US biodiesel is made from soybeans, some of the larger scale biodiesel plants can process the more cost-effective, imported palm oil feedstock. It is known that palm oil biodiesel has poorer low temperature operability properties than most other biodiesels. In the future, biodiesel can also be made from algae, with a yet unknown impact for the fuel properties. More information regarding these findings can be found in Appendix D.

3 Conclusion

Appendix A through Appendix D of the report presents the work carried out for this study and shows that non-biodiesel compatible materials are still in use in some locomotive fuel system components, primarily in consumable fuel filters and associated gaskets. However, at 5 percent (B5) levels, and due to the fact that these filters are generally replaced every 92 days, there does not seem to be a short-term problem with material compatibility. However, if there are future initiatives or incentives to use high blends of biodiesel such as 20 percent (B20) fuel in locomotives, continued use of non-biodiesel compatible materials could be a problem.

US railroads generally specify ASTM International (ASTM) D975 diesel fuel in their fuel procurement for use in their locomotives. However, due to the Renewable Fuel Standard-2 (RFS-2) requirements, 5 percent of pure biodiesel can be blended into ASTM D975 diesel fuel as sold as diesel fuel. This has resulted in widespread use of low blends of biodiesel in the railroad industry. The biodiesel industry continues to ensure that the 100 percent biodiesel meets ASTM D6751 specifications, and actively participates in the ASTM process to refine test procedures and specifications. However, the potential adverse effects of blends of biodiesel higher than B5 on locomotive engine components were of concern to the rail industry. This report summarizes work performed by the Southwest Research Institute (SwRI®) to support the railroad industry in assessing biodiesel fuel issues in locomotives.

If it is the intent of the railroads to use biodiesel in locomotives, it is recommended that a comprehensive B20 locomotive field test plan be developed and implemented to assess the overall long-term effects of B20 on engine components. The Fuel Lubricants & Environmental (FL&E) Committee of the Locomotive Maintenance Officers Association (LMOA) has outlined such as a test plan and should be considered as a starting point in planning expanded use of B20 biodiesel fuel in locomotive engines.

4 References

Fritz, S. G., and Hedrick, J. C. (2014, December 31). *Locomotive Emissions Measurements for Various Blends of Biodiesel Fuel.* Technical Report, DOT/FRA/ORD-14/39. Federal Railroad Administration. Washington, DC: U.S. Department of Transportation. Available at: https://www.fra.dot.gov/eLib/details/L16191#p1_z5_gD_kLocomotive%20Emissions%20Measurements%20for%20Various%20Blends%20of%20Biodiesel%20Fuel.

Appendix A.
Topical Report No. 1 - FTIR Characterization of Biodiesel Markers in Elastomer and Fuel Filter Components in Locomotive Engines

FTIR Characterization of Biodiesel Markers in Elastomer and Fuel Filter Components in Locomotive Engines

Topical Report No. 01

by

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for

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Gary B. Bessee, Director

Fuels and Lubricants Technology Department

SOUTHWEST RESEARCH INSTITUTE (SwRI®)

Executive Summary

The goal of this research was to develop a technique to identify if unknown fuel wetted elastomers in locomotive engine fuel systems had been exposed to biodiesel. This goal was accomplished by conducting FTIR tests on a selection of commercially available elastomers and comparing it to locomotive fuel system elastomers exposed to biodiesel. These tests were conducted under pre-soak conditions, where the elastomers were tested as received without being exposed to biodiesel and post-soak conditions, where the elastomers had exposure to biodiesel. By comparing the FTIR spectra of locomotive fuel system elastomers to the spectra of commercially available elastomers, the general material type of the locomotive elastomers were determined. It was also concluded that FTIR technique could confirm the absorption of biodiesel in the elastomer matrix by the presence of a carbonyl peak (C=O) ranging from 1737.62 cm^{-1} to 1743.49 cm^{-1}.

Six new elastomers used in locomotive engines were tested at pre-soak and post-soak conditions. The method was able to identify if these elastomers have absorbed biodiesel, irrespective of elastomer identity for all the six locomotive elastomers. Four sets of new locomotive engine fuel filters were subjected to pre-soak and 100% biodiesel post-soak FTIR analysis. It was concluded that the presence of biodiesel was identified in all filter elements and O-rings. Five in-service elastomers and O-rings that showed signs of wear and degradation were tested for identity and the presence of biodiesel using FTIR. It was concluded that most of the degraded in-service elastomers and O-rings have evidence of biodiesel diffusion into the seal material.

Overall, it can be concluded that FTIR can be used as a suitable tool to identify the presence of biodiesel in fuel wetted locomotive elastomer and fuel filter components. Future tests should focus on correlation between the percentage biodiesel content and the extent of degradation in physical property such as O-ring squeeze, hardness and tensile strength, for a statistically significant number of O-rings.

Acknowledgements

The U.S. Army Tank Automotive Research Development and Engineering Center (TARDEC) Fuels and Lubricants Research Facility (TFLRF) which is a part of the Fuels and Lubricants Technology Department located at Southwest Research Institute (SwRI) in San Antonio, TX, performed this work outlined.

The SwRI investigators are Steve Westbrook and Nigil Jeyashekar. The grant manager at SwRI was Steve Fritz, Manager of the Medium-Speed Diesel Engine Section in the Design and Development Department, a part of the SwRI Engine and Vehicle Research Division. Mr. Dennis McAndrew, an independent consultant to SwRI, served as a project technical monitor. The authors would like to acknowledge the contribution of the TFLRF technical support staff along with the administrative support staff.

1 Introduction – Objective and Scope

There are primarily two mechanisms that affect a material exposed to fuel. The diffusion of fuel components into the polymer material, and simultaneous loss of polymer material into fuel. These two mechanisms are accelerated by other factors such as pressure, temperature and forces exerted on the material resulting from reciprocating, rotary or oscillating motions in dynamic seals. Fuel–material compatibility research is primarily concerned with change in physical properties of fuel wetted materials. These properties include thickness, hardness, volume swell, and tensile strength. In dynamic seals, Scanning Electron Microscope (SEM) studies are often conducted to determine the change in morphology due to wear.

Fuel–material compatibility has become increasingly important with the use of fuel blends containing biodiesel. Extensive research has been conducted to study the effect of biodiesel on fuel system components in automotive engines. However, there is limited literature on the impact of biodiesel fuel blends on fuel wetted and fuel system components for locomotive engines. In light of this technical void, the objective of the current research is to use Fourier Transform Infrared (FTIR) spectroscopy technique to determine if the elastomers and certain fuel filter components, used in locomotive engines, have absorbed any biodiesel component from the fuel blend. It should be noted that determining the exposure and absorption of biodiesel was only the first step in the process, and quantifying the changes in physical, chemical and mechanical properties that stem from biodiesel absorption was beyond the scope of this research study.

The objective of this research was accomplished by conducting the following studies:

a. FTIR spectra were obtained for standard elastomers, namely, Fluorosilicone, Buna-N and Viton with and without the presence of biodiesel. A comparison of the FTIR spectra were made to identify and label suitable biodiesel markers on these elastomers.

b. FTIR spectra were obtained from new locomotive fuel filter components and elastomers, and also the same components that were soaked in 100% biodiesel (B100). A comparison was made to identify and label biodiesel markers on each of these components.

c. A blind study was conducted on elastomers that were used in-field to identify the type of elastomer and determine the presence of biodiesel in those elastomers.

Since biodiesel comprises primarily of fatty acid methyl esters, the marker that is sought to identify the presence of biodiesel is the carbonyl (C=O) peak in the ester functional group.

2 FTIR Study of Standard Elastomers

FTIR spectra were obtained for a selection of commercially available Fluorosilicone, Buna-N and Viton elastomers. These elastomers were soaked separately in B100 for two weeks. The residual biodiesel on the surface of soaked elastomers was removed and the samples were left to dry in the fume hood for one week, prior to acquiring FTIR spectra for the soaked elastomers. Figure A1, Figure A2, and Figure A3 shows the spectra for all three neat and soaked elastomers in B100.

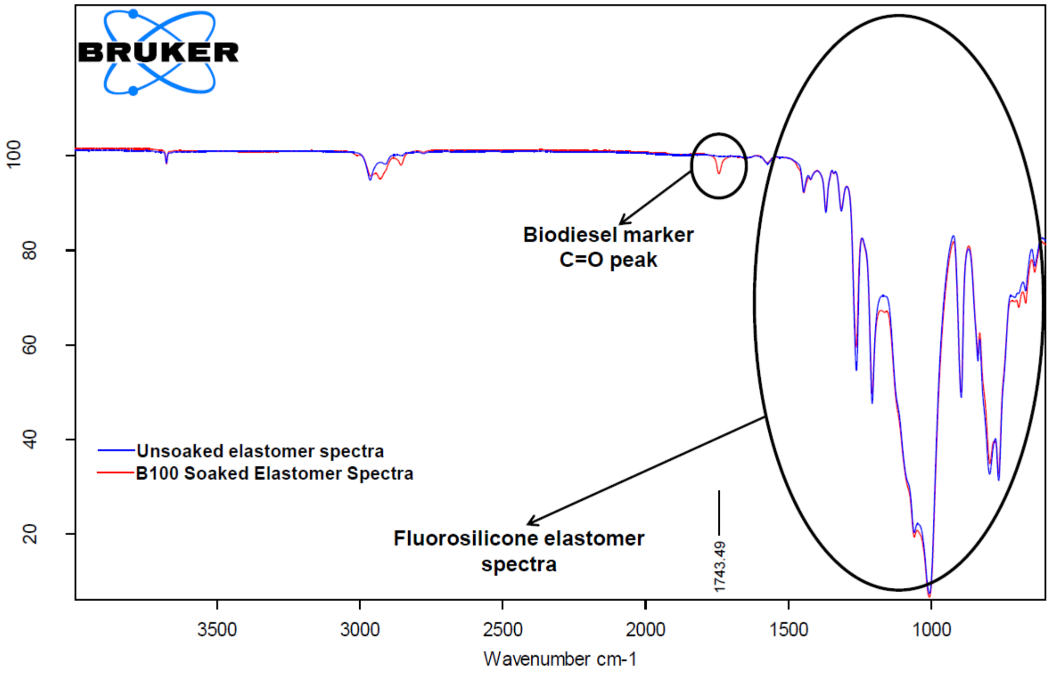

Figure A1. FTIR Spectra of Fluorosilicone Elastomers

The FTIR spectra for unsoaked Fluorosilicone elastomer and that soaked in biodiesel, shown in Figure A1, has nearly identical spectral signatures. The difference in the FTIR spectra is the presence of carbonyl peak that corresponds to an ester, at 1743.49 cm^{-1}, indicating the absorption of biodiesel by the polymer matrix. A similar comparison between new elastomers and those soaked in biodiesel, for Buna-N and Viton, show carbonyl peaks at 1737.62 cm^{-1} and 1741.86 cm^{-1}, in Figure A2, and Figure A3 respectively, confirming the absorption of biodiesel by the elastomer matrix. Therefore, the presence of biodiesel was confirmed by the presence of carbonyl peak ranging from 1737.62 cm^{-1} to 1743.49 cm^{-1}, for all three elastomers. This peak will be used as a marker to determine if an elastomer under investigation has been exposed to biodiesel.

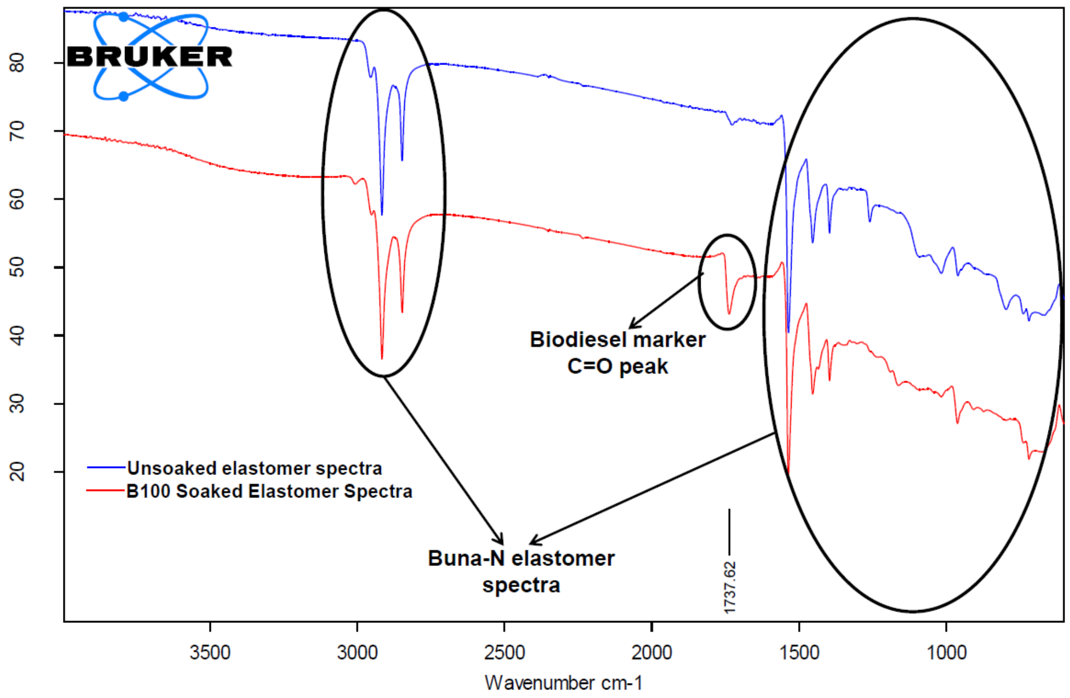

Figure A2. FTIR Spectra of Buna-N Elastomers

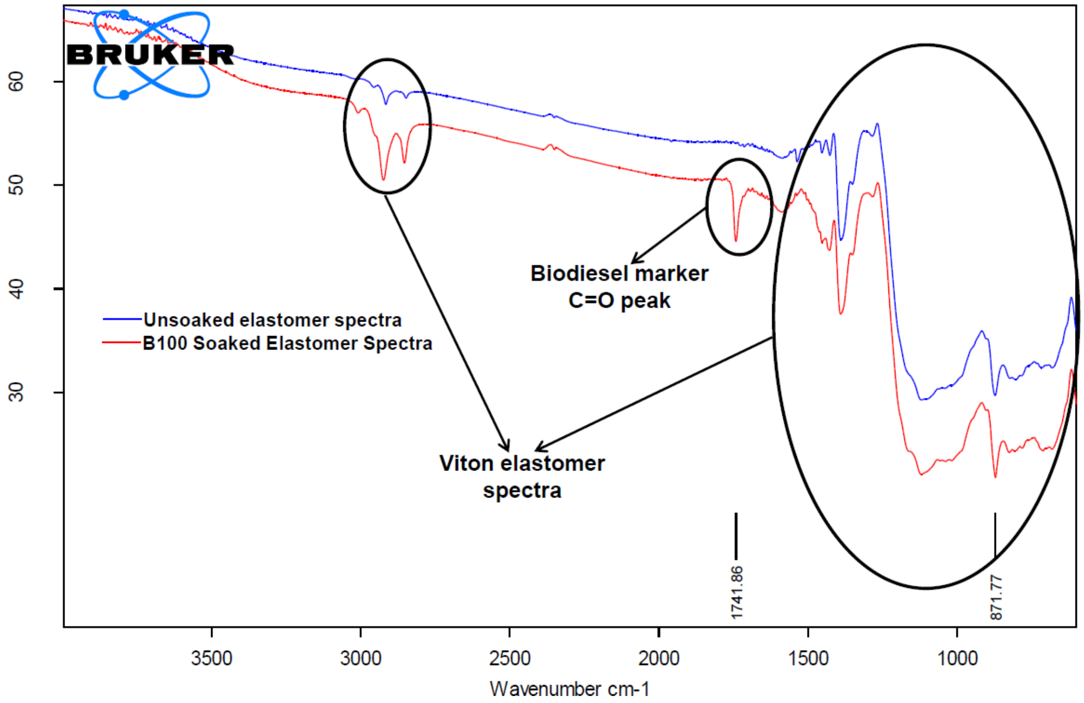

Figure A3. FTIR Spectra of Viton Elastomers

Based on the FTIR study of the three standard elastomers and those soaked in biodiesel, it can be concluded that:

a. The carbonyl peak corresponding to the ester component in fatty acid methyl esters can be clearly identified as a biodiesel marker, ranging from 1737.62 cm^{-1} to 1743.49 cm^{-1}, for all three types of elastomers.

b. The FTIR spectra of unsoaked elastomers can be used as reference spectra to identify the type of elastomer under investigation.

c. Hence, the ultimate goal of this research work is to identify an unknown fuel wetted elastomer in a locomotive engine and determine if it had been exposed to biodiesel.

3 Locomotive Elastomer Tests

SwRI procured six sets of new (unused) locomotive fuel system elastomers that have not been exposed to any fuel. In the interest of confidentiality, the suppliers name and part numbers associated with the elastomers are not provided. The elastomers are identified with a code, beginning with letters “CL13-” followed by four numbers. The elastomer picture is provided in this report along with the FTIR spectra for unsoaked and soaked elastomers. The elastomer samples were soaked in B100 for two weeks. The residual biodiesel on the surface of soaked elastomers were removed and the samples were left to dry in the fume hood for one week, prior to acquiring FTIR spectra for the soaked elastomers.

3.1 CL13-5137: Green O-Ring

The green O-ring for a locomotive primary fuel filter housing is shown in Figure A4. The test on this O-ring was conducted prior to formulating the actual goals for this project which involved soaking these new elastomers in biodiesel. This O-ring was subjected to pyrolysis in a test tube and liquid was coooled prior to collecting the FTIR spectrum. By comparing the FTIR spectra of the pyrolyzed condensate to the standard spectrum shown in Section 2, it can be concluded that this locomotive O-ring sample is a Viton elastomer.

Figure A4. CL13-5137 – Green O-Ring

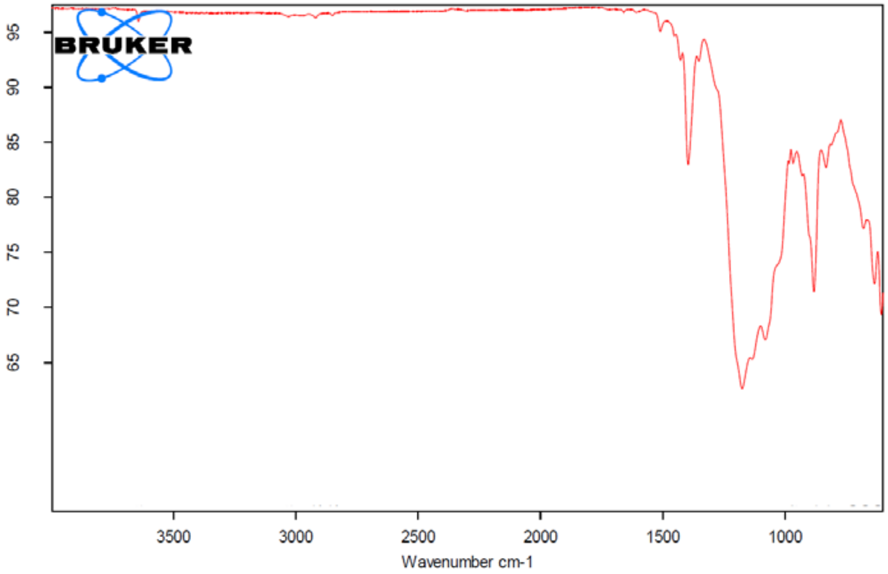

Figure A5. FTIR Spectrum of CL13-5137 – Green O-Ring

3.2 CL13-5138: Black O-Ring

The black O-ring provided by the supplier is shown in Figure A6. The FTIR spectra of unsoaked and B100 soaked elastomer are shown in Figure A7. Based on the reference spectra in Section 2, it can be concluded that:

a. The black O-ring is Viton elastomer.

b. The carbonyl peak at 1714.24 cm-1 and alkyl peaks in 2800–3000 cm-1 range indicates that there is strong absorption of biodiesel by the elastomer.

Figure A6. CL13-5138 – Black O-Ring

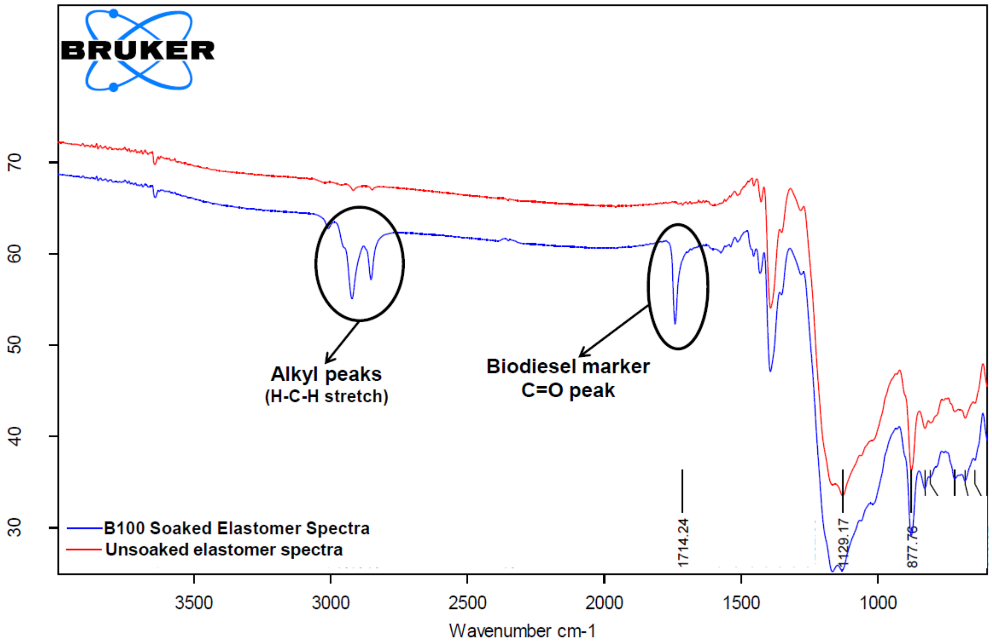

Figure A7. FTIR Spectra of CL13-5138 – Black O-Ring

3.3 CL13-4998 and CL13-4999: Fuel Filter Elastomer Set – I

Two fuel filter elastomer sets were provided, with each set containing two elastomer samples as shown in Figure A8 and Figure A11. Both unsoaked and B100 soaked-elastomer FTIR spectra were obtained and are shown in Figure A9 and Figure A10, for CL13-4998; and Figure A12 and Figure A13, for CL13-4999. Based on the FTIR spectra, it can be concluded that both fuel filter elastomer sets are Buna-N and the fact that the elastomers have absorbed biodiesel is indicated by the presence of carbonyl peak. CL13-4999 contains H–C–H peak in soaked and unsoaked elastomers. The soaked specimen has a stronger alkyl peak due to biodiesel absorption.

Figure A8. CL13-4998 – Fuel Filter Elastomer Set – I: Sample-1 (Left), Sample-2 (Right)

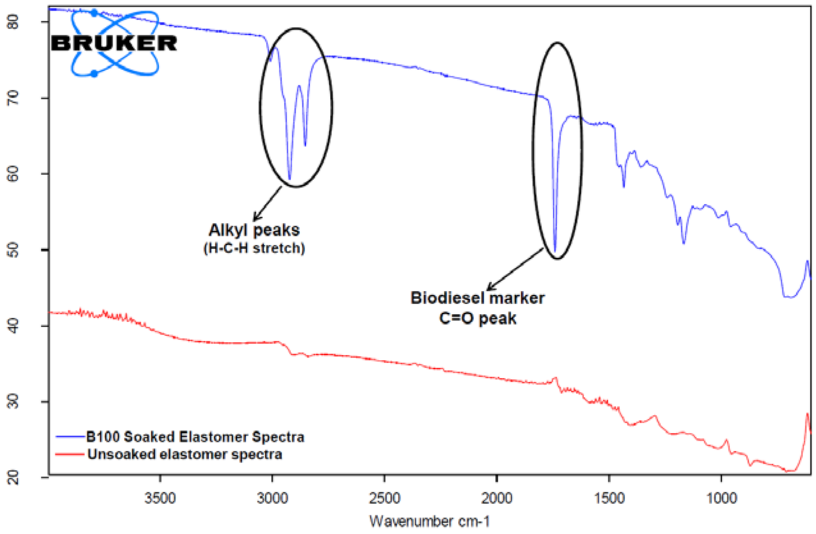

Figure A9. FTIR Spectra of CL13-4998 – Sample-1

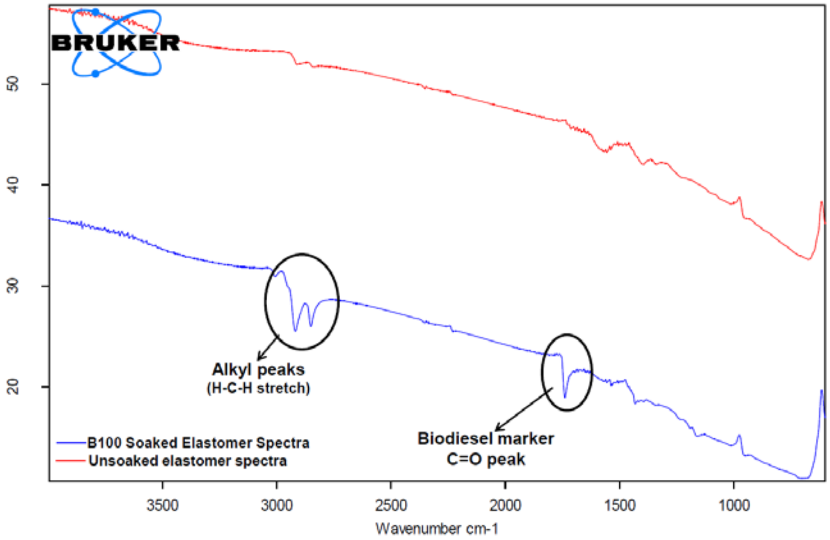

Figure A10. FTIR Spectra of CL13-4998 – Sample-2

Figure A11. CL13-4999 – Fuel Filter Elastomer Set – I: Sample-1 (Left), Sample-2 (Right)

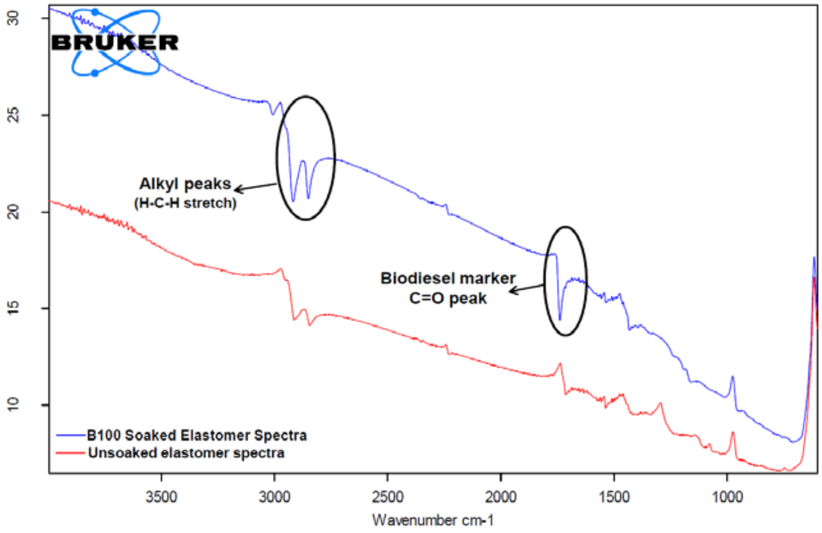

Figure A12. FTIR Spectra of CL13-4999 – Sample-1

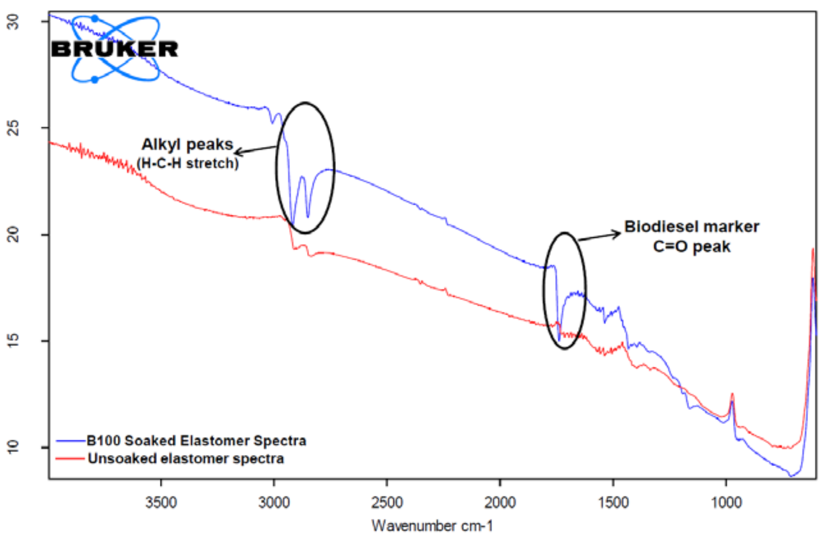

Figure A13. FTIR Spectra of CL13-4999 – Sample-2

3.4 CL13-5000 and CL13-5001: Fuel Filter Elastomer Set – II

Two fuel filter elastomer sets were provided, with each set containing two elastomer samples as shown in Figure A14 and Figure A17. Both unsoaked and B100 soaked-elastomer FTIR spectra were obtained and are shown in Figure A15 and Figure A16, for CL13-5000; and Figure A18 and Figure A19, for CL13-5001. By comparing the unsoaked elastomer FTIR spectra against the standard spectra in Section 2, it can be concluded that both samples in CL13-5000 is a Buna-N elastomer.

The samples in CL13-5001 have marked differences. Prior to biodiesel soak, sample-1 in CL13-5001 breaks into amorphous small clumps, while Sample-2 breaks into thread like polymer and further breaks down into loose powdery structure. Sample-1 in CL13-5001 is similar to samples in CL13-4998, CL13-4999 and CL13-5000. The FTIR spectra for Sample-1 in CL13-5001 indicates that it is a Buna-N elastomer, while the elastomer in Sample-2 does not match either of the three reference elastomers in Section 2.0.

However, in both the elastomers, biodiesel absorption is indicated by the presence of a carbonyl peak. It should be noted that Sample-2 in CL13-5001, has a significantly strong carbonyl peak and a large H–C–H peak is due to biodiesel absorption in soaked elastomer. Overall, it can be concluded that, the presence of biodiesel in an elastomer sample, irrespective of its identity, can be inferred by the presence of a carbonyl peak.

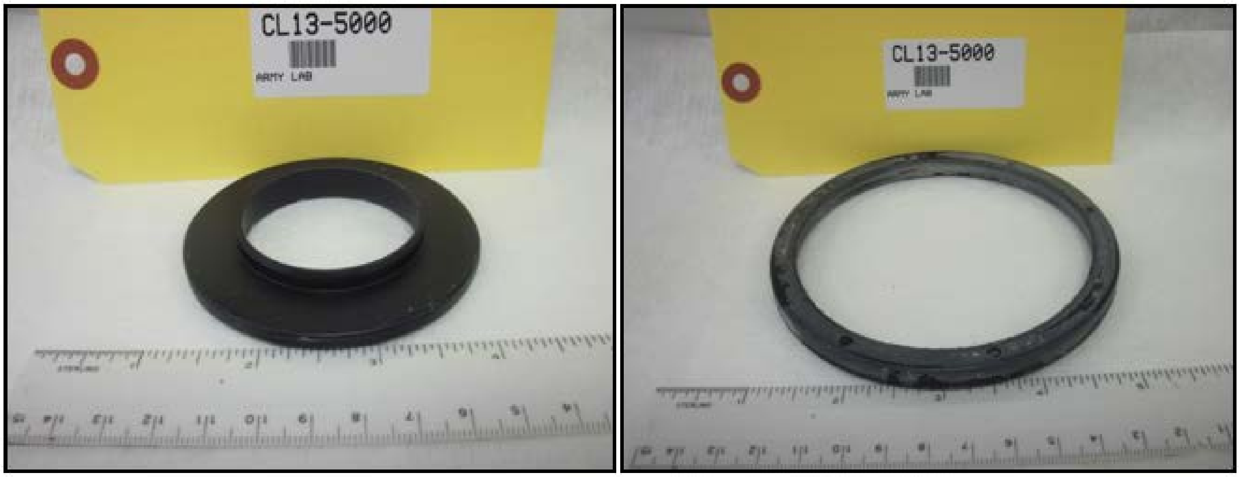

Figure A14. CL13-5000 – Fuel Filter Elastomer Set – II: Sample-1 (Left), Sample-2 (Right)

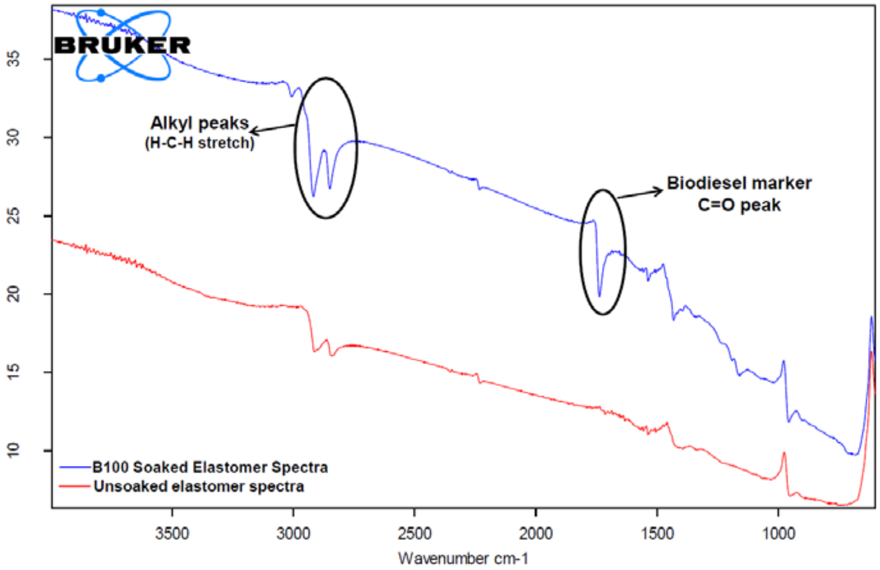

Figure A15. FTIR Spectra of CL13-5000 – Sample-1

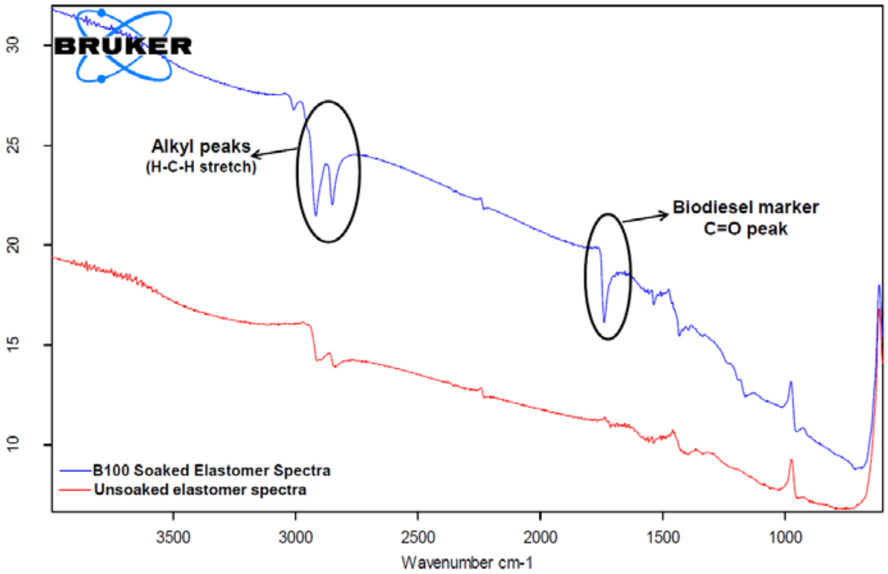

Figure A16. FTIR Spectra of CL13 5000 Sample 2

Figure A17. CL13-5001 – Fuel Filter Elastomer Set – II: Sample-1 (Left), Sample-2 (Right)

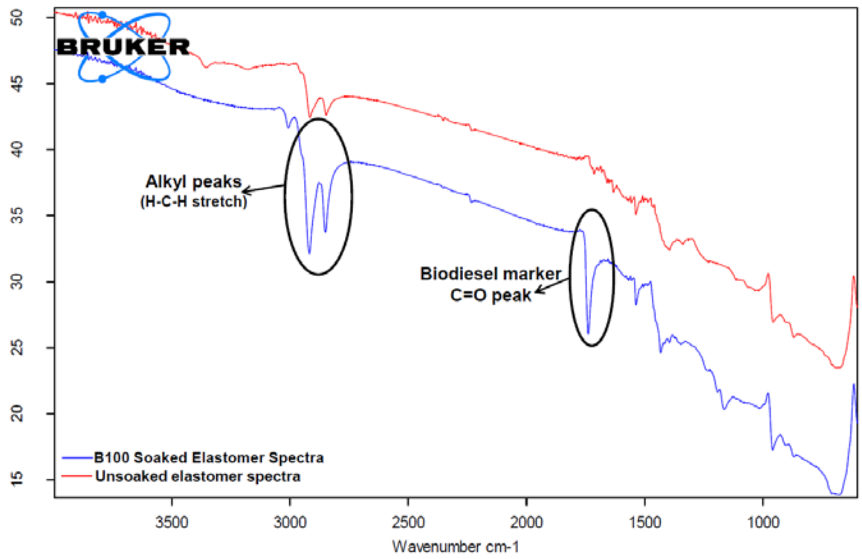

Figure A18. FTIR Spectra of CL13-5001 – Sample-1

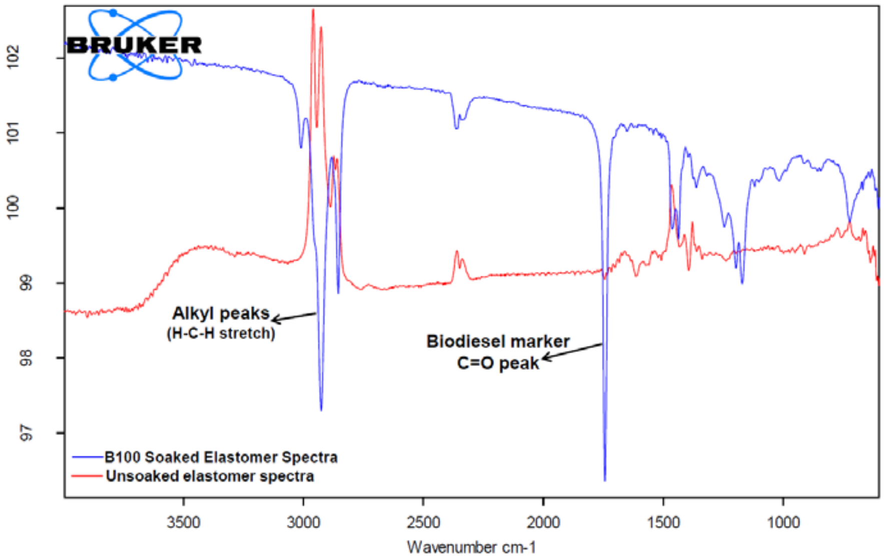

Figure A19. FTIR Spectra of CL13-5001 – Sample-2

4 FTIR Study of in Service Elastomers

Five in service elastomers, potentially from the locomotive wayside fueling systems, that were exposed to fuel were sent to SwRI for testing. The duration of exposure to fuel and other details on the elastomer were not provided to SwRI. All elastomers were given the same identification code, CL13-5860, followed by a short description of the elastomer to serve as a unique identifier. FTIR spectra were acquired for all the in service elastomer samples to determine the presence of biodiesel. In addition to the spectra, physical properties such as thickness, hardness, weight and tensile strength were measured and listed.

4.1 CL13-5860: Blue Elastomer O-Ring

The blue O-ring is shown in Figure A20. The FTIR spectrum, in Figure A21, indicates that the O-ring is a Fluorosilicone elastomer and that it has a carbonyl peak confirming the presence of biodiesel in the elastomer sample. The physical properties of the elastomer are listed in Table A1.

Figure A20. CL13-5860 – Blue Elastomer O-Ring

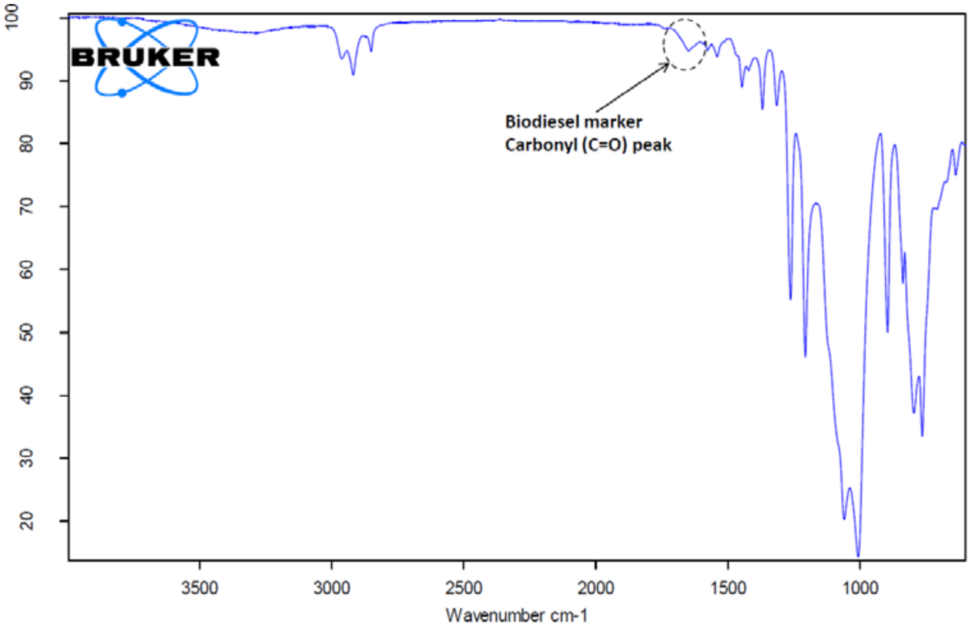

Figure A21. FTIR Spectra of CL13-5860 – Blue Elastomer O-Ring

Table A1. Physical Properties of CL13-5860 – Blue Elastomer O-Ring

Property	Value
Thickness (inches)	0.1329
Hardness (Shore M)	61.40
Weight (g)	2.3854
Tensile Strength (psi)	624.33

4.3 CL13-5860: Small Black Elastomer O-Ring

The small black O-ring is shown in Figure A22. The FTIR spectrum, in Figure A23, indicates that the O-ring is a Buna-N elastomer with no carbonyl peak confirming the absence of biodiesel in the elastomer sample. The physical properties of the elastomer are listed in Table A2.

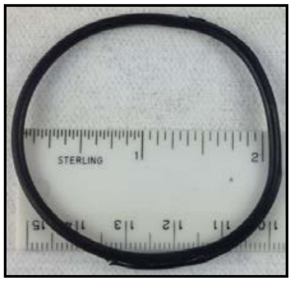

Figure A22. CL13-5860 – Small Black Elastomer O-Ring

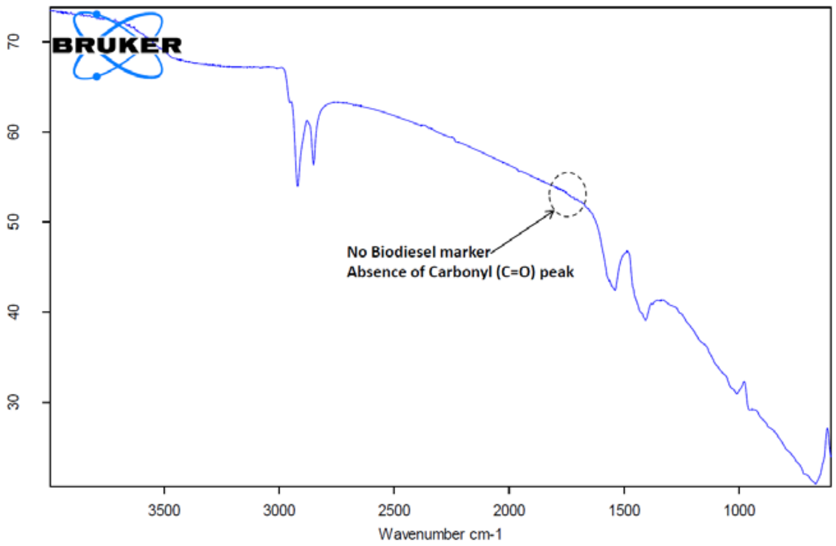

Figure A23. FTIR Spectrum of CL13-5860 – Small Black Elastomer O-Ring

Table A2. Physical Properties of CL13-5860 – Small Black Elastomer O-Ring

Property	Value
Thickness (inches)	0.0998
Hardness (Shore M)	71.40
Weight (g)	1.0473
Tensile Strength (psi)	1688.06

4.4 CL13-5860: Large Black Elastomer O-Ring

The large black O-ring is shown in Figure A24. The FTIR spectrum, in Figure A25, indicates that the O-ring is a Buna-N elastomer and a carbonyl peak confirming the presence of biodiesel in the elastomer sample. The physical properties of the elastomer are listed in Table A3.

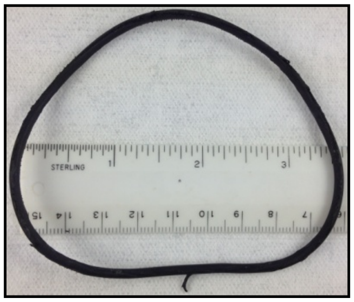

Figure A24. CL13-5860 – Large Black Elastomer O-Ring

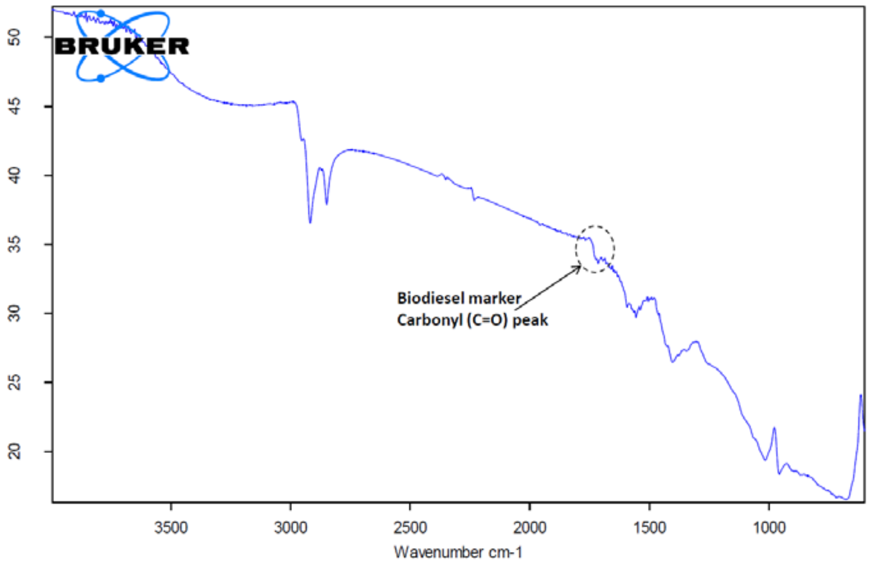

Figure A25. FTIR Spectrum of CL13-5860 – Large Black Elastomer O-Ring

Table A3. Physical Properties of CL13-5860 – Large Black Elastomer O-Ring

Property	Value
Thickness (inches)	0.1020
Hardness (Shore M)	68.80
Weight (g)	1.7744
Tensile Strength (psi)	1336.10

4.5 CL13-5860: Elastomer Specimen-I

The elastomer specimen-I is shown in Figure A26. The FTIR spectrum, in Figure A27, indicates that the elastomer is Viton and a carbonyl peak confirms the presence of biodiesel in the elastomer sample. The physical properties of the elastomer are listed in Table A4.

Figure A26. CL13-5860 – Elastomer Specimen-I

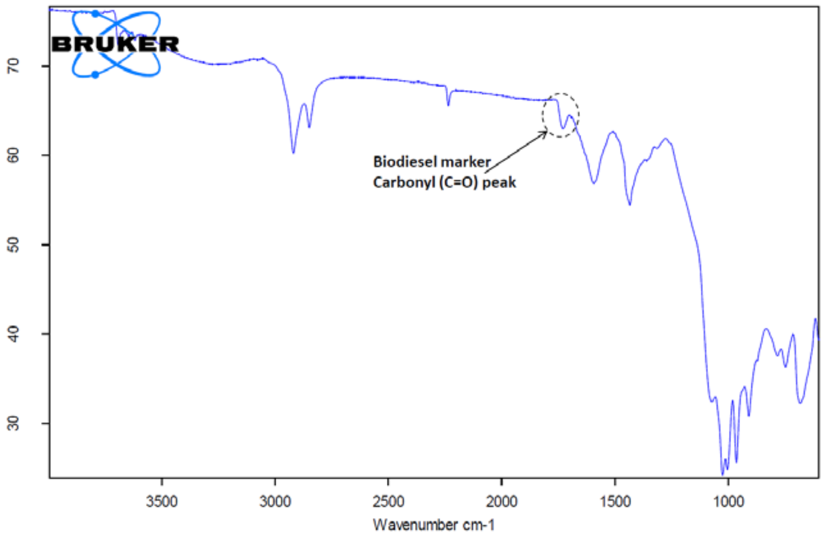

Figure A27. FTIR Spectrum of CL13-5860 – Elastomer Specimen-I

Table A4. Physical Properties of CL13-5860 – Elastomer Specimen-I

Property	Value
Thickness (inches)	0.2017
Hardness (Shore A)	72.82
Weight (g)	13.5826
Tensile Strength (psi)	2145.10

4.6 CL13-5860: Elastomer Specimen-II

The elastomer specimen-II is shown in Figure A28. The FTIR spectrum, in Figure A29, indicates that the elastomer is Viton and a carbonyl peak confirms the presence of biodiesel in the elastomer sample. The physical properties of the elastomer are listed in Table A5.

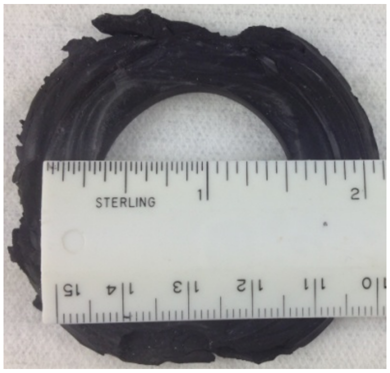

Figure A28. CL13-5860 – Elastomer Specimen-II

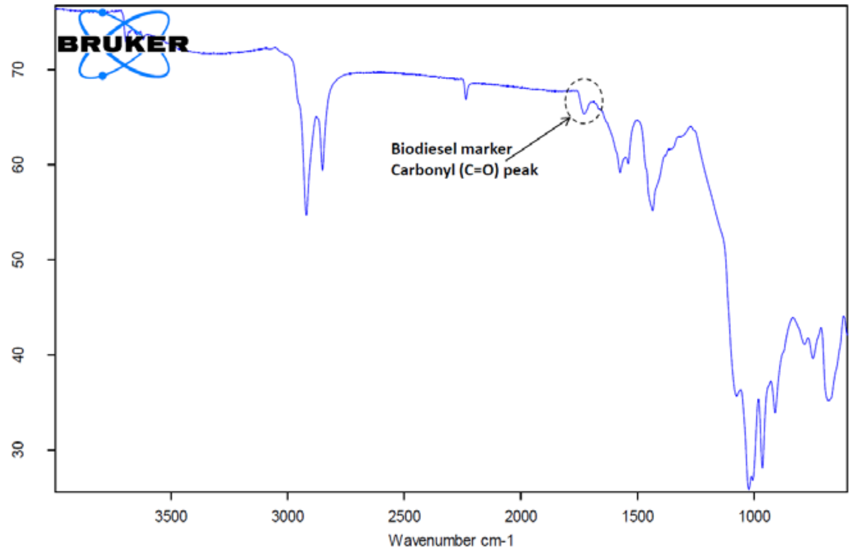

Figure A29. FTIR Spectrum of CL13-5860 – Elastomer Specimen-II

Table A5. Physical Properties of CL13-5860 – Elastomer Specimen-II

Property	Value
Thickness (inches)	0.1919
Hardness (Shore A)	72.38
Weight (g)	10.4452
Tensile Strength (psi)	1503.97

5 Fuel Filter Component Study

Four sets of new (unused) fuel filters were provided to SwRI to conduct FTIR studies on components such as filter elements, O-rings, and polymers in these filters. The supplier for the filter components and detailed description of these filter components are not included in this report, in the interest of confidentiality. The filter components are identified with a code, beginning with letters “CL13-” with four numbers followed by identification of the component as either a filter element or a polymer or an O-ring. The individual components for FTIR study were soaked in B100 for 2 weeks. The residual biodiesel on the surface of soaked elastomers were removed and the samples were left to dry in the fume hood for one week, prior to acquiring FTIR spectra for the soaked components. The identification codes for the four sets of locomotive fuel filter components are CL13-5139, CL13-5140, CL13-5141(female end) and CL13-5142 (male end), CL13-5143 (female end) and CL13-5144 (male end). The male and female end of the filter are essentially the same filter element and polymer, and are therefore represented by one FTIR spectra.

5.1 CL13-5139 – Filter Element, O-Ring and Polymer

The filter element, O-ring and polymer FTIR spectra at unsoaked and soaked conditions are shown in Figure A30, Figure A31, and Figure A32 respectively. In all three FTIR spectra, the presence of carbonyl peak, indicates that the absorption of biodiesel of in service filters could be detected by this FTIR marker. In Figure A31, it should be noted that there is a carbonyl peak in both soaked and unsoaked O-ring and that the soaked elastomer has a stronger carbonyl peak. There is also a slight shift in the carbonyl peak in the soaked elastomer from the unsoaked sample. At this time, there is no reason that can be attributed to this shift. However, it does change the final conclusion in detecting the presence of biodiesel using the carbonyl peak marker. The FTIR spectra indicates that the O-ring is a Viton elastomer.

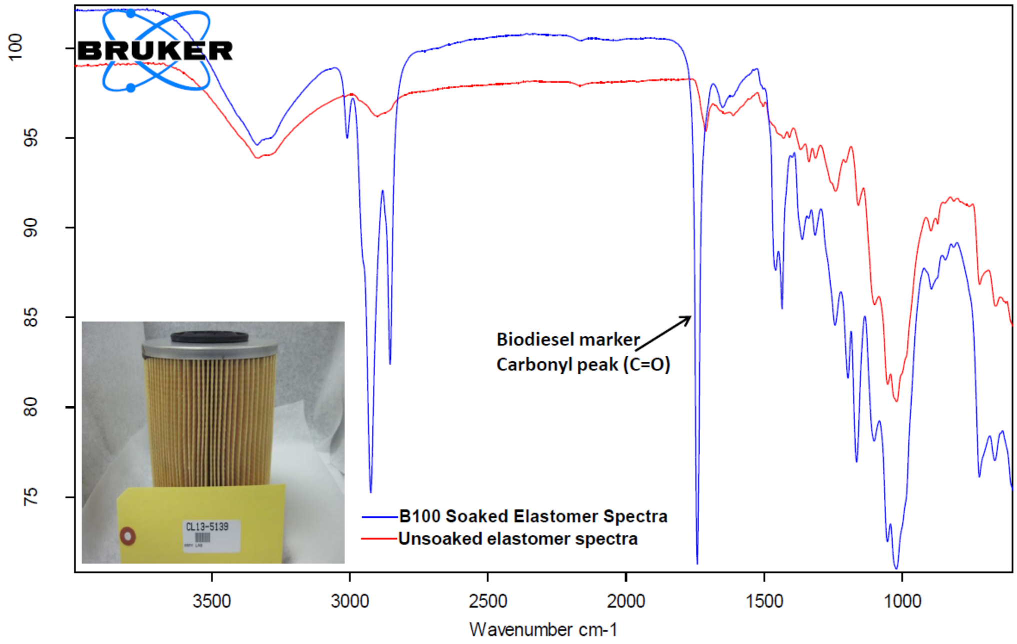

Figure A30. CL13-5139 – FTIR Spectra of Filter Element

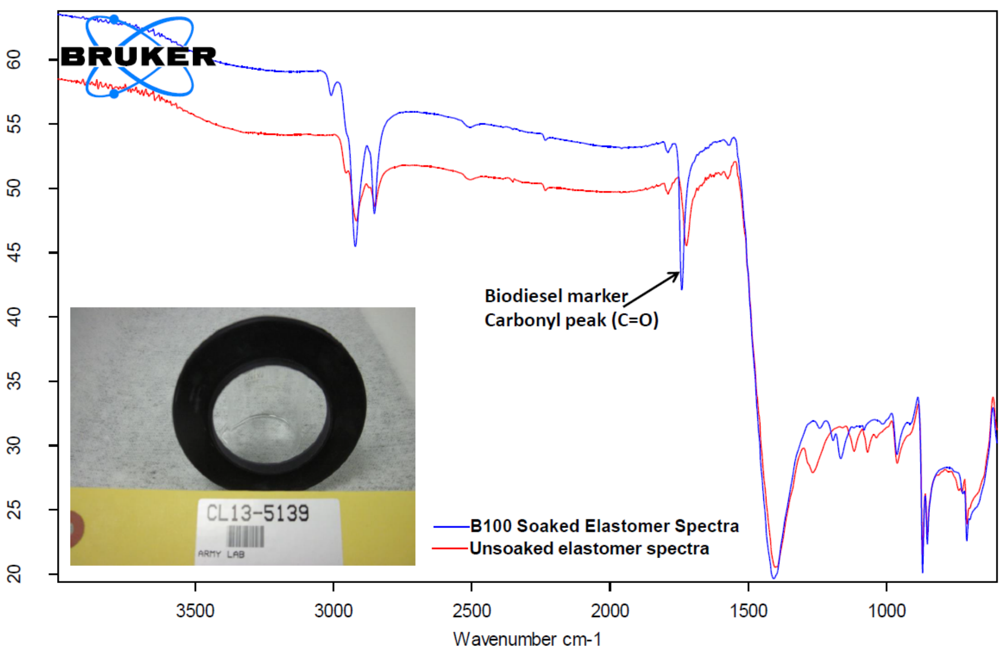

Figure A31. CL13-5139 – FTIR Spectra of O-Ring

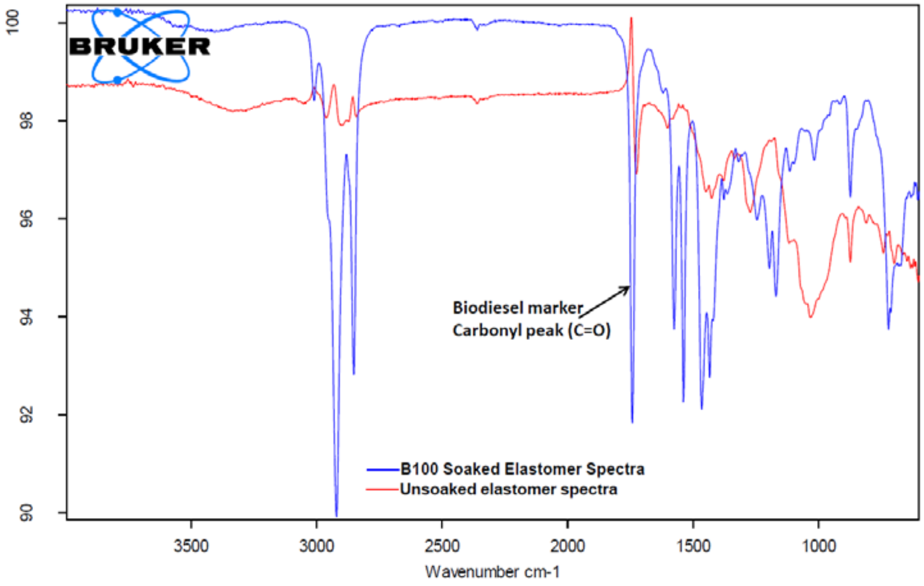

Figure A32. CL13-5139 – FTIR Spectra of Polymer

5.2 CL13-5140 – Metal Filter Element, O-Ring and Polymer

The FTIR spectra of metal filter element, O-ring and polymer material at unsoaked and soaked conditions are shown in Figure A33, Figure A34, and Figure A35 respectively.

a. The unsoaked metal filter element has a blank FTIR spectrum while the soaked metal filter element contains FTIR signature of biodiesel.

b. The O-ring contained in this filter did not belong to the three standard elastomers (Fluorosilicone, Buna-N and Viton). The O-ring contains a carbonyl peak before soak conditions. However, there is a presence of a stronger carbonyl peak in the soaked O-ring FTIR spectra indicated the absorption of biodiesel.

c. The FTIR spectra for the polymer contains the same carbonyl peak at pre-soak and post-soak and therefore, FTIR method is unable to determine absorption of biodiesel by this polymer.

Hence, the presence of biodiesel can be predicted using FTIR for the metal filter element and O-ring. FTIR is unable to determine the absorption of biodiesel by the polymer.

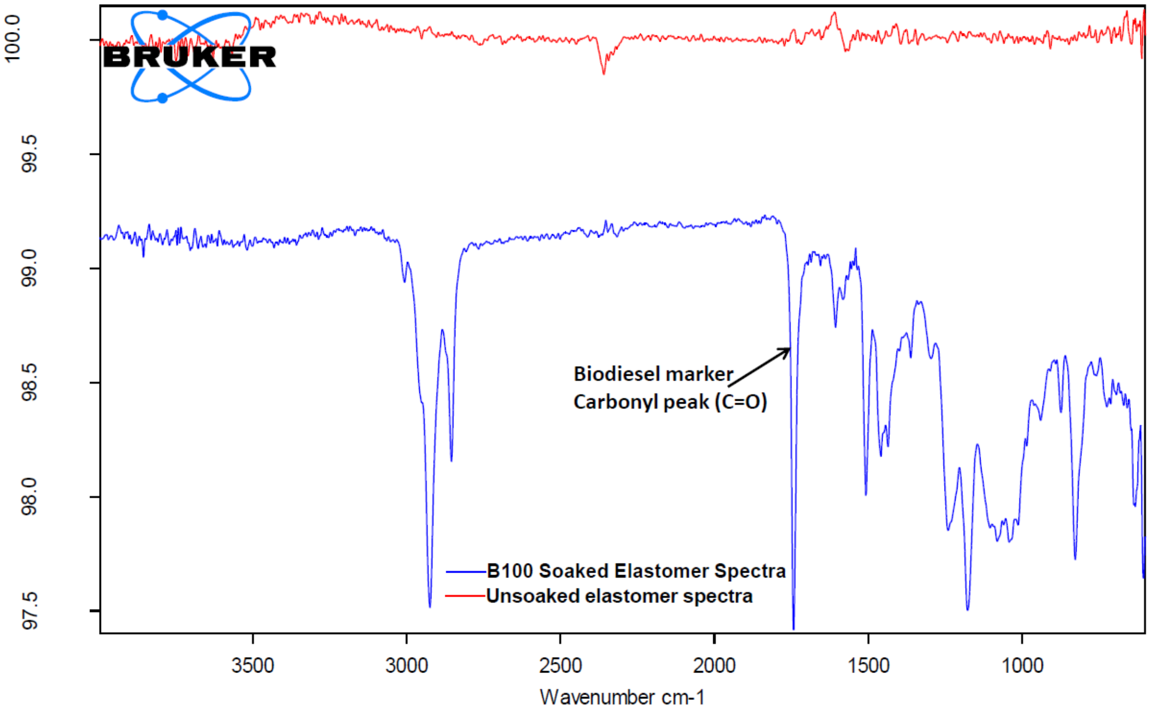

Figure A33. CL13-5140 – FTIR Spectra of Metal Filter Element

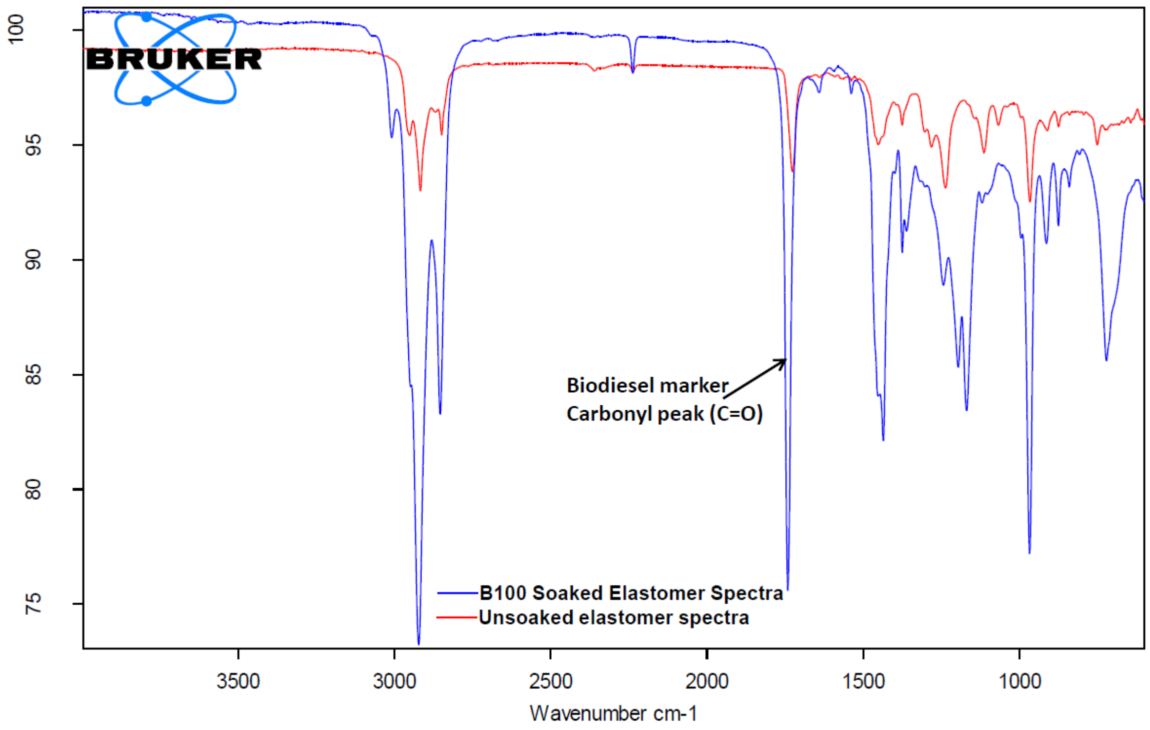

Figure A34. CL13-5140 – FTIR Spectra of O-Ring

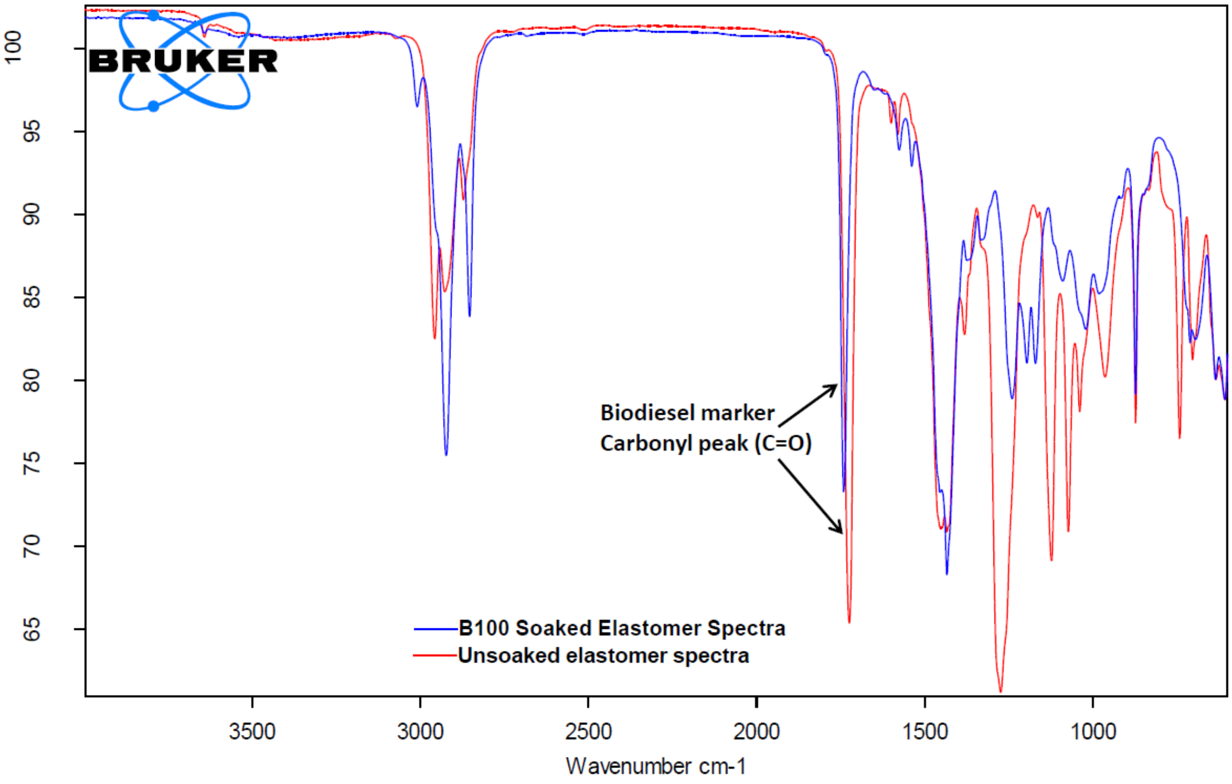

Figure A35. CL13-5140 – FTIR Spectra of Filter Element

5.3 CL13-5141, CL13-5142, CL13-5143, CL13-5144 – Filter Element and Polymer

a. FTIR method was able to determine the presence of biodiesel from the carbonyl marker in the filter element as shown in Figure A36 and Figure A38.

b. There were no O-rings associated with these filters. The polymer FTIR spectra are shown in Figure A37 and Figure A39. The identity of the polymers are unknown. However, both the polymers have carbonyl peaks of the same strength in pre-soak and post soak samples. Hence, it is not possible to predict the absorption of biodiesel using FTIR method for these polymers.

c. The above results are applicable for filter elements and polymers for male and female ends of both sets of fuel filters.

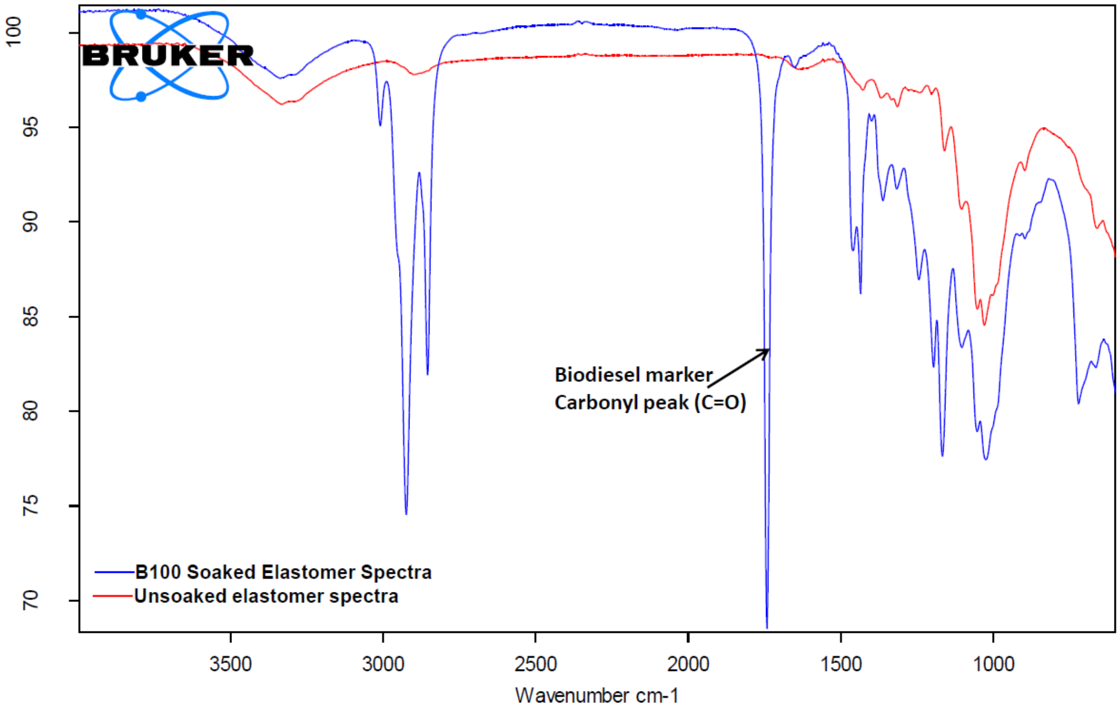

Figure A36. CL13-5141 and CL13-5142 – Filter Element FTIR Spectra

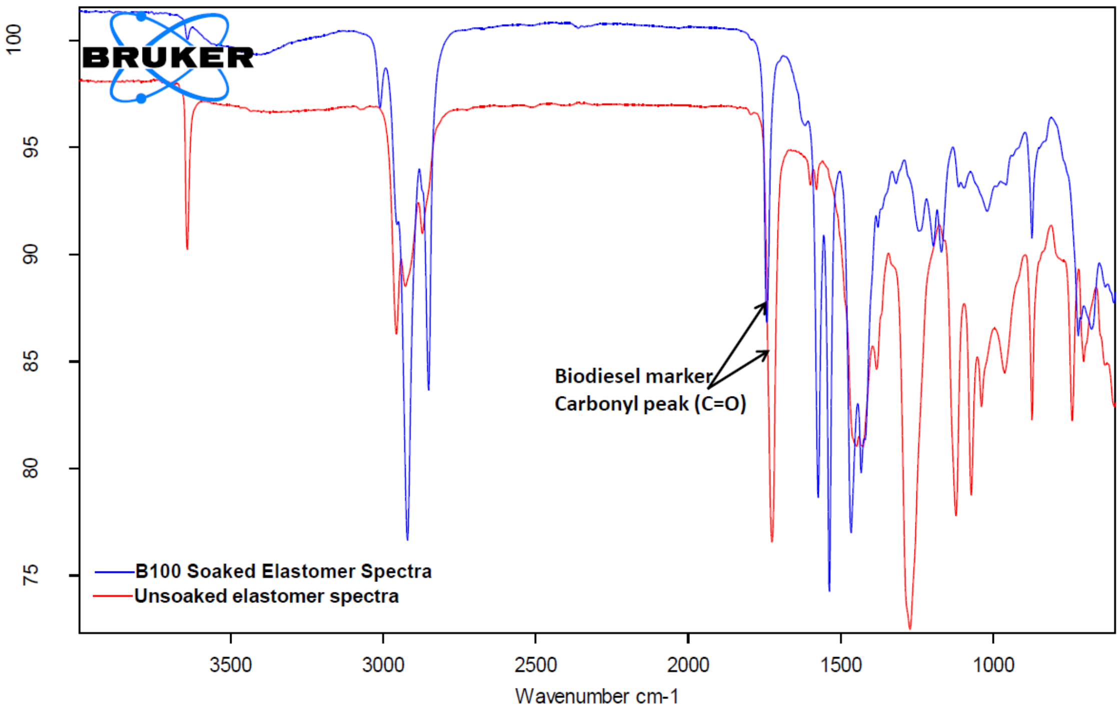

Figure A37. CL13-5141 and CL13-5142 – Polymer FTIR Spectra

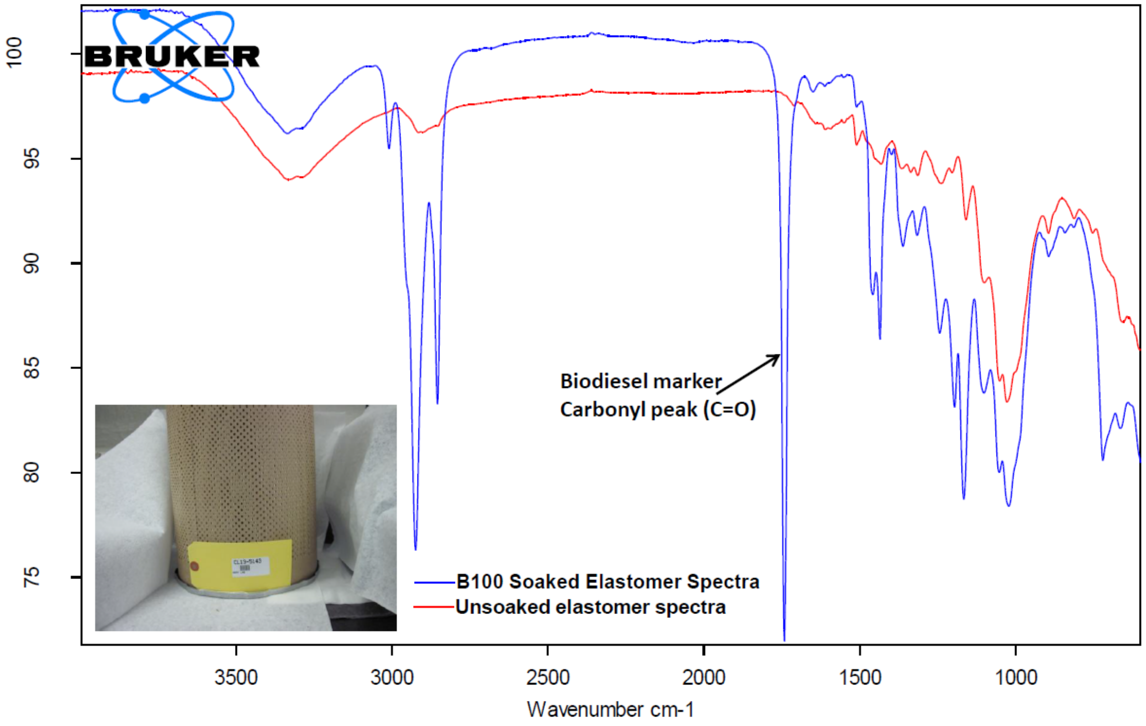

Figure A38. CL13-5143 and CL13-5144 – Filter Element FTIR Spectra

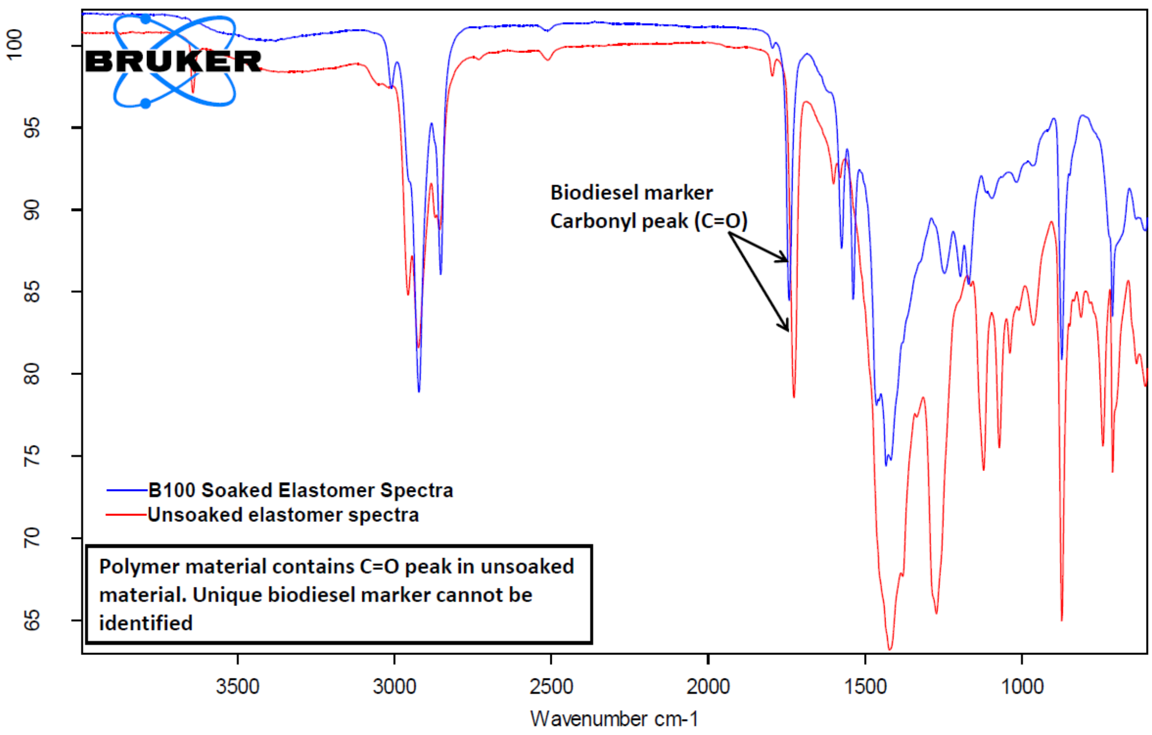

Figure A39. CL13-5143 and CL13-5144 – Polymer FTIR Spectra

6 Conclusions

FTIR studies were performed on commercially available elastomer O-rings (Fluorosilicone, Buna-N and Viton). FTIR spectra of the commercially available elastomers were used to determine the identity of selected locomotive fuel system elastomers. The FTIR spectra were able to confirm the absorption of biodiesel by the presence of carbonyl peak (C=O) for all the three elastomer O-rings. This biodiesel marker was used to identify the presence of biodiesel in locomotive fuel system elastomers.

Six new elastomers used in locomotive engine fuel systems were tested at pre-soak and post-soak conditions. FTIR method was able to determine if the identity of these elastomers were the same as the three standard elastomers listed earlier. The method was also able to identify if these elastomers have absorbed biodiesel, irrespective of elastomer identity for all the six locomotive elastomers. Four sets of locomotive engine fuel filters were subjected to FTIR study with pre-soak and post-soak samples. It was concluded that the presence of biodiesel was identified in all filter elements and O-rings (if present in the fuel filter). Fuel filter polymers that had no carbonyl peak in the pre-soak polymer samples, have showed a strong carbonyl peak in post-soak samples confirming the absorption of biodiesel by the polymer. The presence of biodiesel in certain filter polymers could not be determined due to the presence of a strong carbonyl peak in the pre-soak samples of those polymers. Overall, it was concluded that FTIR can be used as a suitable test to identify the presence of biodiesel in fuel wetted locomotive elastomer and fuel filter components that do not contain a carbonyl peak at pre-soak conditions.

Five in-service elastomers and O-rings that showed signs of wear and degradation were tested for identity and the presence of biodiesel using FTIR. One O-ring was determined to be Fluorosilicone, two O-rings were determined to be Buna-N and two elastomer seals were Viton. Biodiesel markers were identified in all polymers, except one Buna-N O-ring. It was concluded that most of the degraded in-service elastomers and O-rings have evidence of biodiesel diffusion into the seal material. Future tests should focus on correlation between the percentage biodiesel content and the extent of degradation in physical property such as O-ring squeeze, hardness and tensile strength, for a statistically significant number of O-rings.

Appendix B.
Topical Report No. 2 – Locomotive Engine Fuel Injector Deposit Characterization Using FTIR

Locomotive Engine Fuel Injector Deposit Characterization Using FTIR

Topical Report No. 02

by

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US DOT/Federal Railroad Administration

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Approved by:

Gary Bessee

Gary B. Bessee, Director
Fuels and Lubricants Technology Department
SOUTHWEST RESEARCH INSTITUTE (SwRI®)

Executive Summary

The goal of this research work was to determine the chemical composition of internal injector deposits on selected locomotive fuel injectors. The effort was to determine if the formation of internal injector deposits could be due to the presence of biodiesel in the locomotive fuel. The internal deposits formed in locomotive engine fuel injectors were characterized by Fourier Transform Infrared (FTIR) spectroscopy analysis of deposits collected from the control valve area of a locomotive engine fuel injector. The scope of this study was limited to high-pressure common-rail (HPCR) fuel injectors from Cummins QSK19 non-road diesel engines used in genset switcher locomotives.

It was concluded that the highest concentration of internal injector deposits were metal carboxylate salts that resulted from trace metal contaminants. The second highest deposit concentration were polymeric amide deposits. The injectors that were exposed to biodiesel blends contained deposits that resulted from high temperature oxidation of biodiesel. However, based on FTIR, it was determined that these deposits were relatively lower in concentration compared to the deposits due to trace metal contaminants and polymeric amide based deposits.

Elemental analysis was conducted on deposits from an injector needle. The deposits contained significant concentration of calcium, which correlated with FTIR results on metal (calcium) carboxylate salt deposits, further supporting the fact that primary source of deposits were due to trace metals. The results from elemental analysis also had significant concentrations of chromium with low concentrations of iron, indicating that the source of chromium was not due to wear debris, rather, the source of chromium was the fuel. Overall, it was concluded that most of the internal injector deposits were caused due to trace metal contaminants, followed by varnish like deposits that coated on the injector surface formed from polymeric amide based deposits, followed by soft and sticky deposits likely from FAME in biodiesel.

Acknowledgements

The U.S. Army TARDEC Fuel and Lubricants Research Facility (TFLRF), which is a part of Fuels and Lubricants Technology Department located at the Southwest Research Institute (SwRI) in San Antonio, TX.

The SwRI investigators are Nigil Jeyashekar, Doug Yost and Steve Westbrook. The project manager at SwRI was Steve Fritz, Manager of the Medium-Speed Diesel Engine Section in the Design and Development Department, a part of the SwRI Engine and Vehicle Research Division. Mr. Dennis McAndrew, an independent consultant to SwRI, served as a project technical monitor. The authors would like to acknowledge the contribution of the TFLRF technical support staff along with the administrative support staff.

1 Objective and Scope

This work reported herein was conducted under a grant from the U.S. Department of Transportation, Federal Railroad Administration (FRA). The objective of this research work was to characterize internal deposits formed in fuel injectors used in locomotive engines. With the increasing presence of biodiesel in U.S. commercial diesel fuel there was concern that some injector deposit problems might be caused by biodiesel or biodiesel components.

This study was limited to analysis of high-pressure common-rail (HPCR) fuel injectors from Cummins QSK19 non-road diesel engines used in generator set switcher locomotives.

2 Background

The formation of internal diesel injector deposits (IDID), most notably in high-pressure common rail (HPCR) systems continues to be a significant concern for diesel engine manufacturers and diesel vehicle users. Over the past 10–15 years, numerous researchers have investigated this problem and identified several possible causes/mechanisms for the formation of IDID. Among those possible causes, the four that tend to be reported most often are trace contaminants in the fuel, additives in the fuel, biodiesel, also known as fatty acid methyl esters (FAME) and biodiesel components, and the diesel fuel itself.

Trace contaminants in the fuel can react with themselves and other compounds in the fuel to form a number of different deposit types. The type most often reported is metal-carboxylate salt formed by the reaction of carboxylic acid compounds with metals such as sodium and calcium. Certain types of fuel additives have been shown to degrade in the injector to leave polymeric/lacquer type deposits. Biodiesel and biodiesel components such as glycerin can oxidize to form deposits. Hydrocarbon diesel fuel may undergo thermal and oxidative degradation to form polymeric materials and particles. The relative abundance and problematic significance of these deposit causes tends to vary depending on geographic location, additives in the fuel, and composition of the fuel itself. However, deposits identified as resulting from carboxylate salts and fuel additives are generally of greatest abundance and concern [1][2].

The analysis of diesel injector deposits usually involves several different instrumental and non-instrumental methods. The amount, accuracy, and specificity of the information obtained from these methods depend on the method, the sample size, and, in some cases, interpretation of the results. It is the nature of injectors received for analysis that the physical amount of deposit on any given injector can vary greatly. All these factors combine to make the analysis of some injector deposits difficult, and perhaps inconclusive. As an example, identification of compounds by infrared spectroscopy requires sufficient sample for analysis (yielding clear spectra with minimal noise) and the interpretation/assignment of spectral peaks to specific chemical functionalities. Such interpretations/assignments are often subjective and are hampered by the presence of noise due to small sample size.

The technical literature related to the study of IDID provides assistance and guidance in the interpretation of FTIR results. Metal-carboxylate salts typically have FTIR peaks at 1565, 1438, and 1415 cm^{-1} [2]. Hard, polymeric/lacquer-type deposits are generally found to be polymeric amides (sometimes in conjunction with polyisobutylenes) or amide-related; but, theories as to their origin differ [2][3][4][5][6][7]. FTIR absorbance peaks associated with these types of deposits in 1658, 1470, 1390, 1366, and 1231 cm^{-1}. Deposits associated with biodiesel/FAME are indicated by the presence of a carbonyl peak between 1730 and 1740 cm^{-1}. As stated above, the presence of these FTIR absorbance bands can provide indications of the type and source of deposits but should not be considered proof positive. Additional test results and information should also be considered, when available, when analyzing deposits.

Further complicating the analysis is the tendency of some types of diesel fuel additives to adhere to metallic and non-metallic surfaces throughout the fuel system, whether or not they are part of any deposit. Such compounds can interfere with the detailed analysis of deposits and lead to possibly incorrect conclusions.

It is our judgment that the study of diesel injector deposits continues to be hampered by the lack of a reliable test method with which to conduct a robust parametric study. Until such method is available, the analysis of diesel deposits remains somewhat circumstantial in nature. That is to say, wide-spread, industry acceptance of cause and effect relationships is lacking.

The results presented in this report are based on our best judgment, experience, and interpretation of data. However, for the reasons cited above, we encourage the reader to seek additional information from published literature when evaluating these results. A list of applicable references can be supplied upon request.

3 Analyses and Results

Twelve locomotive fuel injectors, from two different locomotives, were received and disassembled. Individual components were inspected for the presence of internal injector deposits and photographed. Residual fuel from the injectors was analyzed for biodiesel content. The internal deposits that were present in certain injectors were collected for Fourier Transform Infrared (FTIR) spectroscopic analysis. The features of deposits on the tip and other injector characteristics were also recorded. Backscatter imaging and elemental analysis using Energy Dispersive Spectroscopy (EDS) was performed on injector needle deposits. Thus, the goal of this research was to determine the chemical composition of internal injector deposits using FTIR. The effort was to determine if the formation of internal injector deposits were primarily due to the presence of biodiesel in diesel fuel.

The injectors came from two locomotives, CSXT 1309, and UPY2755. Both of these locomotives are 1,500 kW NRE 3GS21B locomotives, equipped with three Cummins QSK19-powered gensets rated at 500 kW each. The CSXT1309 injectors were provided by CSX. The QSK19 "generation 1" fuel injectors were removed from GEN1 of UPY2755 at SwRI. Three of the six injectors did not appear to be firing during a cylinder cutout test (Cyl. 1, 5, & 6), and were selected for analysis in this FRA project.

Diesel fuel was collected from twelve injectors and analyzed for the presence of biodiesel using a *Wilks Infracal–2* analyzer. The results are shown in Table B1. Eight of the twelve injectors had been running on a biodiesel blend at the time the injectors were removed from the locomotive and disassembled. The remaining four injectors had no biodiesel present in the fuel collected during disassembly.

Table B1. Biodiesel Content in Residual Fuel

No.	Engine Group and Biodiesel Content (%)	Injector ID	Notations
1	From 1st engine (Locomotive No. 1309 w/o 3326) 4.3% Biodiesel	CL13-5449	Gen. 3, Cyl. No. 1
2		CL13-5450	Gen. 3, Cyl. No. 4
3		CL13-5451	Gen. 3, Cyl. No. 5
4		CL13-5452	Gen. 3, Cyl. No. 3
5		CL13-5453	Gen. 2, Cyl. No. 2
6		CL13-5454	Gen. 2, Cyl. No. 1
7		CL13-5455	Gen. 2, Cyl. No. 4
8		CL13-5456	Gen. 2, Cyl. No. 3
9	From 2nd engine (UPY2755, GEN 1) 0% Biodiesel	CL13-5562	Cyl. No. 1
10		CL13-5563	Cyl. No. 2
11		CL13-5564	Cyl. No. 5
12		CL13-5565	Cyl. No. 4

3.1 Injector Disassembly

The injectors were disassembled and the deposits were collected from the solenoid area for FTIR analysis. Figure B1 shows the disassembled injectors disassembly; the observations for each disassembled injector are recorded in Table B2.

Table B2. Observations from Injector Disassembly

No.	Injector ID	Observations
1	CL13-5449*	Normal carbon deposits on injector tip. Black deposits on wetted surfaces/tip. Diesel Metering Valve (DMV) needle stuck. Black deposits and heat discoloration observed. Sample sent for back-scatter imaging and elemental analysis of deposits. FTIR was not conducted on deposit sample from this injector.
2	CL13-5450	Black deposits on wetted parts (orifice plate, tip, etc.…) DMV needle stuck. Flushed the solenoid block around electrical connection with isooctane for FTIR.
3	CL13-5451*	Injector looked fairly new – no deposits and hence, no FTIR. DMV needle fell out on this own free weight. Injector had black carbon deposits on the outer tip. Based on this observation, it was concluded that the injector must have run for a short duration.
4	CL13-5452*	On the tip, normal carbon deposits was observed on the exterior. Needle stuck in the nozzle body. Tip Needle fell out by tapping tip body. DMV needle stuck. No deposits were collected from this injector and hence, no FTIR was conducted.
5	CL13-5453	Normal deposits on the outer surface of the tip with free needle. Rubber insulator on the electrical connection (solenoid) had black deposits and was torn. Sample was collected for FTIR. DMV stuck.
6	CL13-5454	Deposits on injector tip with free needle. DMV stuck. Black deposits were flushed from the solenoid area and saved for FTIR. Rubber insulator was highly degraded and was falling apart.
7	CL13-5455	Light carbon deposits on the injector tip with a free needle. Black substance was collected from solenoid area for FTIR and rubber insulator was torn. DMV was stuck.

8	CL13-5456	Deposits were observed outside the injector tip with free needle containing light deposits. Black substance was collected from the solenoid area for FTIR and the rubber insulator was cracked with the presence of debris. DMV was stuck.
9	CL13-5562[‡]	Nut came off tight and squeaky. Light deposits on tip needle. Heavy deposits on solenoid and rubber area were saved for FTIR. DMV was pushed out with ease by hand.
10	CL13-5563[‡]	Nut was tight all the way through, twisted solenoid terminals, black deposits around terminals and rubber insulator was collected for FTIR
11	CL13-5564[*‡]	No deposits around the rubber insulator and hence, no FTIR; DMV was stuck. Light deposits on nozzle tip.
12	CL13-5565[‡]	Deposits were observed on nozzle tip. Heavy deposits were observed around the solenoid and rubber. DMV needle was stuck.

[*] *No FTIR was conducted for these injectors;* [‡]*No Biodiesel was present in the residual fuel for these injectors*

Figure B1. Injector Disassembly

3.2 FTIR Spectra of Injector Deposits

Figure B2 shows the FTIR spectra of deposits collected from the injectors (DMV) that contained biodiesel when they were disassembled.

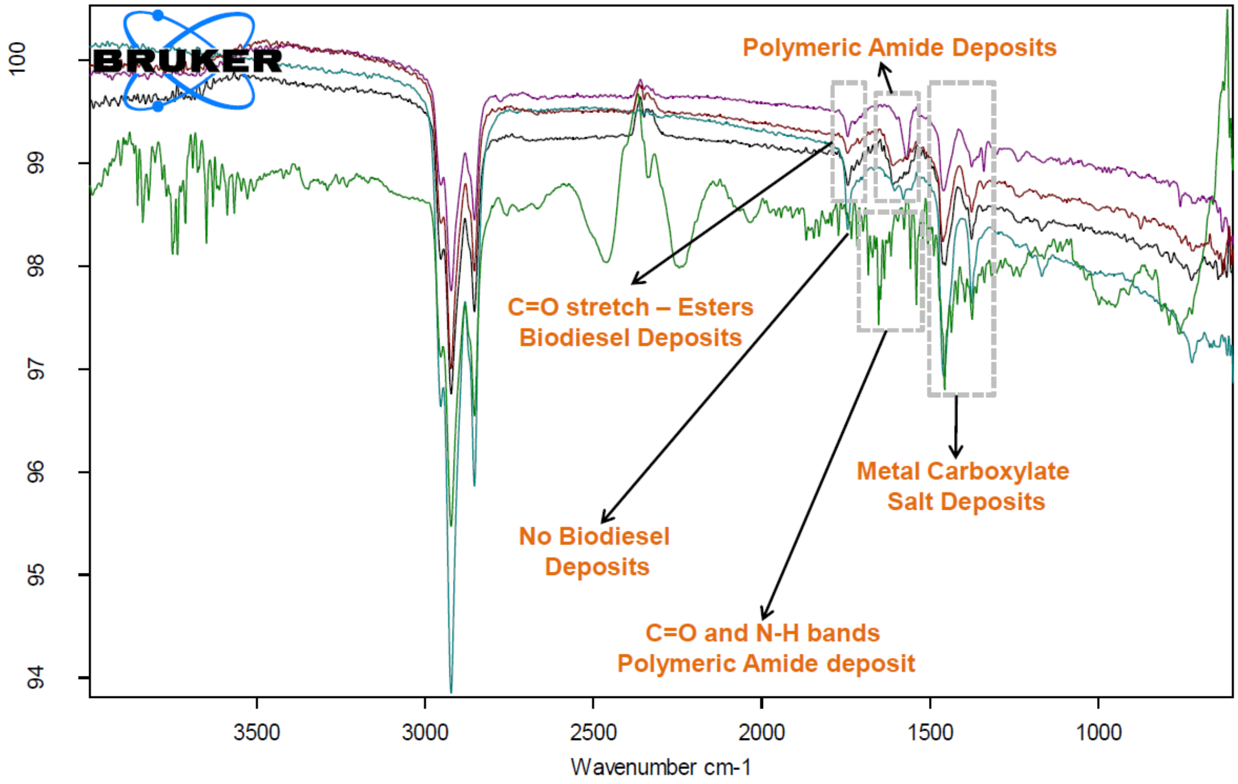


Figure B2. FTIR Spectra of Deposits in Fuel Injectors with Residual Biodiesel

The multiple bands around 1400 cm^{-1} indicate the presence of metal carboxylate salt deposits. As indicated by peak depth, these deposits appear to be the highest in concentration. The presence of polymeric amide deposits was the next highest concentration of deposits. Several of the spectra showed a carbonyl peak around 1740 cm^{-1}, indicative of biodiesel. One FTIR spectra had little or no deposits from biodiesel (absence of C=O band). The polymeric amide deposits were the hard varnish type deposits that formed on the surface of the injector. The soft deposits were possibly formed from biodiesel in the fuel during exposure to prolonged periods of high temperature. It can be concluded that the use of biodiesel did contribute to internal fuel injector deposits, only to an apparently-lesser extent, in comparison to trace metal contaminants and polymeric amide based deposits.

Figure B3 shows FTIR spectra of deposits collected from injectors from UPY2755. These deposits primarily contained metal carboxylate salts and polymeric amide based deposits.

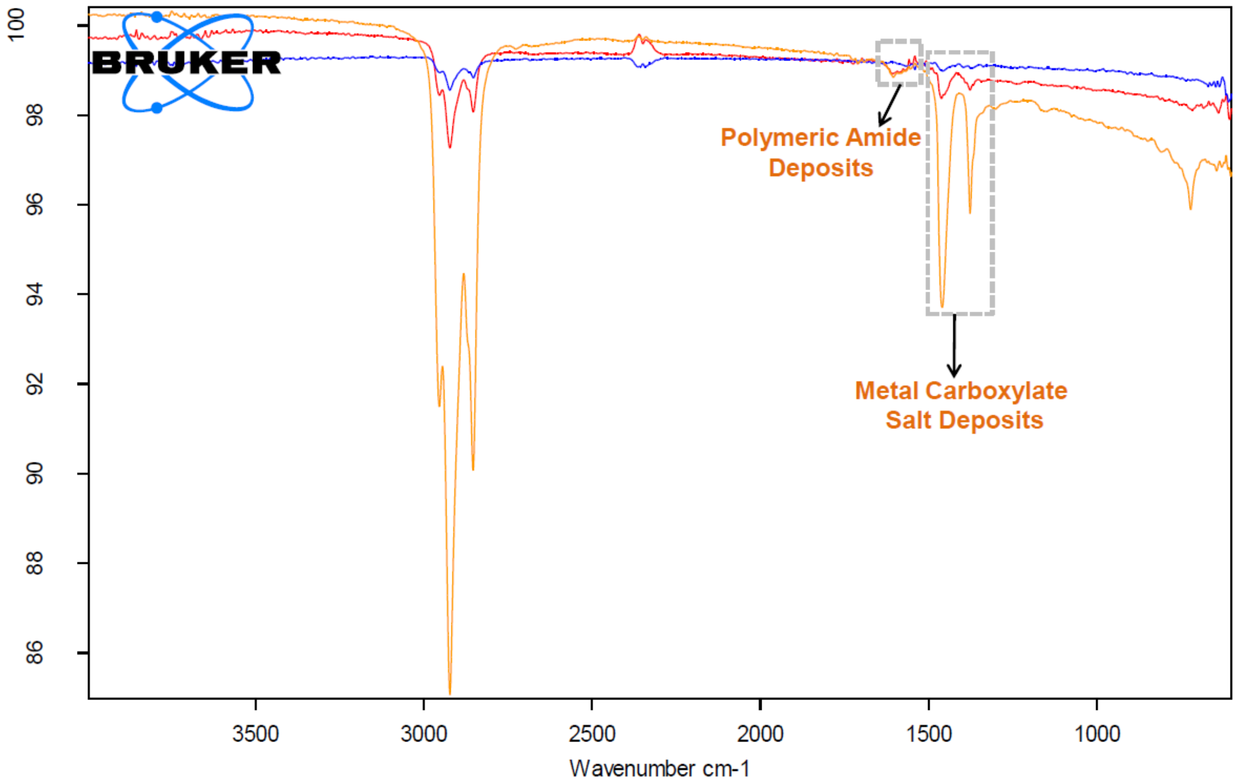


Figure B3. FTIR Spectra of Deposits in Fuel Injectors from UPY2775

3.3 Elemental Analysis of Injector Needle Deposits

Figure B4 shows image of the injector needle, CL13-5449 (CSXT 1309, GEN3, Cyl.No.1), with deposits in the center groove and to the left end of the groove (also called off groove, as shown in Figure B4). Figure B5 shows the backscatter image of the deposits at these locations.

Figure B4. Injector Needle – CL13-5449

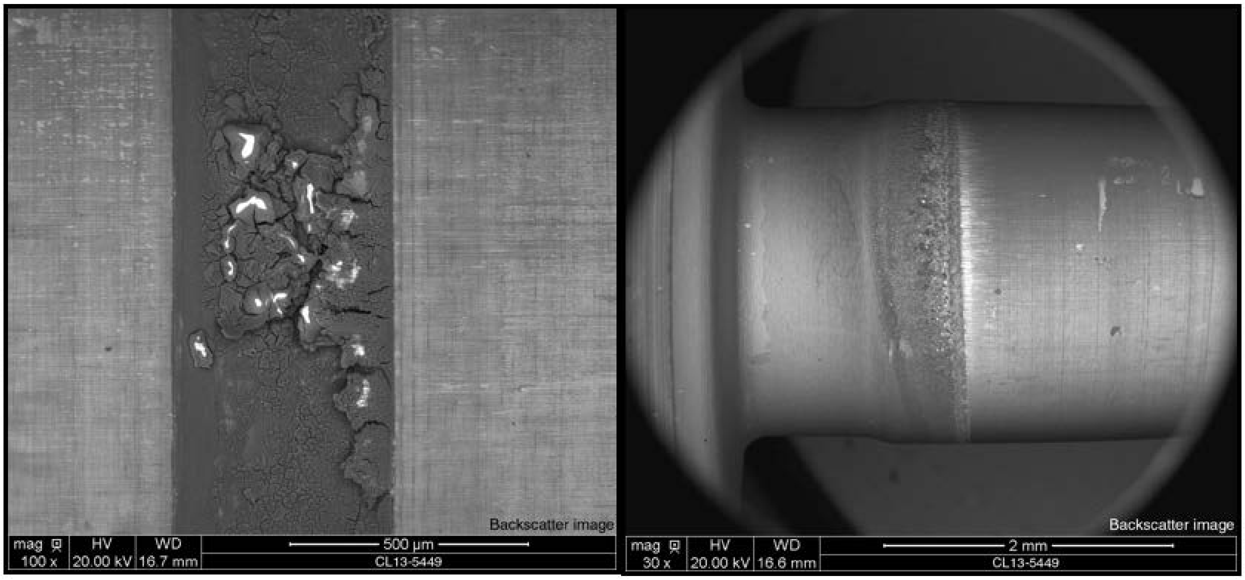
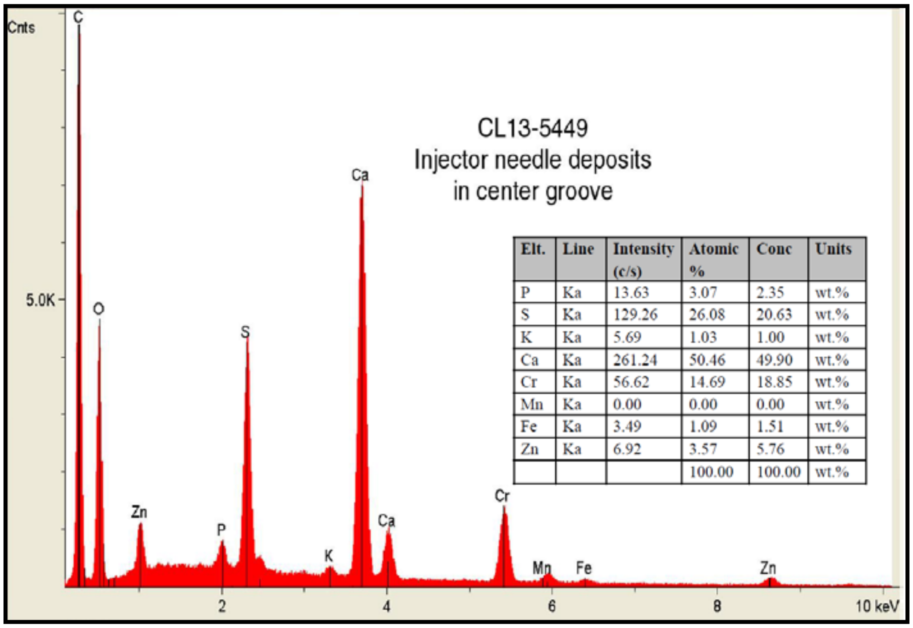


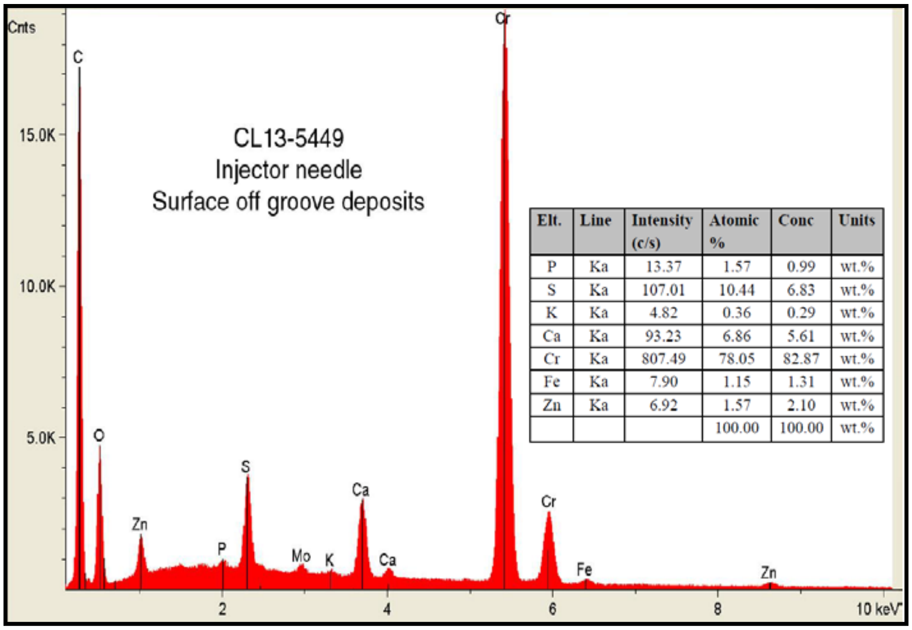
Figure B5. Backscatter Image of Deposits in Center (Left) and Off Groove (Right)

The elemental analysis of these deposits were conducted using Energy Dispersive Spectroscopy (EDS) and are shown in Figure B6, for center groove deposits, and Figure B7, for off groove deposits. While the deposits in the center groove contains a high percentage of carbon, there is a significant quantity of calcium, indicating that carboxylate salts of calcium could constitute a significant portion of the deposit present in the center groove. The surface off groove deposits have significantly high amounts of chromium. Since the intensity of iron is very low on both center groove and off groove EDS spectra, it can be concluded that chromium peaks did not occur due to the presence of wear debris.



Elt.	Line	Intensity (c/s)	Atomic %	Conc	Units
P	Ka	13.63	3.07	2.35	wt.%
S	Ka	129.26	26.08	20.63	wt.%
K	Ka	5.69	1.03	1.00	wt.%
Ca	Ka	261.24	50.46	49.90	wt.%
Cr	Ka	56.62	14.69	18.85	wt.%
Mn	Ka	0.00	0.00	0.00	wt.%
Fe	Ka	3.49	1.09	1.51	wt.%
Zn	Ka	6.92	3.57	5.76	wt.%
			100.00	100.00	wt.%

Figure B6. Elemental Analysis of Deposits in Center Groove Deposits



Elt.	Line	Intensity (c/s)	Atomic %	Conc	Units
P	Ka	13.37	1.57	0.99	wt.%
S	Ka	107.01	10.44	6.83	wt.%
K	Ka	4.82	0.36	0.29	wt.%
Ca	Ka	93.23	6.86	5.61	wt.%
Cr	Ka	807.49	78.05	82.87	wt.%
Fe	Ka	7.90	1.15	1.31	wt.%
Zn	Ka	6.92	1.57	2.10	wt.%
			100.00	100.00	wt.%

Figure B7. Elemental Analysis of Deposits in Off Groove Deposits

Based on the elemental analysis of deposits in the injector needle, it can be concluded that there were significant concentrations of calcium and chromium metals. The deposits in the center groove consisted of metal carboxylate salts from calcium in addition to sodium, while the off groove deposits contained carbon and significant amounts of chromium.

4 Conclusions

The deposits from locomotive fuel injectors were analyzed using several techniques. The highest concentration of internal injector deposits appears to be metal carboxylate salts. The second highest concentration was hard polymeric amide deposits. The injectors that contained biodiesel in the residual fuel, contained deposits that resulted from high temperature oxidation of biodiesel. However, deposits due to biodiesel are relatively lower in concentration compared to deposits that resulted from trace metal contaminants and polymeric amides. Elemental analysis was conducted on one injector needle that contained deposits in the center groove and off groove. The center groove deposits contained high amounts of calcium indicating calcium carboxylate salts, in addition to sodium carboxylate salts, while the off groove surface deposits contained high concentrations of chromium.

5 References

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Appendix C.
Topical Report No. 3 – Analytical Characterization of Locomotive Injector Tip Deposits

Analytical Characterization of Locomotive Injector Tip Deposits

Topical Report No. 03

by

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May 2015, Revised

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Gary Bessee

Gary B. Bessee, Director
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Executive Summary

This work reported herein was conducted under a grant from the U.S. Department of Transportation, Federal Railroad Administration (FRA). The objective of this research work was to characterize internal deposits formed in fuel injectors used in locomotive engines. With the increasing presence of biodiesel in U.S. commercial diesel fuel, there was concern that some injector deposit problems might be caused by biodiesel or biodiesel components. This study was limited to high-pressure common-rail (HPCR) fuel injectors from a 4,500 HP, Tier 3, GE AC45CCTE locomotive.

The injector tip deposits from three locomotive fuel injectors were collected for chemical characterization. The residual fuel was collected and the biodiesel content was measured to be 2.2 percent. Analytical characterization of injector tip deposits by EDS and XRD indicated that the deposits were primarily carbon. EDS characterization indicated some silicon and sulfur content. While sulfur content could be related to fuel, the source of silicon cannot be conclusively related to diesel fuel. FTIR characterization indicated that the injector tip deposits could be the result of high temperature thermal oxidation of biodiesel present in the diesel fuel, and that the deposits also contained polymeric amide-based deposits. It can be stated that the deposit characterization from the injector tips was similar in nature to internal injector deposits found on these injectors. The only exception was that the internal injector deposits also indicated that deposits could have formed from metal carboxylate salts.

Acknowledgements

The U.S. Army TARDEC Fuels and Lubricants Research Facility (TFLRF), which is a part of the Fuels and Lubricants Technology Department located at the Southwest Research Institute (SwRI) in San Antonio, TX, performed this work.

The SwRI investigators are Dr. Nigil Jeyashekar, Mr. Kevin Shannon and Mr. Steven R. Westbrook. The project manager at SwRI is Mr. Steve Fritz, Manager of the Medium-Speed Diesel Engine Section in the Design and Development Department, a part of the SwRI Engine and Vehicle Research Division. Mr. Dennis McAndrew, an independent consultant to SwRI, served as a project technical monitor. The authors would like to acknowledge the contribution of the TFLRF technical support staff along with the administrative support staff.

1 Objective and Scope

This work reported herein was conducted under a grant from the U.S. Department of Transportation, Federal Railroad Administration (FRA). The objective of this research work was to characterize internal deposits formed in fuel injectors used in locomotive engines. With the increasing presence of biodiesel in U.S. commercial diesel fuel, there was concern that some injector deposit problems might be caused by biodiesel or biodiesel components. This study was limited to high-pressure common-rail (HPCR) fuel injectors from a 4,500 HP, Tier 3, GE AC45CCTE locomotive.

2 Background

The formation of internal diesel injector deposits (IDID), most notably in high-pressure common rail (HPCR) systems continues to be a significant concern for diesel engine manufacturers and diesel vehicle users. Over the past 10–15 years, numerous researchers have investigated this problem and identified several possible causes/mechanisms for the formation of IDID. Among those possible causes, the four that tend to be reported most often are trace contaminants in the fuel, additives in the fuel, biodiesel, also known as fatty acid methyl esters (FAME) and biodiesel components, and the diesel fuel itself. Trace contaminants in the fuel can react with themselves and other compounds in the fuel to form a number of different deposit types. The type most often reported is metal-carboxylate salt formed by the reaction of carboxylic acid compounds with metals such as sodium and calcium. Certain types of fuel additives have been shown to degrade in the injector to leave polymeric/lacquer type deposits. Biodiesel and biodiesel components such as glycerin can oxidize to form deposits. Hydrocarbon diesel fuel may undergo thermal and oxidative degradation to form polymeric materials and particles. The relative abundance and problematic significance of these causes tend to vary depending on geographic location, additives in the fuel, and composition of the fuel itself. However, deposits identified as resulting from carboxylate salts and fuel additives are generally of greatest abundance and concern [1][2].

The analysis of diesel injector deposits usually involves several different instrumental and non-instrumental methods. The amount, accuracy, and specificity of the information obtained from these methods depend on the method, the sample size, and, in some cases, interpretation of the results. It is the nature of injectors received for analysis that the physical amount of deposit on any given injector can vary greatly. All these factors combine to make the analysis of some injector deposits difficult, and perhaps inconclusive. As an example, identification of compounds by infrared spectroscopy requires sufficient sample for analysis (yielding clear spectra with minimal noise) and the interpretation/assignment of spectral peaks to specific chemical functionalities. Such interpretations/assignments are often subjective and are hampered by the presence of noise due to small sample size.

The technical literature related to the study of IDID provides assistance and guidance in the interpretation of FTIR results. Metal-carboxylate salts typically have FTIR peaks at 1,565, 1,438, and 1,415 cm^{-1} [2]. Hard, polymeric/lacquer-type deposits are generally found to be polymeric amides (sometimes in conjunction with polyisobutylenes) or amide-related. Theories as to their origin differ [2][3][4][5][6]. FTIR absorbance peaks associated with these types of deposits are at 1658, 1470, 1390, 1366, and 1231 cm^{-1}. Deposits associated with biodiesel/FAME are indicated by the presence of a carbonyl peak between 1730 and 1740 cm^{-1}. As stated above, the presence of these FTIR absorbance bands can provide indications of the type and source of deposits but should not be considered proof positive. Additional test results and information should also be considered, when available, when analyzing deposits.

Further complicating the analysis is the tendency of some types of diesel fuel additives to adhere to metallic and non-metallic surfaces throughout the fuel system, whether or not they are part of any deposit. Such compounds can interfere with the detailed analysis of deposits and lead to possibly incorrect conclusions.

It is our judgment that the study of diesel injector deposits continues to be hampered by the lack of a reliable test method with which to conduct a robust parametric study. Until such method is available, the analysis of diesel deposits remains somewhat circumstantial in nature. That is to say, wide-spread, industry acceptance of cause and effect relationships is lacking.

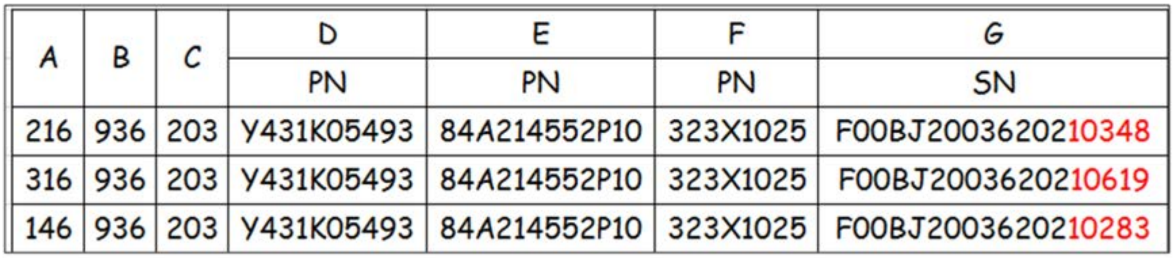
The results presented in this report are based on our best judgment, experience, and interpretation of data. However, for the reasons cited above, we encourage the reader to seek additional information from published literature when evaluating these results. A list of applicable references can be supplied upon request.

3 Analyses and Results

High-pressure common-rail (HPCR) fuel injectors from a 4,500 HP, Tier 3, GE AC45CCTE locomotive were analyzed in this study. A full set of twelve HPCR injectors were supplied by Union Pacific Railroad (UP) from locomotive UP7939. This locomotive was originally manufactured in May 2012, and the HPCR injectors were removed from the locomotive during normally scheduled injector change-out of 18-months, which was December 2013. During those 18-months of operation, UP7939 logged 182,494 miles, producing 5,928.57 MW-hrs of work. This represents approximately 15 percent of the emissions useful life of the engine before the first overhaul. Three of the set of 12 HPCR injectors were randomly selected for analysis, shown in Figure C1, and were disassembled to collect injector tip deposits for analytical characterization

Deposits were characterized using elemental analysis (EDS), x-ray diffraction (XRD), and Fourier Transform Infrared (FTIR) spectroscopy techniques. The fuel collected from the disassembled injector was analyzed for percentage biodiesel content. The subsequent sections present the results from biodiesel analysis of fuel and results from analytical characterization of tip deposits.

Figure C1. HPCR Locomotive Injectors



A	B	C	D	E	F	G
			PN	PN	PN	SN
216	936	203	Y431K05493	84A214552P10	323X1025	F00BJ200362021O348
316	936	203	Y431K05493	84A214552P10	323X1025	F00BJ2003620210619
146	936	203	Y431K05493	84A214552P10	323X1025	F00BJ2003620210283

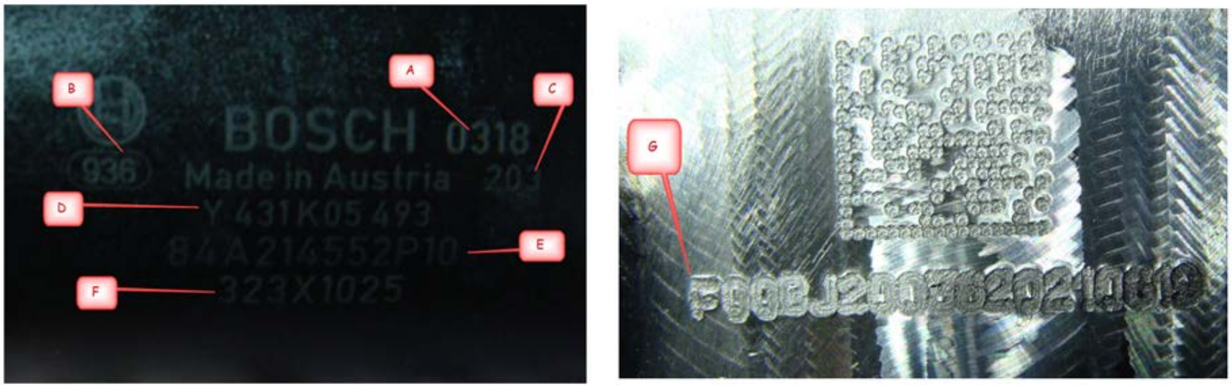


Figure C2. Details of the HPCR Locomotive Injectors Selected for Analysis

3.1 Injector Disassembly

The disassembled locomotive injector tip is shown in Figure C3. The tip deposits were physically removed and collected for analysis. Figure C4 shows the backscatter image of the injector tip before and after removing deposits. Figure C5 shows a closer view of the injector and fuel nozzle openings before and after deposit removal from the injector tip. The fuel collected from all three injectors contained about 2.2 percent biodiesel content.

Figure C3. Injector Disassembly Showing Injector Tip

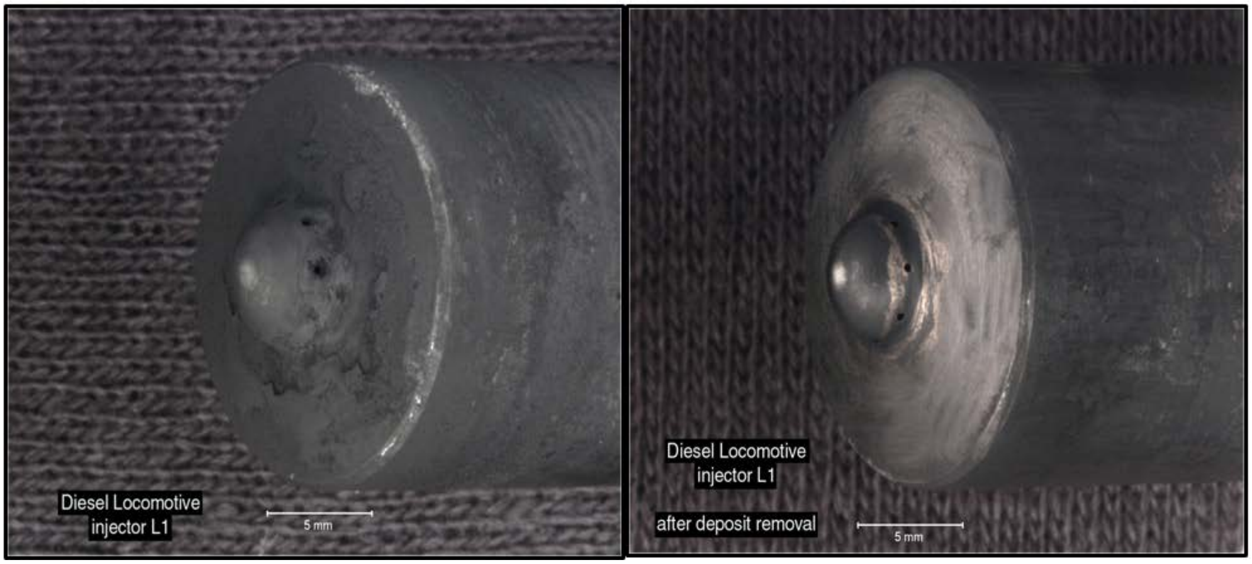


Figure C4. Backscatter Image of Injector Tip, Before and After Deposit Removal

Figure C5. Backscatter Image Showing Fuel Inlet Before and After Deposit Removal

3.2 Analytical Characterization of Injector Tip Deposits

EDS and XRD characterization were performed on the injector tip deposits and the results are shown in Figure C6. The results from EDS characterization indicated that the injector tip deposits primarily consisted of carbon with low concentrations of silicon and sulfur, and trace quantities of calcium. The XRD results indicated that the deposits consisted primarily of carbon. The trace quantity or absence of other elements, especially those associated with engine lubricant additives (such as calcium and zinc), indicates that combusted lubricant was not a significant contributor to the deposits.

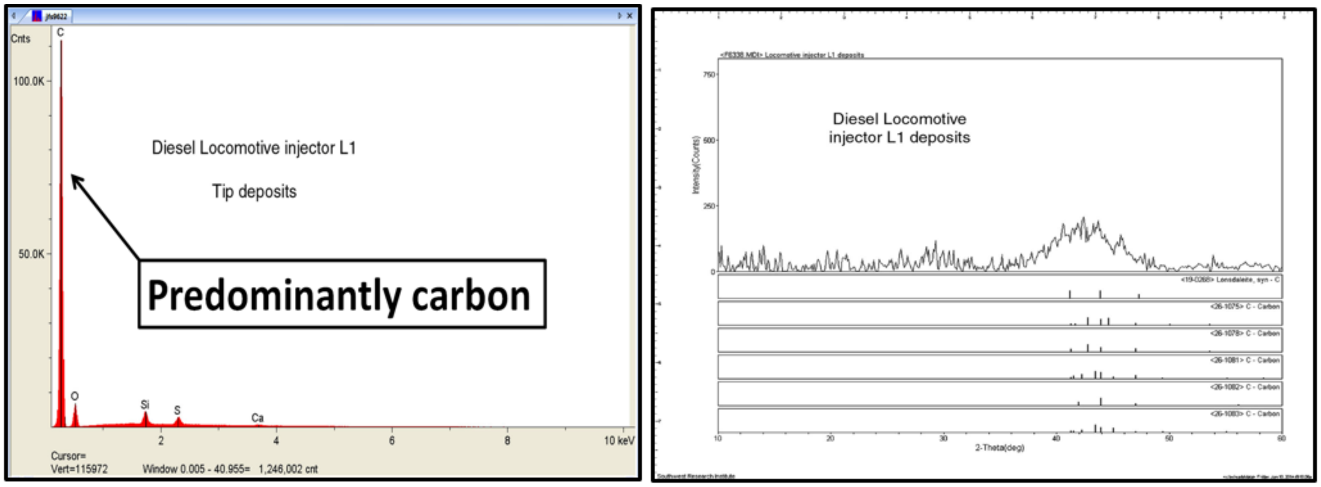


Figure C6. EDS (Left) and XRD (Right) Characterization of Injector Tip Deposits

The FTIR spectrum of injector tip deposits is shown in Figure C7. Because the deposits were primarily carbonaceous-type deposits, the FTIR spectrum has significant signal noise interference. Since carbon is known to be surface-active, any compounds that might be identified may simply be adsorbed onto the carbon deposits and not actually related to the formation of the deposit. As such, the identifiable peaks in the spectrum are not assumed to indicate the source of the deposits. The few peaks that are identifiable can be associated with hydroxyl (O–H), amine (N–H), aromatic amines (C–N), and ester (C–O) compound functional groups. However, at this time, it would be difficult to assign these to specific compounds or to identify specific compounds as the source of the carbon deposits. As stated earlier, a reliable deposit test that allows controlled, parametric studies is needed in order to fully understand these types of deposits.

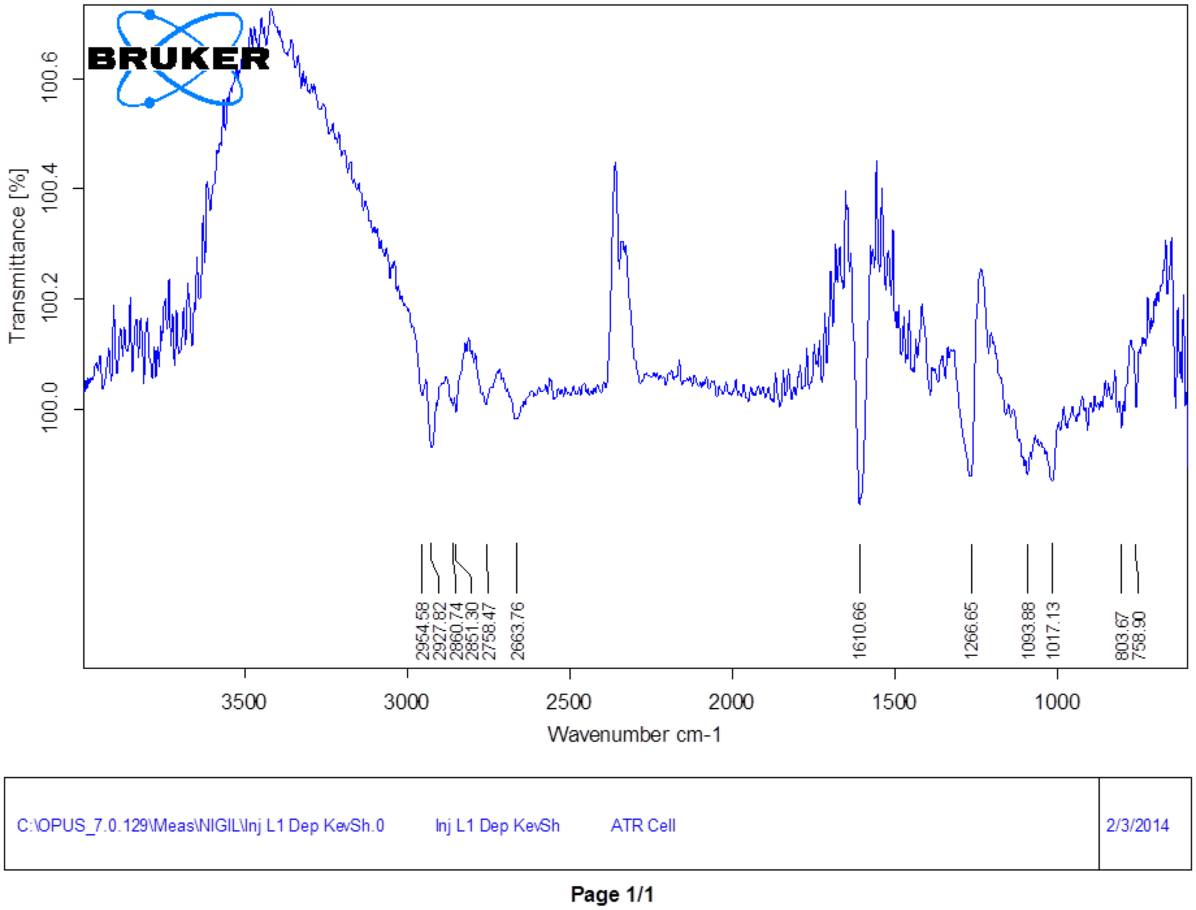


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Figure C7. FTIR Spectra of Injector Tip Deposits

4 Conclusions

The injector tip deposits from three HPCR Tier 3 GE locomotive fuel injectors were collected for chemical characterization. The residual fuel was collected and the biodiesel content was measured to be 2.2 percent. Analytical characterization of injector tip deposits by EDS and XRD indicated that the deposits were primarily carbon. EDS characterization indicated some silicon and sulfur content. While sulfur content could be related to fuel, the source of silicon cannot be conclusively related to diesel fuel. Owing to the carbonaceous nature of the deposits, FTIR characterization was inconclusive. Compounds detected by the FTIR analysis may be simply fuel and additive compounds that adsorbed to the surface of the deposit but played no role in the formation of the deposit.

5 References

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Appendix D.
Topical Report No. 4 – Literature Review: Biodiesel as a Locomotive Fuel

Biodiesel as Locomotive Fuel Literature Review

FINAL REPORT

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February 21, 2014

Acknowledgements

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1 Driving Forces

1.1 Overview

Historically, air pollution used to be one of the main driving forces for engine emission development, and the use of alternative fuels. With ultra-low emission requirements adopted for nearly all categories of diesel and gasoline engines, future environmental priorities have been shifting from exhaust emissions to greenhouse gas (GHG) emissions and energy supply and security.

Three main factors were responsible for the shift in focus in the energy and environmental policy that became apparent in the 2000s:

- *Depletion of oil resources*—As the production capacity of conventional oil resources has been declining, the world has been approaching a point when it reaches the maximum crude oil output (referred to as the *peak oil*), after which the global oil production will begin to decline. There are indications that peak oil could take place (possibly, already has) at some point in the current decade. Use of unconventional oil resources (such as the US shale oil discussed below), alternative fuels and increased energy efficiency could extend the resources, but inevitably a depletion of fossil fuel based energy sources must be faced sooner or later.
- *Energy security*—This factor was particularly important in the United States, where an increasing proportion of crude oil had been imported from the Middle East and other politically unstable regions of the world.
- *Global warming*—Growing emissions of greenhouse gases (GHG) from anthropogenic sources, with fossil fuel-derived CO_2 emissions playing a major role, have been blamed for the increase in the Earth's surface temperature, which has been observed since the industrial revolution in the 19th century. The regulation of GHG emissions in the United States was initiated by a 2007 ruling of the US Supreme Court (US Supreme Court, 2007) which decided that CO_2 is a pollutant under the Clean Air Act and, therefore, CO_2 emissions must be controlled by the US Environmental Protection Agency (EPA).

In the 1990s and in early 2000s, it was generally believed that increased use of biomass-derived fuels—under the US conditions, mostly corn-based ethanol and soy-based biodiesel—could increase domestic production of transportation fuels while also reducing GHG emissions. As a result, renewable fuel mandates were adopted in the mid-2000s in the United States, as well as in the European Union and in other jurisdictions. In the US, the most important biofuel mandate driving the use of biodiesel is the Federal Renewable Fuel Standard (RFS) program.

Since the creation of the RFS program in 2005, the global biofuels outlook has changed. The production of fossil fuels in the United States has grown sharply due to the commercial utilization of unconventional fossil resources, including shale gas and the associated oil, known as light tight oil. Furthermore, scientific evidence that has been accumulated over the last decade indicates that GHG emission reductions from biomass-based fuels have been grossly overestimated, and that most biofuels have very low energy return on investment (EROI) and are not a viable replacement for fossil fuels. These factors could result in at least some relaxation of the renewable fuel mandates in the future.

1.2 EPA Renewable Fuel Standard

Under the U.S. Energy Policy Act of 2005 (EPAct), the EPA adopted the Renewable Fuel Standard which required blending certain volumes of ethanol into gasoline. Under the Energy Independence and Security Act (EISA) of 2007, the RFS program was expanded in several ways, including the addition of renewable diesel fuel requirements. The expanded legislation, finalized by the EPA in 2010, is referred to as the RFS-2 standard.

Under the RFS-2 legislation, some renewable fuels must achieve lifecycle GHG emission reductions—compared to the gasoline and diesel fuels they displace—in order to be counted towards compliance with volume standards. The RFS-2 volume requirements are set for four categories of fuels:

- Cellulosic biofuel—To be classified in this category, fuels must provide a 60 % lifecycle GHG emission reduction.
- Biomass-based diesel—A 50% GHG emission reduction.
- Advanced biofuel—A 50% GHG emission reduction.
- Total renewable fuel—The remaining renewable fuel volumes must provide a 20% GHG emission reduction if produced at new facilities (those that commenced construction after December 19, 2007).

These categories are not exclusive—biodiesel, for example, qualifies as both advanced biofuel and as biomass-based diesel, while the total renewable fuel—in accordance with the designation—represents the total pool of renewable fuels including all of the other categories, as well as other renewable fuels providing GHG reductions from 20 to 50% (corn-ethanol).

The GHG emissions are determined by the EPA as the aggregate quantity of greenhouse gas emissions—including direct emissions and significant indirect emissions such as emissions from land use changes. The emission reductions are relative to the 2005 petroleum fuel baseline.

In the final rulemaking, the EPA relaxed their GHG estimates for a number of conventional biofuels which are now meeting the RFS-2 requirements, but were to be disqualified under the RFS-2 proposal. In particular, the EPA determined that ester-based biodiesel and renewable diesel from soy oil or waste oils, fats, and greases meet the 50% GHG threshold for biomass-based diesel. Biodiesel and renewable diesel produced from algal oils will also comply with the 50% threshold should they reach commercial production.

The RFS-2 requires annual biofuels production to grow from the 2009 level of 11.1 billion gallons to 36 billion gallons in 2022, with 21 billion gallons to come from “advanced biofuels”. The exact requirements are listed in the following table.

Table D1. RFS-2 Renewable Fuel Volume Requirements, Billion Gallons

Year	Cellulosic Biofuel	Biomass-Based Diesel	Advanced Biofuel	Total Renewable Fuel
2008	n/a	n/a	n/a	9.0
2009	n/a	0.5	0.6	11.1
2010	0.1	0.65	0.95	12.95
2011	0.25	0.80	1.35	13.95
2012	0.5	1.0	2.0	15.2
2013	1.0	a	2.75	16.55
2014	1.75	a	3.75	18.15
2015	3.0	a	5.5	20.5
2016	4.25	a	7.25	22.25
2017	5.5	a	9.0	24.0
2018	7.0	a	11.0	26.0
2019	8.5	a	13.0	28.0
2020	10.5	a	15.0	30.0
2021	13.5	a	18.0	33.0
2022	16.0	a	21.0	36.0
2023+	b	b	b	b

a - To be determined by EPA through a future rulemaking, but no less than 1.0 billion gallons.
b - To be determined by EPA through a future rulemaking.

The minimum volumes of biomass-based diesel after 2012 must be 1 billion gallons or more, to be determined by the EPA. For 2013, EPA adopted a biomass-based diesel volume at 1.28 billion gallons. For 2014 and 2015, EPA proposed to maintain the biomass-based diesel volume at the 2013 level of 1.28 billion gallons (EPA, 2013). The National Biodiesel Board has criticized the EPA proposal and has called to increase the volume requirements to 1.7 billion gallons in 2014 (NBB, 2013).

Biodiesel can be used to fulfill the requirements for both *biomass-based diesel* and for *advanced biofuels*. Under EPA classification, US-made soy-based biodiesel reduces GHG emissions by more than 50%, which is the minimum reduction for both categories. Biodiesel represents nearly 100% of the biomass-based diesel volumes, as the North American production capacity of the main alternative—the refinery-made renewable diesel—remains insignificant.

Biodiesel also represents the majority of the advanced biofuel volumes. At the 2012 production level of almost 1.1 billion gallons, biodiesel filled 87% of the 2012 advanced biofuel requirement and can be expected to fill a majority of the 2013 quota.

The RFS-2 biodiesel enters the supply stream blended with No. 2 diesel for both onroad and nonroad use, typically as B5. In colder climates, biodiesel is blended into diesel only during Spring and Summer. Under ASTM D975-12a, biodiesel content up to B5 is allowed in No. 2 diesel without labeling. Therefore, it is believed that since around 2009, US railroads have been using B5 blends for their locomotives, whether knowingly or not.

Every year, the EPA develops percentage-based standards for the particular renewable fuel categories to be met during the following year by fuel suppliers. The percentage standards specify the minimum volume of renewable fuels—as a percentage of the total volume of gasoline and/or diesel—that must be blended into transportation fuels by each fuel refiner and importer. The 2013 requirements and the proposed 2014 requirements (EPA, 2013) are listed below.

Table D2. Proposed 2014 and Final 2013 RFS-2 Fuel Volumes and Percentage Standards

Category	**Proposed 2014 Standards**		*Final 2013 Standards*	
	Volume*	**Percentage**	*Volume**	*Percentage*
Cellulosic biofuels	17 million gallons	0.010%	*6 million gallons*	*0.004%*
Biomass-based diesel	1.28 billion gallons	1.16%	*1.28 billion gallons*	*1.13%*
Advanced biofuels	2.20 billion gallons	1.33%	*2.75 billion gallons*	*1.62%*
Total renewable fuels	15.21 billion gallons	9.20%	*16.55 billion gallons*	*9.74%*

*Volumes are ethanol-equivalent, except for biomass-based diesel which is actual.

It may be noted that for 2014, the EPA proposed to lower the total and advanced biofuel requirements relative to the 2013 requirements. It is the first deviation since the beginning of the RFS-2 program from the EISA-mandated targets (Table D1.

1.3 Canadian Renewable Fuel Requirements

In September 2010, Canada finalized the federal Renewable Fuels Regulations which require gasoline producers and importers to have an annual average renewable fuel content of at least 5% based on the volume of gasoline produced and imported. The 5% requirement came into force on December 15, 2010.

For diesel fuels, the Regulations require an average 2% renewable fuel content in diesel fuel and heating distillate oil, effective July 1, 2011. The technical feasibility of the 2% requirement was assessed based on the results of the National Renewable Diesel Demonstration Initiative, NRDDI (NRC, 2010). Fuel suppliers in Canada comply with this mandate by blending typically 5% biodiesel into diesel fuels during summer weather months. Only in certain limited geographical areas of a mild climate, such as Vancouver, B5 fuels intended for local use may be supplied over the entire year (Mitchel, 2013).

1.4 State Mandates

Obligatory blending of biodiesel into the diesel fuel has been mandated by several States. Typically, the mandate requires that all diesel fuel sold in a state contain a minimum of a two to five percent biodiesel (B2-B5) blend. Some States are adding language that would increase the B2-B5 blend to a higher blend level after a designated period.

The first State that adopted biodiesel blending requirements was Minnesota, where a B2 mandate applied since 2005. A new bill adopted in May 2008 envisioned increasing the mandatory blend level on the following schedule: 5% from May 1, 2009; 10% from May 1, 2012; and 20% from May 1, 2015. The above minimum biodiesel content levels would be required during the months from April through October. Two categories of diesel equipment are exempted from the biodiesel requirements: (1) engines located at an electric generating plant regulated by the Nuclear Regulatory Commission, and (2) railroad locomotives. The legislation introduced an approval process before moving to higher blends, which allows assessing the supply and demand situation before moving to a higher blend. On September 30, 2013, the Minnesota Legislature formally announced the move to the 10% biodiesel mandate in the state (MN, 2013)]. Since the final B10 regulation has not yet been published, the exact deadlines are still unknown and it remains unclear whether locomotive engines will continue to be exempted.

Some States tie their biodiesel requirements to the local feedstock or biodiesel fuel production. Pennsylvania, for example, passed bill HB1202 in July 2008, requiring that all on-road diesel transportation fuels sold in Pennsylvania include increasing amounts of biodiesel, based on levels of in-state production. HB1202 sets a scaling biodiesel requirement beginning at 2% (B2), one year after in-state production reaches an annualized volume of 40 million gallons and is sustained for three months. Subsequent blend requirements are: B5 at 100 million gallons in-state production; B10 at 200 million gallons; and B20 at 400 million gallons. The biodiesel requirement in Pennsylvania may be fully substituted by coal-to-liquid diesel. Renewable diesel, such as hydrotreated oils and fats, may be used in place of biodiesel only up to 25% of the biodiesel requirement.

A number of other States either adopted or are considering the adoption of some form of biodiesel requirement, including California, Florida, Louisiana, Kansas, Connecticut, Missouri, Oregon, Mississippi, Arkansas, Montana, New Mexico, as well as some Canadian provinces (e.g., Ontario). In some cases the legislation requires that a certain percentage of diesel sold in a state be biodiesel, rather than introducing blending requirements.

1.5 California Low Carbon Fuel Standard

California's Low Carbon Fuel Standard (LCFS) requires a 10% reduction in the carbon intensity of transportation fuels by 2020, as measured on a lifecycle basis. The LCFS program is a potential future source of biodiesel demand in California, including blends up to B20.

Forecasted diesel consumption in California indicates that diesel will generate about 20% of deficits in the LCFS program (ICF, 2013). However, fuels that substitute diesel, including biodiesel, renewable diesel, and natural gas, have the potential to generate 40–55% of LCFS credits. Although biodiesel consumption in California has been modest, the LCFS may create a significant potential to blend biodiesel at levels of 5 to 20% (ICF, 2013).

Since biodiesel tends to increase diesel NOx emissions, the fuel enjoyed little support from the California Air Resources Board (ARB). To facilitate market introduction of biodiesel and other diesel alternatives, the ARB has initiated the development of the "Alternative Diesel Fuels" regulation, intended to control the emissions of criteria pollutants that may result from the new alternative diesel fuels.

1.6 Prices and Commercial Factors

Figure D1 outlines the average US retail prices for No. 2 diesel fuel and B100 for the dates indicated (DOE, 2013). The dashed line represents the price of B100 adjusted for energy content, expressed in dollars per diesel gallon equivalent (DGE). With the exception of a short period around April–July 2008, the price of one gallon of B100 has been always higher than that of diesel. (Owing to the rapid rise in diesel prices and a lower rise in B100 prices in April–July 2008, the price of B100 had matched that of diesel fuel for a short period of time). When the energy content is taken into account, biodiesel (B100, $/DGE in the chart) has been always more expensive than diesel fuel.

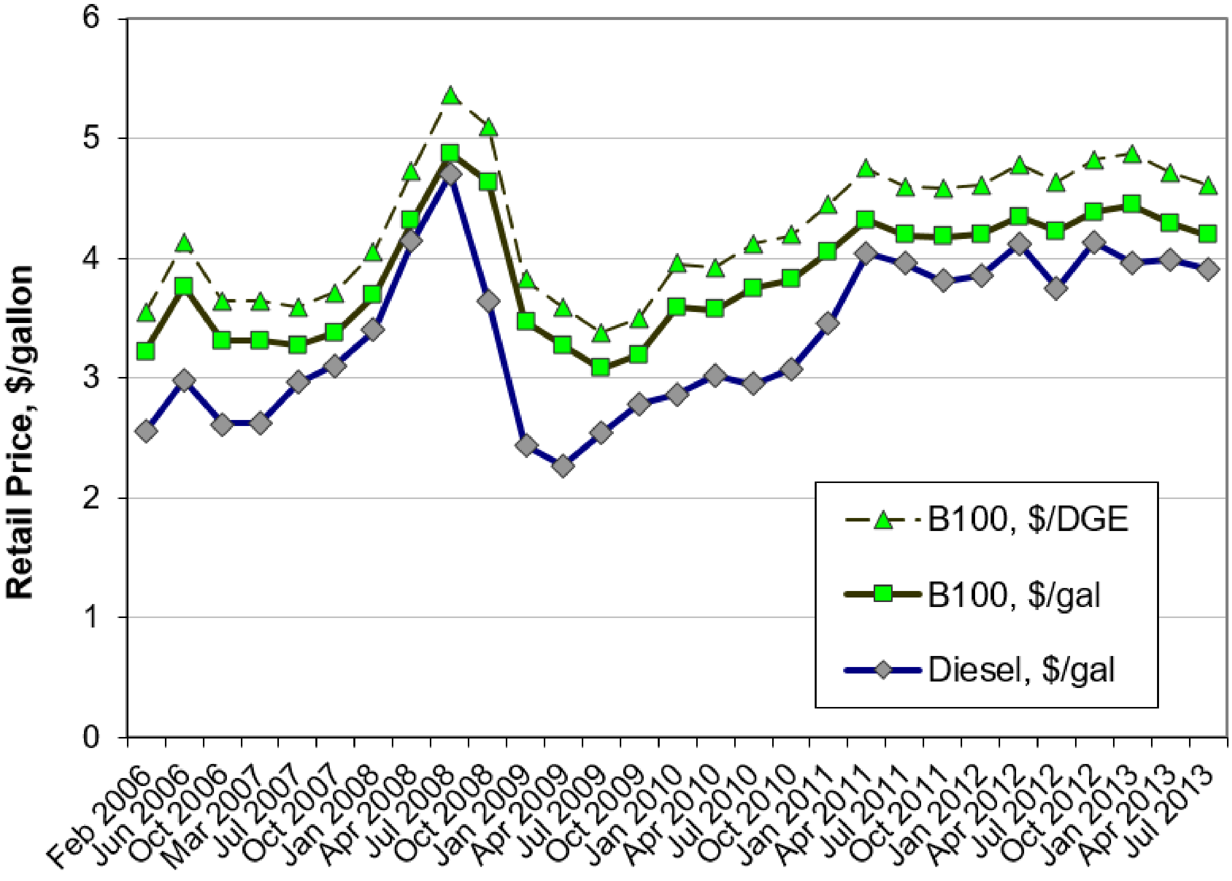

Figure D1. Average US Retail Prices for Diesel and B100

The US price of biodiesel is affected by the Federal Excise Tax Credit (so-called "blenders credit") that has been in place since January 1, 2005. This provides blenders with $1/gallon for B100 made from agricultural products and $0.50/gallon for B100 made from other oils (e.g., cooking oils). The tax credit lapsed in December 2009—which resulted in a 42% drop in US biodiesel production in 2010—but was reinstated from December 2010.

According to a statement issued by the National Biodiesel Board in January 2008, annual production capacity for biodiesel in the United States was 2.24 billion gallons. However, prior to the adoption of the RFS-2 program, the utilization of biodiesel production capacity in the United States was very low. Actual production from October 1, 2006, to September 20, 2007, was 450 million gallons or 20% of production capacity. A rapid rise in production occurred in 2007–2008 (Figure D2), followed by a 2009 decline due to the economic recession and a further decline in 2010 due to the expiry of the blenders tax credit.

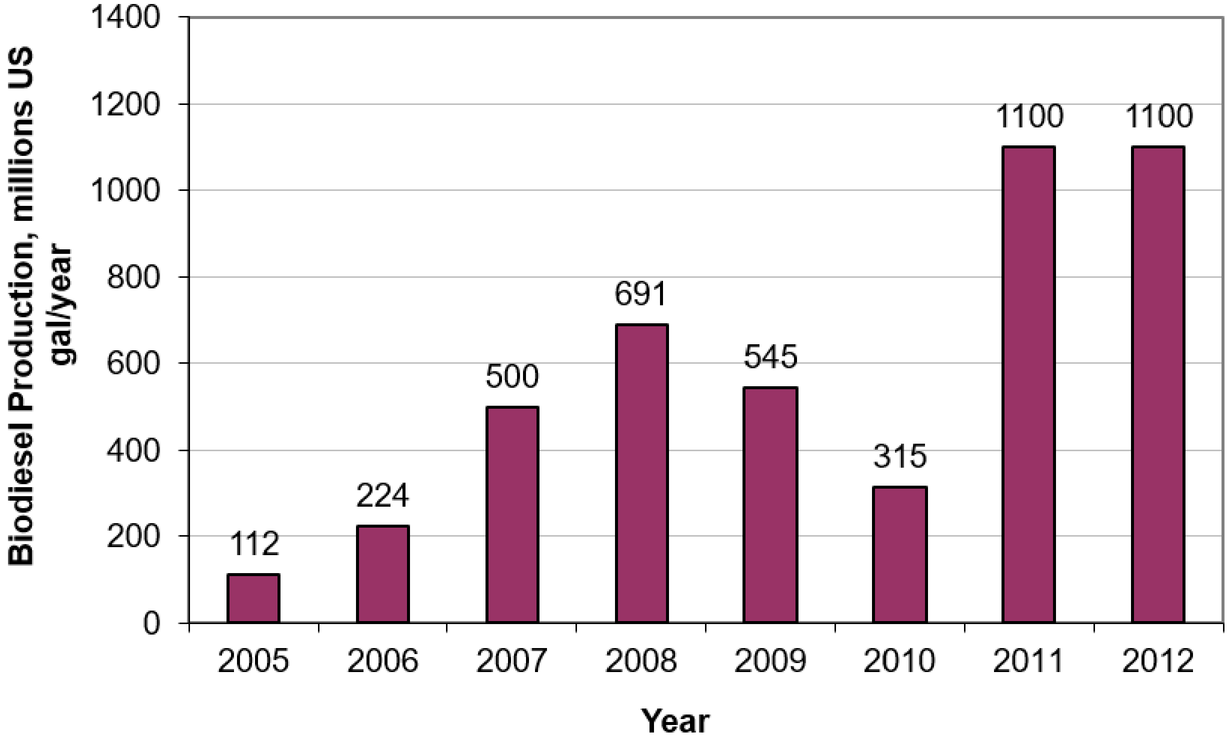

Figure D2. US Biodiesel Production

(Source: National Biodiesel Board)

Since the adoption of the RFS-2 program by the EPA in 2010, Federal biofuel requirements have become the major driver in biodiesel demand. The increase in biodiesel production from 2011 was also driven by the reinstatement of the blenders tax credit.

An important factor affecting biodiesel prices and sales volumes are feedstock costs. Most feedstocks used in biodiesel production (e.g., soybeans) compete with food production, and the increase in food commodities also affects biodiesel feedstock costs. This may have the effect of shifting from high cost feedstocks, such as virgin vegetable oils, to less costly feedstocks, such as imported palm oil or used cooking oil and animal fat. However, because of the EPA-assigned GHG emission reduction factor of less than 50%, palm oil biodiesel does not currently qualify as RFS-2 biomass-based diesel fuel.

The history of biodiesel production in the Unites States shows that, in spite of the growing production volumes and the significant financial incentives, biodiesel remains more expensive than petroleum diesel. This may be an economic reflection of the poor energy return on investment of biofuels. If a biofuel requires a significant fossil energy input over its life cycle production process, it must remain more costly than fossil fuels. In this case, future biodiesel sales volumes would be largely determined by the government mandates.

If, on the other hand, biodiesel retail prices could become competitive with petroleum diesel—due to reduced production costs or increased government subsidies—biodiesel sales would grow likely above the volumes mandated by the government(s). The price flexibility of biodiesel demand can be illustrated by the purchasing decisions among the US railway industry. In mid-2011, the Norfolk Southern Corporation began fueling locomotives in Chicago and Decatur, IL with "an approximately 10% biodiesel blend" (NS, 2011) (NS, 2012). The switch to biodiesel was enabled by a state tax credit that eliminates payment of Illinois' 6.25% fuel tax on biofuel blends of more than 10 percent biodiesel—an incentive that made B11 blends very common across the state. The use of B11 in Illinois was also reported by other railways (McAndrew, 2013).

By 2013, the Norfolk Southern Corporation was using 1 million to 1.5 million gallons of the biodiesel blend every month to run locomotives fueled in Illinois (NSC, 2013). While the report is not specific on how the B11 is used, railways typically blend the B11 into their main storage tanks to dilute the biodiesel level to B5 or less.

1.7 Future Regulatory Trends

US domestic oil and gas production has grown rapidly since the mid-2000s due the commercialization of horizontal drilling and fracturing (fracking) drilling technologies which allowed the utilization of shale gas and light tight oil reserves. In the mid-term—about 10-20 years—the US oil imports are predicted to decrease significantly, with some forecasts anticipating that the United States may even reach energy independence. Considering the combined production of gas liquids and oil, the US production is expected to match the production of Saudi Arabia in 2013.

In the long term—despite the gas and oil production increase in the United States—the world must face increasing energy resource scarcity. Forecasts vary in estimating the duration of the current US gas and oil boom. According to a recent analysis by the IEA, US production (combined with the Brazilian deep water oil) will supply most of the world's growth in oil demand over the next 10 years, while future growth beyond 2025 would increasingly depend on OPEC oil supplies (IEA, 2013). According to forecasts by the US DOE, US crude oil production increases sharply until 2016, when it comes close to the historical high achieved in 1970 (EIA, 2013). After 2016, US oil production is projected to level off and then slowly decline after 2020. Natural gas production, however, grows steadily with a 56% increase between 2012 and 2040.

Indeed, notwithstanding some optimistic opinions, the shale gas and oil production is unlikely to avert the peak oil. *Peak oil* does not suggest the world is running out of oil, but that a peak in conventional oil production will create an increasing reliance on more expensive, unconventional forms of oil and gas which have a far lower energy output (Murray, 2013). Geologists, economists, environmentalists, and resource managers are looking with interest at when the use of fossil fuels is expected to peak, and whether that occurrence will be driven by the oil supply or by market demand.

Concerns about the depletion of conventional oil resources combined with the realities of the climate change clearly indicate the need for alternative energy sources and alternative fuels. In this context, the future of biodiesel is linked to a broader question about the sustainability of biomass-derived fuels.

The Future of Biofuels. In the mid-2000s, at the time biofuel mandates were first adopted in the United States and in Europe, fuels made from agricultural crops (and from biomass in general) were considered the best solution to the world's energy and environmental problems. Biofuels were believed to have the potential to displace fossil fuels, reduce greenhouse gas emissions, increase energy security, and stimulate national economies. These beliefs have been questioned or invalidated by the science developed over the last decade.

One of the best reviews of current scientific knowledge on the environmental, economic, and social effects of biomass-based fuels has been presented in a discussion paper published by a US Navy analyst, Captain T.A. 'Ike' Kiefer (Kiefer, 2013) (Kiefer, 2013). Biofuel science from the 1980s and 1990s viewed biomass-derived liquid fuels as a prospective replacement for petroleum-based transportation fuels. However, most of the early biofuel studies were overly focused on the conversion of solar energy and ambient CO_2 into biomass during plant growth, while overlooking a number of important lifecycle, or "well-to-wheel", effects. In many media reports, crop-based biofuels such as ethanol or biodiesel are still seen as being able to increase domestic fuel supply and improve energy security, while reducing greenhouse gas emissions and stimulating the economy. These arguments all fall apart under scrutiny, states the paper. Uncultivated biofuel yields are far too small and diffuse to displace any meaningful fraction of US primary energy needs, and boosting yields through cultivation consumes more energy than it adds to the biomass.

Energy return on investment (EROI) is the key metric used in the paper to assess and compare fuels. EROI is defined as the ratio of usable energy in newly produced fuel to the energy consumed in producing the fuel. In a modern civilization, EROI must be significantly greater than unity, as survival and standard of living depend upon the size of this margin. The ancient Roman civilization achieved EROI (calculated as the ratio of their output physical work to the input of crop farming resources and labor necessary to feed them) of between 1.8:1 and 4.2:1. A significant increase of EROI was possible when steam engines were developed that could extract high EROI work from coal. Later, petroleum's high EROI, combined with high energy density and versatility, enabled the transportation revolution of aircraft and rockets. The magnitude of the energy revolution can be appreciated when one realizes that a car's tank of gasoline contains approximately two man-years of energy.

In 2010, the overall EROI in the United States was at 12:1. Based on studies of historical economic performance, a modern developed nation must maintain an EROI of at least 6:1 to avoid slipping into recession. When the overall EROI drops below 3:1, energy starvation sets in.

Energy sources with the highest EROI include hydro power, followed by coal, natural gas, oil and nuclear energy, continues the paper. Among newer energy sources, reasonably high EROI levels—matching or exceeding the current US 12:1 average—may be possible with solar, wind, geothermal, as well as wood and waste-derived energy. Tar sand fuels are estimated to have EROI of up to about 10:1.

By comparison, crop-based fuels offer EROI performance at energy starvation levels. Food crop-based ethanol and biodiesel have EROI below 3:1, while hydrotreated and cellulosic crop fuels have EROI of less than 0.7:1. The low EROI of biofuels is caused by high (petroleum) energy consumption in their production. In the case of US-based corn ethanol (EROI ~ 1.25), nitrogen fertilizers represent a very significant input of fossil energy (the fertilizers are based on ammonia which is manufactured from natural gas). Hence, the life cycle of corn-ethanol is described as transformation of high quality fossil fuel into an approximately equivalent amount of lower quality gasoline additive, accompanied by release of CO_2 emissions and consumption of significant quantities of water.

The EROI methodology presented in the paper shows that biofuels in the United States are not displacing fossil fuels—they are accelerating their use. The only way to displace imported petroleum and improve national security—points out the paper—is to domestically produce fuels with higher EROI than refined petroleum.

The evidence of the poor EROI of biofuels is their high price—due to the amount of petroleum energy consumed in their production they cannot compete with petroleum-based fuels and can exist in the market place only with the support of government subsidies and mandates. The cheapest price the US Navy has ever paid for any biofuel is $25.73 per gallon ($6.80 per liter), according to the paper. Since 2007, the US military has spent $67.8 million on 1.35 million gallons of biofuel, averaging more than $50 a gallon ($13.20 per liter) and costing $60 million more than if conventional fuel had been purchased.

The paper analyzes a number of other social and environmental costs and impacts of biofuels, including *energy sprawl* (i.e., low power density of energy crops and high demand for arable land); "*green grabbing"* of land and resources*; GHG emissions* (the low EROI of biofuels translates into high CO_2 emissions); c*ompetition of fuel and food*; and high w*ater demand* of energy crops.

The author concluded that biomass is an inefficient middleman between solar energy and fuel—a better approach would be to bypass the creation of biomass completely and directly synthesize liquid fuel from sunlight. In its concluding remarks, the paper called on the US government to end subsidies and market-distorting policies that encourage low-EROI biofuels over high-EROI energy sources.

Faced with the new scientific evidence, the European Union has been considering lowering their biofuel mandates or, possibly, dropping them entirely. One example of the ongoing political discussion is a recent EU proposal to amend their biofuel regulations—which currently require a 10% biofuel share in transportation fuels by 2020—and to freeze the use of agricultural biofuels at around 6%, which is approximately equal to the current EU biofuel consumption. The gap would be filled by "advanced biofuels", such as those made from seaweed or certain types of waste. A limit of about 6% would deliver a serious blow to the once booming European biofuels industry and require some biofuel production plants to close. In the recently proposed EU 2030 framework for climate and energy policies that covers the period beyond 2020, biofuel targets for the transportation sector have been dropped and replaced by economy-wide GHG and renewable energy targets, which reflects the realization that biofuels present one of the more costly approaches to reduce GHG emissions (EU, 2014).

In the United States, Congress has launched a review of the RFS-2. While the current energy supply trends and the biofuel science both seem to suggest that the RFS-2 requirements should be dropped or at least reduced, the outcome of the discussion is in the realm of politics and largely depends on the balance of power between the various groups opposing the legislation and the agricultural and biofuel lobbies who support it.

From the technical point of view, if biomass-based fuels are to be used, hydrocarbon fuel formulations are preferred over ester based fuels (FAME). In their Biodiesel Guidelines, international vehicle and engine manufacturers called for limiting the maximum FAME blend level to 5% (B5) (ACEA, 2009). The latest edition of the worldwide Fuel Charter introduces Category 5 gasoline and diesel fuels for markets with highly advanced requirements for emission control and fuel efficiency (ACEA, 2013). For diesel fuels, Category 5 establishes a high quality hydrocarbon-only specification that allows certain advanced biofuels (including hydro-treated vegetable oil, HVO, and biomass-to-liquid, BTL, provided all other specifications are respected and the resulting blend meets defined legislated limits) while disallowing ester-based biodiesel (FAME).

2 Biodiesel Definition and Properties

2.1 What Is Biodiesel

While a wide variety of materials could potentially carry the label "biodiesel" in that they are biologically derived fuels that can be used in diesel engines, the label is generally applied to a specific class of compounds. In the U.S., the ASTM International (formerly American Society for Testing and Materials) Biodiesel Task Force adopted a definition of biodiesel that limits it to "mono alkyl esters of long chain fatty acids derived from renewable lipid feedstocks, such as vegetable oils and animal fats, for use in compression ignition (diesel) engines" (Howell, 1997). The mono alkyl ester definition eliminates pure vegetable oils as well as monoglycerides and diglycerides from consideration as biodiesel. This review will limit the term biodiesel to mono alkyl ester fuels.

Other jurisdictions do not necessarily align their definition with that used by ASTM definition and considerable variation in the definition of biodiesel exists both in North America and worldwide. Biodiesel may occasionally refer to material other than alkyl esters. For example:

- Developments after about 2005 created pressure to expand the usage of the term biodiesel to include renewable diesel-like fuels made with other processes and composed of chemically different compounds. For several years, the term biodiesel was used to describe hydrocarbon-based fuels manufactured through refinery hydrogenation of fats or vegetable oils—an increasingly more important type of biofuel. For various reasons, the use of the term biodiesel to describe hydrocarbon fuels produced by hydrotreating oils at a refinery has fallen out of favor and these fuels are commonly referred to as "renewable diesel" fuels.
- The EPAct defines biodiesel as "a diesel fuel substitute produced from non-petroleum renewable resources that meets registration requirements for fuels and fuel additives established by the Environmental Protection Agency under Section 211 of the Clean Air Act" [10 CFR § 409.702].

In this report, we use the term biodiesel in accordance with the mono alkyl ester definition. Care must be taken to avoid confusion, as the use of the term remains inconsistent. For example, the Norfolk Southern Corporation recently announced that in 2012 the company "became the first U.S. railroad to begin using a 100 percent biodiesel fuel made from waste animal fats and grease" (NSC, 2013). And yet the fuel—made by Dynamic Fuels, LLC, a joint venture of Tyson Foods and Syntroleum–is a hydrocarbon based renewable diesel that meets the ASTM diesel fuel specifications and is outside of the scope of this report.

The most common alcohol used in the production of mono alkyl esters is methanol and the more specific label "methyl ester" is often attached to this type of esterified biodiesel. Higher order alcohols such as ethanol and propanol can also be used in the production of mono alkyl esters. These produce other classes of compounds called "ethyl esters" and "propyl esters" respectively. Further information on biodiesel processing can be found in the literature (Van Gerpen, 2004).

Biodiesel is rarely used in its neat form but is commonly blended with diesel fuel. The resulting blend is commonly referred to as Bx where x is a numerical value representing the volume percentage of biodiesel in the final fuel blend. For example, B2, B5 and B20 are common blend levels and denote a blend of 2%, 5% and 20% biodiesel by volume, respectively, in petroleum diesel fuels. B5 is the highest blend level approved by almost all manufacturers of high speed diesel engines. Under the ASTM D975 “Standard Specification for Diesel Fuel Oils,” up to 5% biodiesel content is allowed in commercial No. 2 diesel fuel. Some engine manufacturers allow higher level blends, such as up to B20. B100 refers to 100% (or “neat”) biodiesel.

2.2 ASTM Standards

2.2.1 Biodiesel Specifications

In the United States, ASTM D6751 defines the properties of biodiesel blending stock to be used in blends with diesel fuel up to a blend level of B20. The technical requirements of ASTM D6751-12 for biodiesel grade No. 2-B are outlined in Table D3

Table D3. Technical Requirements of ASTM D6751-12

Property	**Test Method**	**Limits**		**Units**
		Min.	Max.	
Alcohol control either:				
Flash Point or	ASTM D93	130		°C
Methanol	EN 14110		0.2	% vol.
Flash Point	ASTM D93	93		°C
Kinematic Viscosity @40°C	ASTM D445	1.9	6.0	mm^2/s
Sulfated Ash	ASTM D874		0.02	% mass
Sulfur:				
S15	ASTM D5453		0.0015	% mass
S500	ASTM D5453		0.05	% mass
Copper Corrosion	ASTM D130		No. 3	
Cetane Number	ASTM D613	47		
Cloud Point	ASTM D2500	Report		°C
Carbon Residue	ASTM D4530		0.05	% mass
Acid Number	ASTM D664		0.50	mg KOH/g
Free Glycerin	ASTM D6854		0.020	% mass
Total Glycerin	ASTM D6854		0.240	% mass
Distillation, 90%	ASTM D1160		360	°C
Water & Sediment	ASTM D2709		0.05	% vol.

P	ASTM D4951		0.001	% mass
Ca + Mg	EN 14538		5	mg/kg
Na + K	EN 14538		5	mg/kg
Oxidation Stability	EN 14112	3		hours
Cold soak filtration time (CSFT)	ASTM D7501		360	s

In 2012, a new biodiesel grade No. 1-B was added to the ASTM D6751. Biodiesel grade 1-B has improved cold temperature operability properties, controlled by two specifications:

- A maximum limit on monoglycerides of 0.40% wt (no limit for grade 2-B)
- CSFT of 200 s (down from 360 s for grade 2-B)

Since 2008, biodiesel blends of up to 5% (B5) have been incorporated into the diesel fuel standard, ASTM D975. Up to 5% biodiesel can be blended into No. 1 or No. 2 diesel fuel, provided that:

- the biodiesel component meets the requirements of ASTM D6751, and
- the final blend meets the requirements of ASTM D975.

Labeling of the finished blend is not required. It may not be possible for the purchaser to know whether or not the ASTM D975 diesel fuel contains biodiesel unless an analysis is carried out. This is also consistent with the US Federal Trade Commission (FTC) biodiesel labeling requirements which apply to blends above 5%.

B6 to B20 blends are covered by a stand-alone ASTM specification D7467, Table D4.

Table D1. ASTM D7467 Standard for B6-B20 Blends

Property	**Test**	**Limits**		**Units**
		Min.	Max.	
Biodiesel content	ASTM D7371	6	20	% vol.
Flash Point	ASTM D93	52		°C
Kinematic Viscosity @40°C	ASTM D445	1.9	4.1	mm2/s
Ash	ASTM D482		0.01	% mass
Sulfur:				
S15	ASTM D5453		15	µg/g
S500	ASTM D2622		0.05	% mass

S5000			0.5	% mass
Copper Corrosion	ASTM D130		No. 3	
Cetane Number	ASTM D613	41		
Cloud Point	ASTM D2500	Report		°C
Carbon Residue, 10% bottom	ASTM D524		0.35	% mass
Acid Number	ASTM D664		0.3	mg KOH/g
Distillation, 90%	ASTM D86		343	°C
Water & Sediment	ASTM D2709		0.05	% vol.
Lubricity, HFRR @ 60°C	ASTM D6079		520	µm
Cetane Index or	ASTM D976-80	40		
Aromaticity	ASTM D1319-03		35	% vol.
Oxidation Stability	EN 14112	6		hours

In Europe, EN 14214 establishes specifications for fatty acid methyl esters for diesel engines. In contrast to ASTM D6751, B100 that meets this standard could be used unblended in a diesel engine (if the engine has been adapted to operate on B100) or blended with diesel fuel to produce a blend in accordance with EN 590, the European diesel fuel specification.

2.2.2 Major Standards Development Issues

In the winter of 2005-2006, the first winter after Minnesota's B2 mandate came into existence, there were widespread filter plugging problems across the state. While a large number of these problems occurred with fuel blends where the biodiesel component did not meet the requirements of ASTM D6751, this was not the case for all these problems. A number of problems were encountered with biodiesel that was entirely in compliance with the existing standard. In these cases, filter plugging problems occurred at temperatures above the cloud point of the fuel. These issues suggested that the existing parameters used to define the low temperature operability limit of diesel fuels were not adequate even for low level biodiesel/diesel fuel blends.

An important aspect of these precipitates is that in many cases they do not redissolve after the fuel is warmed up. Contaminants such as sterol glucosides and/or soap in combination with water or saturated monoglycerides are thought to be at the root of such precipitates.

To address the issue, a specific operational type test was developed for biodiesel to reproduce the conditions under which precipitates can form above the fuel's cloud point. In this test, the Cold Soak Filtration Test (CSFT), a 300 ml sample of the biodiesel is cooled to 4.4°C and soaked at this temperature for 16 hours. It is then gently heated to room temperature were the time taken to pass through a 0.7 µm filter is recorded. The CSFT and appropriate test limits have now been included into ASTM D6751. (It may be noted that GE locomotive fuel filters were nominally 5 µm filters[1]).

While the CSFT test appears to address many of the filter plugging concerns encountered in vehicle fuel systems, not everyone is in agreement that this is sufficient to entirely address precipitation issues with biodiesel/diesel blends above the cloud point of the fuel. There is evidence to suggest that saturated monoglycerides on their own can come out of solution at low temperatures given sufficient time and collect in the bottom of fuel storage tanks (Brewer, 2007) and unheated distribution system filters (Selvidge, 2007). If other contaminants are not present, these saturated monoglycerides easily redissolve when the temperature of the fuel rises and would not be detected with the CSFT. Unlike vehicle fuel systems, the temperature of fuel storage and distribution system tanks and filters do not generally rise rapidly and the presence of these insolubles could be a problem is some cases.

2.3 Fuel Properties

2.3.1 Energy Content

The energy content of biodiesel is lower and specific gravity is higher than No. 2 diesel. The volumetric energy contents of two typical fuels are shown in Table D5. As a result of these differences, loss of engine power and increased fuel consumption can be expected.

Table D5. Energy Content of Biodiesel and No. 2 Diesel

Fuel	**Net (Lower) Heating Value**	
	MJ/l	*Btu/gal*
Biodiesel (B100)	32.9	118,170
No. 2 diesel	36.0	129,050

A survey by EPA on pre-1998 high-speed engines found that the average fuel consumption increase by mass for a wide range of engines was about 9% for B100 and varied almost linearly with the proportion of biodiesel in the blend (EPA, 2002). For a B20 blend, the average increase expected would then be a little under 2%.

The fuel consumption penalty can however be highly dependent on the particular engine. In one study with three different on-road high-speed diesel engines, the fuel consumption penalty ranged from 13–17% for B100 and 2–7% for B20 over the US FTP Transient test cycle. The same study measured a power loss of about 7% with B100 and about 2% with B20 (Sharp, 2000).

Work with engines used in rail applications is relatively limited but reflects the trends seen with high-speed engines.

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[1] GE has moved from specifying a nominally pore filter size of 5 µm to using an ISO Cleanness Code. The Tier 3 and Tier 4 common rail fuel system on locomotives require cleanness at 4, 6, and 14 µm of an ISO Code of 12/9/7 (Wallon, 2013).

In a study with an EMD GP38-2 locomotive equipped with a 2-stroke EMD roots blown 16-645-E diesel engine, no detectable differences were measured in fuel consumption between B20 and diesel fuel on both the EPA line haul and EPA switch duty-cycles. Power losses ranged from 0.9–2.4% depending on the base diesel fuel. The engine load control system on this particular engine sets a fixed volumetric fueling rate at each notch position (Fritz, 2004).

Tests with a 4-stroke single cylinder medium-speed research engine having a similar power assembly to a GE 7FDL locomotive engine showed a power loss of 1–3% with B20. The impact on fuel consumption was minimal (Su, 2005).

Newer line-haul locomotives are controlled to deliver constant gross power at a given throttle notch position, so there is no loss of power with biodiesel, but rather the fuel consumption increases. A study with a Tier 2 GE ES44DC line-haul locomotive reported volumetric fuel consumption increases of about 1% for B2 and B10 blends, 2% with B20, and almost 7% with B100 (Osborne, 2010).

In another study, two locomotive models were tested, a Tier 2 EMD SD70ACe (2-stroke) and a Tier 1+ GE Dash9-44CW (4-stroke) (Fritz, 2013). Fuel consumption increases were especially apparent with higher biodiesel blend levels. With B20, fuel consumption increases from about 1.25 to about 3.4% were measured. The 4-stroke locomotive appeared to have higher fuel consumption sensitivity to biodiesel than the 2-stroke locomotive. Interestingly, fuels based on CARB diesel (B0–B20) showed about 2% higher fuel consumption compared to fuels based on EPA diesel.

2.3.2 Low Temperature Operability

2.3.2.1 Sources of Low Temperature Operability Problems

Low temperature operability of fuel is critical in cold climates. Biodiesel generally has poorer low temperature operability than petroleum fuels and extra care needs to be taken at colder temperatures to ensure trouble free operation.

With petroleum diesel fuels, a range of options exists to adjust the low temperature operability limits of the fuel including varying fuel composition and use of low temperature operability additives. The wide possible range of hydrocarbons that can be used as diesel fuel allows considerable control of low temperature properties just by controlling the type and amount of some high boiling point components—by controlling the high end distillation temperature of the finished fuel for example. The range of compounds that compose biodiesel, however, are very limited and varying fuel composition provides a much narrower range of adjustment. To add to the challenge, most biodiesel contains a significant proportion of saturated long chain fatty acids that are very similar to the long chain paraffins whose concentration is undesirable in diesel fuels when low temperature operability range is to be extended.

There are several major sources of potential low temperature operability problems with biodiesel:

- Formation of waxes in the fuel—Long chain methyl esters, especially saturated ones, can solidify as the fuel temperatures drops. These can plug filters and cause engines to not start or stall shortly after start-up.

- Formation of precipitates from fuel contaminants—Some fuel contaminants such as saturated monoglycerides, sterol glucosides and soaps can lead to the formation of filter plugging precipitates at temperatures above the fuel's cloud point.
- Fuel system icing—At sub-zero temperatures, water from fuel contamination can freeze, causing the precipitation of ice particles.

Cold flow properties vary depending on the biodiesel feedstock, as illustrated in Figure D3 using a cloud point example.

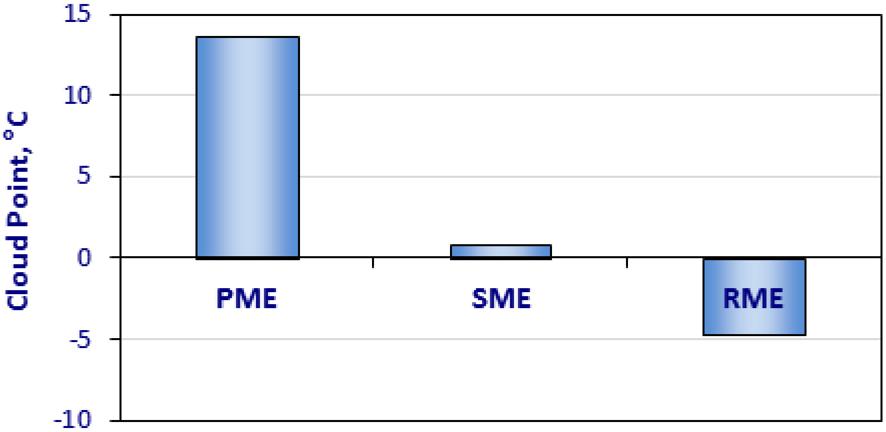


Figure D3. Average Cloud Point for Palm Oil (PME), Soybeans (SME) and Rapeseed (RME) Biodiesel

The main reason for the differences is the content of saturated fatty acid alkyl esters in the fuel, which have a relatively high cloud point (Krishna, 2007). In addition to the total level of saturated alkyl esters, the cloud point can be also affected by the chain length of saturates or the distribution of unsaturates (Imahara, 2006). A third factor affecting the cloud point of biodiesel is the level of some contaminants, an important one being *saturated monoglycerides*. Figure D4 shows the effect of saturated monoglycerides on the cloud point of soy methyl ester (Pfalzgraf, 2007).

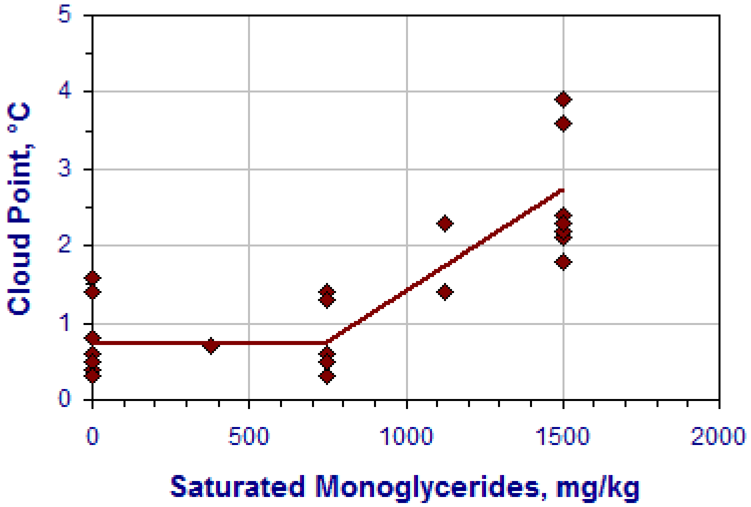


Figure D4. Effect of Saturated Monoglycerides on Cloud Point of Soy Methyl Ester

2.3.2.2 Low Temperature Properties of Blends

The cloud point of biodiesel/diesel fuel blends is affected by the low temperature properties of both the biodiesel and diesel fuel components. Figure D5 shows the difference between the cloud point of B5 blends and their base diesel fuel (cloud point elevation) as a function of the difference in cloud points of the biodiesel and diesel fuel components of the blend (the data was compiled from a variety of sources) (Jääskeläinen, 2009). Also shown is data for a Hydrogenation Derived Renewable Diesel (HDRD) a pure hydrocarbon product derived from vegetable oil.

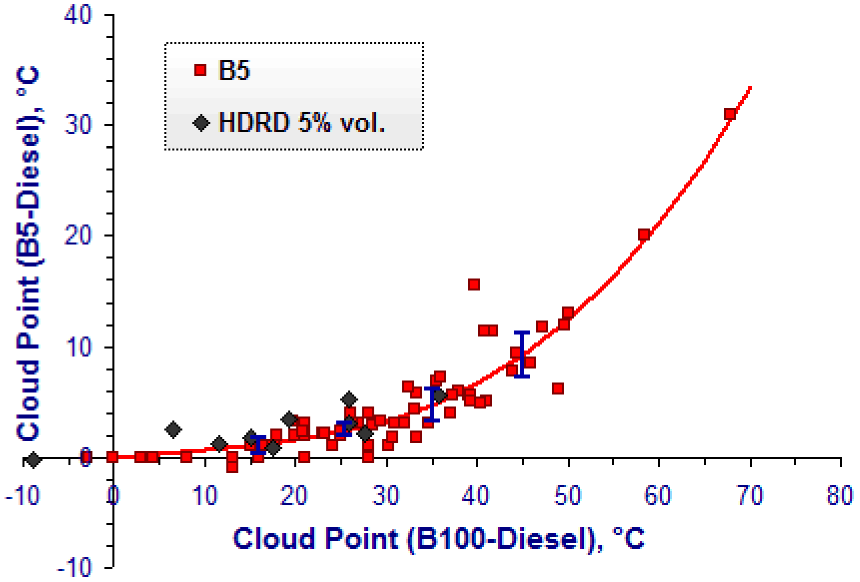


Figure D5. Elevation of Cloud Point for B5 Blends

As apparent from Figure D5, blending 5% biodiesel by volume will elevate the cloud point temperature of the final blend. Even for a difference in cloud point temperature between the blend components as low as 10–20°C, the cloud point elevation is greater than zero. Cloud point elevation can reach 30°C from blend components having a difference in cloud point of 70°C meaning that the successful use of biodiesel in very cold climates can be a major challenge.

2.3.2.3 Precipitate Formation Above Cloud Point Temperature

A major concern with biodiesel is the occurrence of low temperature precipitate at temperatures above the cloud point (Jääskeläinen, 2009). This is problematic because the conventional measures of low temperature operability such as cloud point would no longer be appropriate to estimate the low temperature operability limit of a fuel in which this occurs. These precipitates, which are not due to crystallization of alkyl ester molecules or to oxidation by-products, have been observed to form when blends as low as B2.5 are stored at low temperatures above their cloud point. In many cases they do not redissolve after the fuel temperature rises to about 20°C or even higher. While the formation of precipitates above the cloud point temperature in biodiesel and biodiesel/diesel fuel blends is not completely understood, it is known that they arise from the presence of trace fuel contaminants in the biodiesel as opposed to bulk fuel components such as methyl esters or paraffins. Two contaminants that are believed to contribute to this problem are *sterol glucosides* and *saturated monoglycerides*.

2.3.3 Cetane Number

Biodiesel fuels generally have higher cetane numbers than diesel fuels. The high cetane number of biodiesel arises from the long-chain structure of the alkyl ester molecules, with long chain saturated methyl esters having the highest cetane number. As the number of unsaturated bonds increase, the cetane number decreases.

Rape and soybean oil derived methyl esters are dominated by unsaturated methyl esters and they tend to have average cetane numbers in the range of 50-55 that is reflective of this. Palm oil methyl esters are rich in saturates and have cetane numbers well over 60.

Biodiesel that is stored for a sufficient period of time can start to oxidize. In the early stages of oxidation, the concentration of peroxides in the fuel increases. Peroxides have cetane enhancing properties—they are occasionally used as cetane improvers. Thus the cetane number of biodiesel can increase with time if the fuel undergoes sufficient oxidation, Figure D6 (Van Gerpen, 1996).

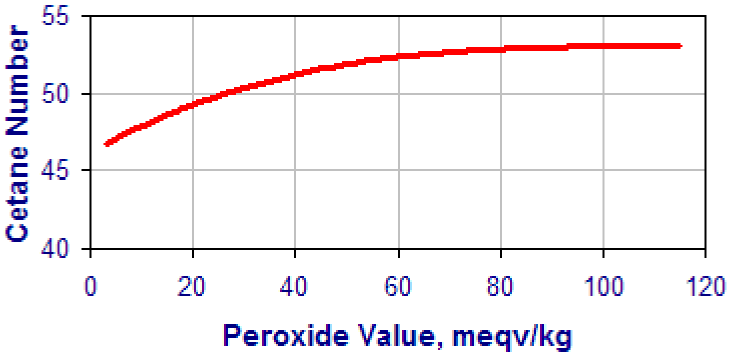


Figure D6. Effect of Peroxide Value on Cetane Number of Biodiesel

2.3.4 Lubricity

It is widely reported that biodiesel has very good lubricity characteristics and that adding 1–2% biodiesel to a diesel fuel that has lost most of its lubricity enhancing compounds through processing can restore this important fuel property. In order to identify the important lubricity imparting compounds in biodiesel, a number of biodiesel components were tested (Knothe, 2005). It was found that the main components of biodiesel, methyl esters, do provide some lubricity benefit but that they are not the primary lubricity enhancing components in biodiesel. When common contaminants often found in biodiesel were blended into the methyl ester at a 1% level and the mixture then blended into ULSD at low levels, lubricity improved substantially. In particular, the study demonstrated that free fatty acids and monoglycerin give biodiesel its excellent lubricity enhancing characteristics.

Free fatty acids and monoglycerin are considered biodiesel contaminants. If their level becomes excessive, significant fuel system problems can occur. Significant effort is therefore made to eliminate them from the fuel even though they are the most important lubricity enhancing compounds.

2.3.5 Distillation Temperature

Biodiesel has a very narrow distillation temperature range. The atmospheric pressure boiling temperature range of methyl esters in biodiesel generally falls in the range of 330 to 357°C. The maximum 90% distillation temperature for ASTM D6751 biodiesel is set just above this range at

360°C. Including the distillation characteristics in the biodiesel specification serves a different function than that for petroleum fuels. Rather than defining the compounds that make up the fuel, the maximum distillation specification for biodiesel serves to ensure that the fuel has not been adulterated with high boiling point contaminants.

Compared to No. 2 Diesel, biodiesel also has lower volatility (i.e., higher distillation temperatures). This property (combined with the higher surface tension and higher density of biodiesel) is the source of oil dilution problems when using biodiesel fuels.

2.3.6 Flash Point

Minimum flash point limits have been set for fuels to meet legal requirements and safety precautions for fuel handling and storage. The value for biodiesel is set much higher than that for diesel fuel because for biodiesel, flash point can also be used to limit any unreacted alcohol left over from the fuel production process.

For ASTM D6751, the flash point of biodiesel, when used to control the level of unreacted alcohol, is intended to be 100°C minimum. Due to the high variability of the test method, the minimum flash point temperature has been set to 130°C to ensure that the minimum of 100°C will be met. A flash point of 100°C will be exceeded only if the alcohol content of the fuel is less than 0.18% to 0.22% (Van Gerpen, 1997). Typical flash points of biodiesel are over 160°C.

2.3.7 Kinematic Viscosity

Biodiesel has an allowable range on viscosity of 1.9 to 6.0 mm^2/s (ASTM D6751). The upper limit is higher than the upper limit of 4.1 mm^2/s for No. 2 Diesel fuel defined by ASTM D975. Blending biodiesel into No. 2 Diesel fuel that has a viscosity near its upper limit can result in a final blend with a viscosity that exceeds 4.1 mm^2/s.

2.3.8 Fuel Quality Properties

2.3.8.1 Fuel Stability

Fuel stability is an important consideration to ensure that fuel properties remain constant from the time a fuel is produced to the time it is consumed. In most cases, this time period can extend from several days to months. A fuel that has insufficient stability can result not only in changes to fuel properties such as cetane number and viscosity but can lead to the formation of fuel system deposits and acids. Deposits can lead to filter blockage and sticking of fuel injectors or pumps. Acids can corrode fuel system components such as fuel tanks. Such problems have been shown to be possible when vehicles are fueled with biodiesel.

Biodiesel stability can be broadly categorized as oxidative stability and thermal stability. The olefinic unsaturated structure of the fatty acid chains that make up the mono-alkyl ester molecules of biodiesel is an important source of biodiesel instability (Waynick, 2005). The different pathways available for methyl ester decomposition and for deposit formation include (Fang, 2006):

- *Peroxidation*. This can proceeds through two possible routes. One is through formation of cyclic peroxides that will ultimately decompose to form aldehydes, ketones, and acids. These can react further to form oligomers (i.e., polymers that consist of a few monomers). The second is through reactions with fatty acid chains to form dimer or higher oligomers with peroxide or ether linkages. Deposits form when the polarity and molecular weight of oligomers by either pathway becomes high.

- *Reverse transesterification*. A reaction of the methyl ester with glycerin, or mono- or di-glycerides present in the sample as impurities can form intermediates that are highly reactive for oligomer formation. Samples with high levels of glycerin may indicate the formation of glycerides by reverse transesterification followed by formation of oligomer precursors.
- *Perester formation.* The interaction of biodiesel methyl esters with hydroperoxides to form peresters.
- *Ester hydrolysis*. The hydrolysis of methyl esters by reaction with dissolved water in the fuel can form acids. These acids can enhance other degradation reactions such as reverse transesterification and oxidation. The water required for hydrolysis can be present as a contaminant or be a product of oxidation reactions.
- *Thermal polymerization*. Polymerization of molecules with fatty acid chains can occur if the fuel temperature reaches 250–300°C. This degradation pathway may be of some importance in engine fuel systems that allow fuel to be heated by the engine and then recycled to the fuel tank. Biodiesel made from used cooking oils may also contain some products resulting from thermal instability.

2.3.8.2 Acid Number

The acid number property is a measure of the concentration of acid in the fuel. A number of factors can influence the acid number of biodiesel. Free fatty acids that were not fully removed during the fuel processing and acids formed during fuel degradation are two important contributing factors to biodiesel acid number. Biodiesel fuels with a high acid number have been correlated with increased fuel system deposits and increased the risk of corrosion (Jääskeläinen, 2009).

Setting an acid number limit for biodiesel/diesel fuel blends is complicated by the fact that weak acids are sometimes used as diesel fuel additives. A limit on blends that allows for reasonable biodiesel acidity and still allows for some use of acidic diesel fuel additives may not be sufficient to protect fuel system components from corrosion.

2.3.9 Contaminants

2.3.9.1 Glycerin

It is important to ensure that biodiesel has low levels of free glycerin (glycerol) and total glycerin. Free glycerin is a major byproduct of biodiesel production and is separated from the alkyl esters during the production process. It is however possible for small amounts to remain in the fuel. Bound glycerin is the molecular structure that forms the backbone of the triglyceride molecules from which biodiesel is produced when free fatty acids are still connected to it. Bound glycerin includes mono-, di- and triglycerides. Total glycerin is the sum of free glycerin and bound glycerin.

Excess free glycerin can build up in storage and fuel tanks, cause injector deposits or clog filters. Excess total glycerin can result from the incomplete conversion of oil or fat into alkyl esters. This can also lead to injector fouling, the formation of deposits at injection nozzles, pistons and valves and it can result in poor low temperature operability (Jääskeläinen, 2009).

The current limits on free and total glycerin in ASTM D6751 are 0.020% mass and 0.240% mass respectively.

2.3.9.2 Water and Sediment

Water and sediment in fuel can be major sources of contamination. Water especially can cause corrosion and support microbiological growth. Free water and the formation of ice in fuel systems is also an important source of cold weather operating problems. It is important that water and sediment be kept to a minimum. Water contamination can occur in numerous places of the fuel handling chain. While fuel may contain little water as it leaves the production facility, it can pick up water and atmospheric humidity as it passes through the distribution and storage system.

Normally water can exist in fuel as either free water or dissolved in solution. With free water, there is a distinctive boundary between the fuel and water phases. The amount of water that a fuel can hold in solution depends on the fuel. Upon cooling of the fuel, the solubility of water in the fuel decreases and some of the dissolved water can separate into tiny droplets making the fuel hazy. Given sufficient time, this free water can settle to the bottom of the tank.

Petroleum diesel fuels reach water saturation at values typically less than 100 ppm, while B100 can reach saturation at levels over 1000 ppm, Figure D7 (He, 2006). The solubility of water in blends of biodiesel and petroleum diesel does not scale linearly. The solubility of water in B20 is less than would be predicted based on the contributions from saturated biodiesel and saturated diesel fuel (Van Gerpen, 1997) (He, 2006). It is therefore possible when blending a diesel fuel and a biodiesel, neither of which has any free water, to end up with a fuel blend that has significant quantities of free water.

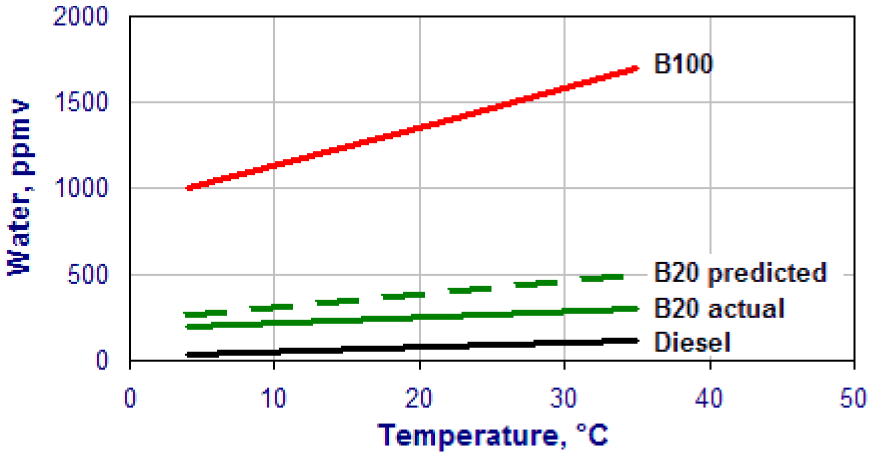


Figure D7. Saturation Moisture Content of Biodiesel

The specification for biodiesel, ASTM D6751, and the specification for diesel fuel, ASTM D975, allow up to 0.05% (500 ppm) by volume of free water and sediment. In practice, 500 ppm of free water in any fuel would be unacceptable and would lead to significant problems. The free water and sediment test (ASTM D2709) and the associated high limit, while useful to detect extremely high levels of contamination, is not considered sufficient to provide real protection (Jääskeläinen, 2009).

2.3.9.3 Phosphorus

Phosphorus is a known catalyst poison. Phosphorus specifications have been introduced to protect diesel emission control catalysts from exposure to excessive phosphorus levels. The ASTM D6751 specification requires that the phosphorus level be less than 10 mg/kg (ppm) by mass. The same limit was specified by EN 14214:2003, but it was lowered to 4 mg/kg in the 2012 edition of the standard. The 4 mg/kg limit has been preferred by automobile and engine manufacturers.

Based on tests using B100 fuel, it has been suggested that a limit of 10 mg/kg is not low enough to prevent damage to diesel aftertreatment systems (Krahl, 2006). Blending biodiesel with diesel fuel will result in a final blend with significantly lower levels of phosphorus than that in the original B100.

2.3.9.4 Metals

EN 14214 and from 2006 on, ASTM D6751, have limits on sodium, potassium, calcium and magnesium. The limit for the sum of Na + K is 5 mg/kg, as is the limit for the sum of Ca + Mg. These metals may be present as abrasive solids or soluble metallic soaps. Abrasive solids can contribute to wear of fuel system components, pistons and rings as well as contribute to engine deposits. Soluble metallic soaps have little impact on wear but may contribute to filter plugging and engine deposits.

These metals can also accumulate in diesel particulate filters, causing increased pressure drop and shorter times between maintenance intervals. A level of 1 mg/kg of trace metal in the fuel has been estimated to result in the accumulation of about 22 g of trace metal in the diesel particulate filter per 100,000 miles assuming a fuel economy of 15 mpg and 100% trapping efficiency (Sappok, 2007). Some of these metals are also known catalyst poisons.

2.3.9.5 Sulfur

ASTM D6751 defines two different grades of biodiesel; S15 with a sulfur level less than or equal to 15 mg/kg and a S500 grade with a sulfur level less than or equal to 500 mg/kg. While most biodiesel fuels can easily meet the S15 grade requirement, some produced from animal fats cannot and may therefore not be suitable for blends used as ultra-low sulfur fuel unless further processed to remove sulfur.

2.3.9.6 Ash/Sulfated Ash

Ash forming materials may be present in fuel as abrasive solids and soluble metallic soaps. In biodiesel, residual catalyst from the fuel production process may also be present. Abrasive solids and residual catalyst can result in excessive wear of the fuel injection equipment and/or the piston and piston rings, and can contribute to engine deposits. Soluble metallic soaps have little impact on wear but can contribute to fuel filter plugging and engine deposits (Jääskeläinen, 2009).

2.3.9.7 Carbon Residue

The term carbon residue—when used in the context of a fuel property—refers to the carbonaceous residue formed during the evaporation and pyrolysis of a fuel under specific test conditions. Carbon residue tests are intended to give a measure of the tendency of a fuel to form carbon deposits under conditions where volatile fuel components evaporate quickly such as in the combustion chamber. Although the results of carbon residue tests are not directly related to engine deposits, this property is considered an indication of the carbon deposit forming tendency of petroleum diesel fuels. It is known that non-volatile coke forming compounds that were not adequately separated during distillation and other refinery processes can contribute to engine deposits if they end up in diesel fuel.

The compounds that affect carbon residue test results in biodiesel are very different from those in diesel fuel. The carbon residue content of biodiesel shows a strong correlation with free fatty acids, glycerides, soaps, inorganic impurities, polymers, additives like pour point depressants, and the content of higher unsaturated fatty acids (Prankl, 2000). It is not known if a correlation exists between carbon residue values in biodiesel and engine deposits.

2.4 Fuel Handling and Storage

2.4.1 Introduction

The railroads handle large amounts of fuel and have numerous fuel facilities, including large size wayside diesel fuel tanks and fueling facilities. Due to the different properties of biodiesel compared to petroleum diesel—mainly stability and low temperature operability—special fuel handling demands apply to biodiesel. Special handling procedures or completely new infrastructure and/or storage facilities may be required to address the following issues:

- General handling and storage guidelines (stability)
- Blending facilities
- Solvency effect of biodiesel
- Heated storage for B100
- Free water.

Biodiesel handling and use guidelines have been published by the US DOE, Concawe, as well as—for marine fuels—by CIMAC (NREL, 2009) (Concawe, 2009) (CIMAC, 2013). In August 2013, API finalized their Recommended Practice 1640 dealing with storage and handling of fuels, which includes a number of sections on biodiesel (API, 2013). These general recommendations are summarized below, while the initial experience of railroads with biodiesel handling and storage is discussed in Section 5.2.

2.4.2 Compatibility with Storage Facilities

Existing supply and distribution facilities for hydrocarbon-only diesel fuels are in general considered adequate for handling diesel fuels containing biodiesel, but it is recommended to review the need for hardware modifications consideration of potential material incompatibilities and the increased risk of deposit formation (API, 2013). The following points should be considered:

- dedicated lines may be needed for imports and exports at terminals to avoid water and other contamination;
- gaskets should be compatible with B100 including those fitted in flanges and swivel joints;
- lagged or heat traced pipelines may be appropriate depending on the ambient temperatures and the cold flow properties of the diesel blend; and
- the design of product filters should be considered as well as the frequency of change.

Because of the chemical difference between hydrocarbons and biodiesel, various components in the fuel distribution system may be less compatible with biodiesel than they are with hydrocarbon-only fuels. Sensitive materials may swell or lose their integrity after prolonged contact with biodiesel. They may also promote fuel degradation reactions due to their chemical composition.

Biodiesel may degrade some hoses, gaskets, seals, elastomers, glues and plastics after prolonged exposure. Biodiesel may also permeate some types of plastics (polyethylene, polypropylene) over time and they are not recommended for use in storing B100. Natural or nitrile rubber compounds, polypropylene, polyvinyl, and plasticized PVC tubing materials are particularly sensitive. Polytetrafluoroethylene, fluoroelastomers or synthetic rubber materials, and nylon are not sensitive to biodiesel and are among the materials that can be used to update incompatible materials in equipment.

Most tanks that are designed to store diesel fuel should also be adequate for storing B100. Acceptable storage tank materials include aluminum, steel, fluorinated polyethylene, fluorinated polypropylene, polytetrafluoroethylene, and most fiberglass products.

Brass, bronze, copper, lead, tin and zinc may catalyze the oxidation of biodiesel accelerating the formation of insoluble gels and salts. Lead solders and zinc linings should be avoided, as should copper pipes, brass regulators, and copper fittings. Affected equipment should be replaced with stainless steel, carbon steel or aluminum.

Table D6 lists selected materials that are either recommended for use or should be avoided when handling B100 (API, 2013).

Table D6. Material Compatibilities with Biodiesel (B100)

	Material Recommended	**Not Recommended**
Metals	Carbon steel	Brass
	Stainless steel	Bronze
	Aluminum	Copper
		Lead
		Tin
		Zinc
Elastomers	Fluorocarbon	Nitrile rubber
	Nylon	Neoprene

	Polytetrafluoroethylene	Chloroprene
	Fluoroelastomer	Natural rubber
		Hypalon
		Styrene-Butadiene rubber
		Butadiene rubber
Polymers	Carbon filled acetal	Polyethylene
		Polypropylene
		Polyurethane
		Polyvinylchloride
Others	Fiberglass	

Diesel fuels containing lower biodiesel concentrations should generally have smaller effect on materials used in the fuel distribution system. With blends of B10 and lower, the effects are not likely to be appreciable although some sensitivity of nitrile rubbers has been reported (API, 2013).

Among the reported underground storage tank (UST) problems related to storing biofuels—such as corrosion or breakup of tanks or tank equipment—most cases appear to be related to ethanol-gasoline blends, rather than biodiesel blends (ASTSWMO, 2013).

2.4.3 Temperature of Storage

Biodiesel (B100) should be stored at temperatures at least 6 °C higher than the cloud point (API, 2013). Therefore, most underground storage facilities are adequate. Above ground storage tanks (depending on the climate) should be protected with insulation, heating systems or other methods. This precaution includes piping, tanks, pumping equipment, and trucks used to transport biodiesel. Heating should be designed to minimize hotspots and prolonged exposure of the biodiesel to high temperatures.

If the temperature does drop and precipitates begin to form, the precipitates should dissolve if the fuel is warmed up, although residual monoglycerides and sterol glucosides may be difficult to dissolve. Precipitates formed in biodiesel or in diesel blends can also settle to the bottom of the tank and begin to form a gel layer.

Slow agitation can prevent precipitates from building up on the tank bottom and agitation can also help to redissolve precipitates once they are present in the fuel. If the biodiesel product has gelled completely, it is advisable to raise the temperature up to 40 °C to 60 °C in order to melt the most saturated biodiesel components (API, 2013).

During colder seasons, B100 is sometimes pre-blended with low cloud point diesel fuel in order to prevent precipitation. Preblends vary depending on environmental conditions. Pre-blends are prepared before blending into the diesel fuel. The recommendations for biodiesel also apply to these diesel blends.

2.4.4 Storage Duration

Due to the inherent instability of biodiesel, it is recommended to limit the storage of biodiesel—including low level biodiesel blends—to no more than 6 months (API, 2013) (CIMAC, 2013). Even shorter storage periods have been recommended by some diesel engine manufacturers. John Deere, for instance, requires that biodiesel blends up to B20 be used within 90 days of the date of biodiesel manufacture, and blends from B21 to B100 within 45 days of the date of manufacture (DEERE, 2007).

Because biodiesel ages in storage, the acid number tends to increase, the viscosity can increase and gums and varnish can form. To monitor biodiesel quality during storage, oxidation stability, acid number, viscosity, water, and sediment may all be used as indicators to ensure that the biodiesel complies with ASTM D6751.

A fuel condition monitoring program is recommended if the fuel is intended for long term storage of 6–12 months or more to ensure the fuel has not degraded to the point it will be problematic (CIMAC, 2013). This involves drawing samples periodically, recommended every 3 months, and having a laboratory check the acid number and oxidation stability of the fuel. It is possible in some instances to increase the stability value of a biodiesel blend that has lost some of its oxidation stability by re-additising the fuel or blending with a fuel that has additional stability additives.

When oxidized or aged biodiesel is blended with diesel, some of the sediments and gums that are soluble in the B100 may become insoluble in the diesel blend and form sediments (API, 2013). For this reason, biodiesel that does not comply with ASTM D6751 should not be used for blending.

2.4.5 Minimum Headspace

As a fuel tank is emptied, air will enter through the vent pipes to displace the fuel that was in the tank. The extra air drawn into the tank may lead to more oxidation, particulate contamination and increased water levels of the biodiesel. In order to limit the effects of air in the tanks, it is recommended that biodiesel and diesel blends are not stored for long periods of time in partially empty tanks without the use of oxidation stabilizing additives (API, 2013).

2.4.6 Water Contamination

Biodiesel is susceptible to water-related problems. Desiccant filters are recommended on breathing vents to reduce water condensation in the storage tank (API, 2013). All tanks should have an effective drainage arrangement and as best as possible be kept clean. The tanks must be drained regularly to limit the degree of water and sludge build up. In marine applications, it is recommended that tanks with biodiesel blends up to B7 be drained at least twice daily (as recommended for conventional marine distillate fuels) (CIMAC, 2013). This high draining frequency reflects the high level of attention to reliability and safety in marine engine operation.

Both free and dissolved water accelerate corrosion and fuel degradation. Free water may enter bulk fuel tanks by condensation, by carry-over from the fuel distribution system, or by leakage through the fill cap, spill containment valve or piping.

In addition to accelerating the degradation of the fuel product, water also provides a suitable environment for microbial growth, which primarily occurs at the water-fuel interface (Passman, 2003). Poor tank design can make it almost impossible to completely remove free water once it is present; therefore, it is important to take steps to prevent water from entering the fuel storage tank.

2.4.7 Biocides

The preferred approach to prevent microbiological contamination is a good tank housekeeping program. If microbiological problems are encountered, a biocide shock treatment can be used as a temporary measure, but biocides should not be used on a continuous basis (API, 2013).

The continuous application of biocide does not compensate for the introduction of water, and is therefore not a suitable preventative measure against water related problems. The regular use of biocides may even increase the resistance of micro-organisms to treatment. Furthermore, the regular use of biocides also has some drawbacks that must be properly managed (e.g. biocides are toxic chemicals and produce bio-sludges that must be removed). More information on microbial contamination of fuel systems can be found in ASTM D6469: *Standard Guide for Microbial Contamination in Fuels and Fuel Systems*.

Regulations may restrict the use of biocides and special measures may be required when disposing of water from tanks treated with biocides.

2.5 Biodiesel Blending

2.5.1 Blending Strategies

Biodiesel is fully compatible with petroleum diesel; however, some of the significant characteristics of biodiesel can impact blending (API, 2013):

- Biodiesel typically has a higher density and viscosity compared to diesel fuel. If blend components are added sequentially into a blending tank, the higher density component (B100) should be added first in order to avoid the formation of an unmixed bottom layer.
- When blending into a storage tank, documented procedures should be established to create and validate a homogenous blend. These procedures must be controlled following a formalized approach called the Management of Change (MOC).
- Biodiesel generally has a higher cloud point than diesel. If different components are added into the blending tank, the temperature of all of the components should be well above the biodiesel cloud point to ensure easy flow and prevent formation of precipitates that may be difficult to redissolve. In other words, biodiesel should not be blended with extremely cold diesel.

Several blending strategies can be used to achieve proper mixing, including:

- in-tank sequential blending;
- in-line blending into a tank;
- in-line ratio blending at the loading rack; and
- splash or sequential blending at the load rack.

2.5.2 In-Tank Sequential Blending

The required volumes of biodiesel and diesel fuel are pumped separately into a tank. Proper mixing shall be achieved and tested prior to releasing the diesel blend.

2.5.3 In-Line Blending into a Tank

The biodiesel and other blend components are pumped simultaneously under flow control into a common product line to a product storage tank. The turbulent flow conditions at the injection points and in the line promote mixing, but the use of a static mixer is also recommended.

2.5.4 In-Line Ratio Blending at the Loading Rack

Biodiesel is injected continuously into the diesel fuel stream under flow control during truck loading. Alternatively, the biodiesel can be added in small slugs or in pulsed quantities spread evenly throughout the time that the truck is being loaded. This is similar to the way most additives are blended into diesel fuel at the loading rack.

2.5.5 Splash or Sequential Blending at the Loading Rack

Biodiesel and diesel fuel are sequentially loaded into a truck or other vessel. In this case, relatively little mixing occurs as the fuels are loaded into the vessel. After the fuels are in the truck, driving down the road is sometimes considered to be sufficient agitation to allow the biodiesel and diesel fuel to be mixed in transit.

This blending strategy is not recommended, particularly when the ambient temperature is low, because there is some risk that the product may not be homogeneous, and therefore subject to low temperature effects of the biodiesel component, when it arrives at the delivery point.

2.5.6 Biodiesel Blending and Additive Performance

Diesel performance additives (such as cold flow improvers or cetane boosters) should be injected into the diesel fuel stream during blending. The additive dosage in biodiesel blends may be different from hydrocarbon-only diesel fuels in order to achieve the same level of performance.

Additive dosages that should be rechecked include cold flow, cetane improvers, lubricity enhancers, conductivity improvers, performance packages and antifoam additives (API, 2013).

Blending biodiesel into diesel fuel, even at low concentration, can increase the lubricity of the diesel blend. The amount of biodiesel required to achieve adequate lubricity depends on the properties of both the biodiesel and the hydrocarbon-only diesel. Evidence suggests that about 2% biodiesel may provide sufficient lubricity. However, some batches of biodiesel cannot sufficiently improve lubricity to meet specification at any concentration. Consequently, testing should be conducted to confirm the effectiveness of the biodiesel as a lubricity improver.

2.6 Biodiesel Quality Issues

Well publicized fuel quality problems have plagued biodiesel. In the winter of 2005–2006, large numbers of low temperature operability issues were reported in Minnesota. This was the first winter of Minnesota's B2 mandate. Many of these problems were associated with high levels of free and total glycerin from off-spec fuel (however, a number of problems were also reported with fuel that fully met the requirements of D6751 that was in effect at that time).

The DOE’s National Renewable Energy Laboratory conducted biodiesel fuel quality surveys in 2011, 2004, 2006, and 2007 (McCormick, 2005) (Alleman, 2007) (Alleman, 2008) (Alleman, 2013).

The 2006 survey found that 59% of US B100 samples did not meet the requirements of ASTM D6751. 30% of samples failed total glycerin and 20% failed on metals Na+K. Some flash point failures were also noted—indicating that some samples contained significant amounts of methanol. Another interesting observation from the 2006 survey was that of the 39 samples analyzed—nominally B100—32 were B100, 6 were B99 and one was B50.

A follow-up survey in 2007 showed a similar trend with 45% of samples analyzed (25 out of 51) failing to meet the requirements of ASTM D6751 (Alleman, 2008). The most common failures were: low oxidation stability (18/55 samples), free and total glycerin (6/55 samples) and the trace metals Ca+Mg and Na+K (6/55 samples). Additional failures were due to high acid number, methanol control, phosphorous and water and sediment. On a production volume weighted basis, small and medium biodiesel producers failed to meet the oxidation stability specification most often. The study concluded that since most failures were from small and medium sized producers, the high rate of sample failures indicated that about 10% of the biodiesel in the United States failed to meet ASTM D6751.

A significant improvement in biodiesel quality was found in the 2011 survey (Alleman, 2013). Samples of B100 collected from producers (53 samples) and terminals (14 samples) in 2011 were tested for free and total glycerin, flash point, cloud point, oxidation stability, cold soak filterability, and metals. Failure rates for cold soak filterability and oxidation stability were below 5%. A single flash point failure due to excess methanol content was observed. One sample failed multiple properties, including oxidation stability and metal content. Overall, 95% of the samples surveyed met ASTM D6751.

Although D6751 did not include the No. 1-B grade of biodiesel in 2011 when the samples were collected, 70% of the samples would have met the requirements had they been in place. Two samples would not have met the 200 s CSFT requirement, and 19 samples had monoglycerides over the 0.40 wt% limit. Of the 19 samples with monoglycerides above 0.40%, one was from a terminal and the other 18 were directly from producers.

In order to address many of the quality issues, a voluntary BQ-9000 program has been started in the USA that allows biodiesel producers and marketers to certify that not only does their fuel meet ASTM D6751 requirements, but that proper sampling, testing, storage, sample retention, shipping and handling procedures are in place (BQ-9000, 2008).

3 Environmental Impact

3.1 Lifecycle GHG Emissions

One of the main advantages claimed for biodiesel is its renewable character and the potential to reduce petroleum consumption. Biodiesel's raw resources—ranging from food crops such as soybeans and rapeseed to non-edible biomass such as algae—are entirely renewable. However, early studies overestimated the environmental benefits and underestimated the lifecycle GHG emissions from biodiesel by overlooking a number of fossil energy inputs over the full lifecycle of biodiesel production. While biodiesel still appears to be a more sustainable biofuel when compared with some alternatives (e.g., corn-ethanol), the environmental benefits—as currently perceived—are less than it was once estimated.

One of the first life cycle analyses for biodiesel was conducted by the US DOE National Renewable Energy Laboratory (NREL) (Sheehan, 1998) (Sheehan, 1998). According to this early NREL work, substituting B100 for petroleum diesel in buses would reduce the life cycle consumption of petroleum by 95% (while increasing the consumption of coal by 19% and of natural gas by 77% due to the usage of electricity and steam in biodiesel production) (Sheehan, 1998).

Energy Efficiency. In terms of energy, the NREL analysis found that biodiesel yields about 3.2 units of fuel product energy for every unit of fossil energy consumed in its life cycle (EROI = 3.2) (Sheehan, 1998). In other words, 0.31 MJ of fossil energy is needed to produce 1 MJ of biodiesel, thus representing a 69% energy gain over the fossil energy input. Similar figures were reported by other authors. The International Energy Agency reviewed seven European rapeseed biodiesel studies, which were reporting that biodiesel production resulted in fossil energy savings from 30 to 80% (IEA, 2004).

According to newer studies, however, the complex issue of life cycle energy efficiency of biodiesel remains uncertain. There are several fossil fuel energy inputs—such as those in the process of growing biodiesel crops—that might have been underestimated or overlooked. Some authors estimated that growing and processing soybeans requires 32% *more* fossil energy than the energy content in the produced biodiesel (considering the energy value of the byproduct soy meal, biodiesel still produced a net energy loss of 8%) (Pimentel, 2005). The difference between this and the former estimates can be attributed to higher assumed energy inputs in soy agriculture—such as machinery, fuels, fertilizers, lime, herbicides, electricity, etc.

GHG Emissions. Due to the renewable character of carbon in the fuel, biodiesel can also potentially provide reductions of life cycle carbon dioxide emissions. Carbon is biologically cycled when plants such as soybean crops convert atmospheric CO_2 to carbon-based compounds through photosynthesis. Biomass-derived fuels participate in the relatively rapid biological cycling of carbon to the atmosphere (via engine tailpipe emissions) and from the atmosphere (via photosynthesis). Fossil fuel combustion, on the other hand, releases carbon that was removed from the atmosphere millions of years ago. For this reason, shifting from fossil fuels to biomass-derived fuels is thought to reduce the amount of CO_2 in the atmosphere.

According to the estimates in the above NREL study (Sheehan, 1998), the net reduction of the life cycle CO_2 due to biodiesel use amounted to 78%. Newer studies, however, account for an increasing number of additional factors that have an impact on the life cycle greenhouse gas effect of biodiesel. These factors include land use effects from cultivation of soybeans or rapeseed, such as changes in carbon content in the soil (which decreases in cultivated land) and GHG emissions from fertilizers (N_2O), effects related to displaced products, such as glycerin (Delucchi, 2003), and emissions from changes in the use of land, e.g., from converting forests into arable land. The latter effects are referred to as the indirect land use change or ILUC.

Studies that take into account the land use effects have raised significant doubt about the net greenhouse gas emissions reduction potential of alkyl ester biodiesel. A technical analysis by the University of California related to California's Low Carbon Fuel Standard (Arons, 2007) found that the net GHG emissions of biodiesel made from US Midwest soybeans varied significantly depending on how the land use issues were treated. A life cycle analysis methodology (Greenhouse Gases, Regulated Emissions, and Energy Use [GREET] model) that is known to have shortcomings when dealing with land use changes gave US Midwest soybean FAME biodiesel a net GHG intensity of 30 g CO_2 equivalent/MJ. This is about 42% of that for petroleum diesel (71 g CO_2 equivalent/MJ) with the same analysis. However, when an alternative life cycle analysis (LEM) that deals with land use changes in a more comprehensive manner was used, the soy based biodiesel gave an astounding 224 g CO_2 equivalent/MJ—over three times higher than that for petroleum diesel (73 g CO_2 equivalent/MJ) estimated with the same analysis.

Similar concerns have been raised over rapeseed derived FAME. Some authors suggested that if rape is grown on dedicated farmland the life cycle GHG emissions are almost equivalent to those for petroleum diesel (Johnson, 2007). Others, based on a detailed analysis of N_2O release in agricultural production, have negated any climate benefit of rapeseed biodiesel (Crutzen, 2007). It was found that between 3 and 5% of the nitrogen fertilizer used for growing rape is emitted as N_2O—twice the value used by the UN Intergovernmental Panel on Climate Change (IPCC) to calculate the impact of fertilizers on climate change—causing up to 70% *more* GHG emissions than using the equivalent amount of fossil-based diesel.

Even more uncertainty exists about the net GHG effect for tropical biodiesel crops, such as palm oil or soybeans grown over cleared Amazon rainforest. Clearing forests for plantations usually produces a significant GHG release, which may be compensated for only after a very long period of biodiesel use. In the case of palm oil, significant GHG emissions are also generated in the production process (Reijnders, 2008). Palm oil mills produce large amounts of organic waste—up to as much as 80% of the inputs—a part of which enters waste water. During effluent treatment, a large part of the carbon input in the waste water undergoes anaerobic decomposition to methane, a potent greenhouse gas, which makes the overall GHG benefit of palm oil derived biodiesel uncertain.

Locomotive GHG Studies. The US DOE National Renewable Energy Laboratory (NREL) conducted a life cycle assessment of the use of jatropha biodiesel in Indian locomotives (Whitaker, 2009). The assessment was conducted to support the Indian government policy to introduce jatropha biodiesel blends into the nation's transportation sector, including railway locomotives.

The life cycle of jatropha biodiesel examined in the study includes jatropha cultivation, jatropha oil extraction, oil transesterification to biodiesel, and combustion of B5, B10 and B20 blends as well as, for reference, B100 biodiesel in Indian locomotives. The study estimated that substituting petroleum diesel with B5 could reduce net GHG emissions per gross tonne-km by 3%, by 12% for B20, and by 62% for B100.

3.2 Pollutant Emissions

Most testing with biodiesel has been carried out on high-speed diesel engines and only limited data is available for medium-speed diesels. Figure D8 shows average emission trends from pre-1998 high-speed diesel engines from an EPA survey (EPA, 2002) for different blend levels of biodiesel. Light-duty and nonroad engine emissions were predicted poorly by the EPA correlations, but the data set was too limited to allow for statistically valid generalizations. On average, PM, CO and THC emissions decrease while NOx emissions increase with increased proportion of biodiesel in the fuel.

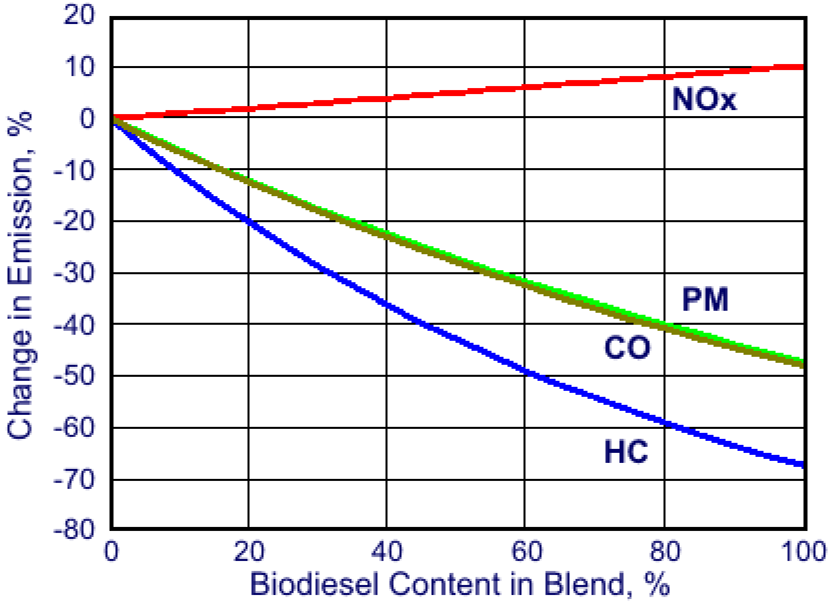


Figure D8. Average Impact of Biodiesel on Emissions for High Speed Diesel Engines

More recent work on 2004 and later on-highway engines suggests that the PM reduction potential may be higher than with the older pre-1998 engines (McCormick, 2005). Part of the PM reduction control strategy for these newer engines is reduced lubricating oil consumption. The relative contribution of combustion generated soot to total PM would be higher and fuel effects on PM accentuated. On the downside, the NOx increase with the newer engines was higher than in the older engines used in the EPA survey (Figure D9).

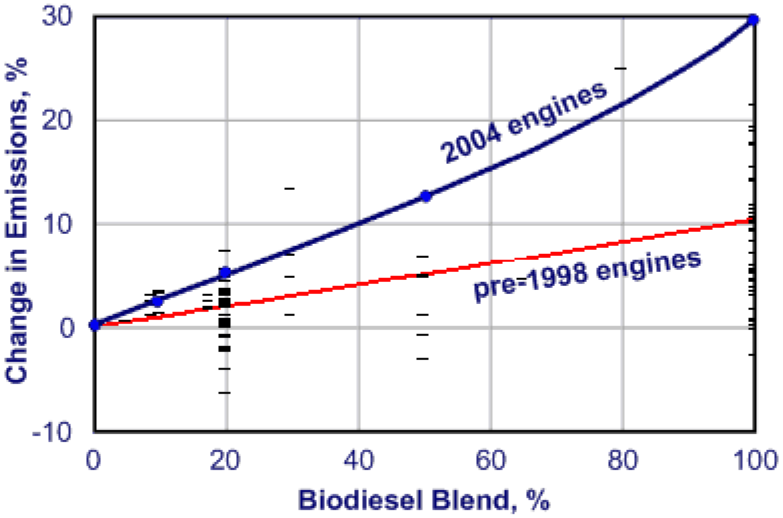


Figure D9. Relative Increase in NOx for Pre-1998 and 2004 On-Highway Diesel Engines

The NOx increase with biodiesel has been fairly consistently noted. One characteristic of this NOx increase is that its magnitude is strongly dependent on engine load. Figure D10 shows the relative NOx increase for B20 and B50 blends from a 2006 Cummins ISB on-road engine measured for different test cycles having different average power demands (Sze, 2007).

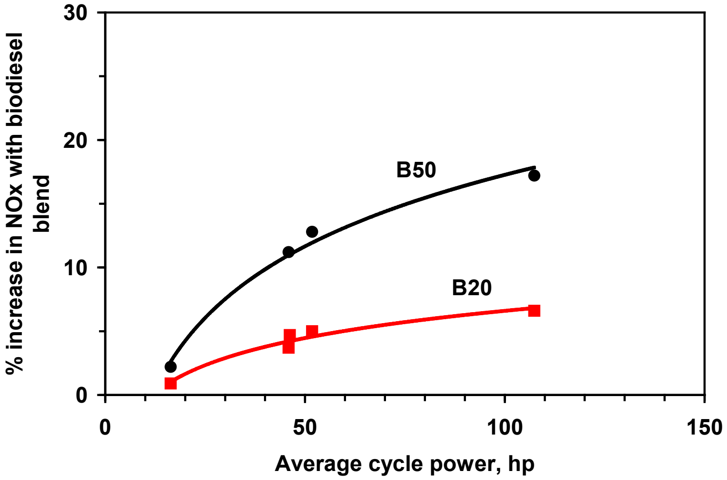


Figure D10. Relative Increase in NOx Measured on Different Drive Cycles Having Different Average Power Requirements

Some have argued that biodiesel can show a NOx decrease in some cases and therefore the claim that biodiesel always causes a NOx increase is unwarranted (McCormick, 2006). However, examination of data used to support this argument shows that NOx decreases only occur on drive cycles with very low average power demands such as those used with some urban buses (Sze, 2007). The data also shows that in cases where a NOx decrease is noted, a significantly higher fuel penalty is observed when compared to cases where NOx increases – suggesting that the NOx decrease at low loads is due to degradation in engine efficiency (Majewski, 2009).

The increases in NOx with biodiesel can be attributed to numerous factors that depend on details of the engine being considered. Changes in controlled parameters such as fuel injection timing, injection pressure and EGR rate can play a major role. However, even in cases where measures to hold these controlled parameters constant have been taken, NOx increases have persisted due to changes in combustion phasing, peak temperatures and mixture stoichiometry (Cheng, 2006] (Majewski, 2009).

3.3 Locomotive Emission Studies

3.3.1 Overview

While a significant body of work exists on the effect of biodiesel on emissions for high-speed engines, only limited data is available for medium-speed diesel engines such as those used in North American rail service.

Tests with an unregulated 2-stroke EMD GP38-2 locomotive with an EMD roots blown 16-645E diesel engine using both EPA line haul and EPA switch duty cycles showed statistically significant increases in NOx of about 5-6% and decreases in CO with B20. No impact on PM or THC was detected (Fritz, 2004). It should be kept in mind, however, that these tests were carried out on an unregulated 2-stroke locomotive with PM emissions of 0.62 g/kWh (0.46 g/bhp-hr) on the EPA line haul duty cycle. PM emissions from this 2-stroke engine are dominated by lubricating oil components and the fuel effects are relatively insignificant. In newer, emission certified locomotives, PM emissions have decreased to the level where fuel effects are detectible. This trend is also more pronounced in 4-stroke engines.

In the work by Su, PM decreases comparable to those in Figure D8 were measured with B20 from an engine with PM emissions of 0.16 g/kWh (0.12 g/bhp-hr) (Su, 2005). The study was conducted using a 4-stroke single cylinder Alco 251 medium-speed research engine (non-emissions regulated) having a similar power assembly to a GE 7FDL locomotive engine. B5 and B20 blends where tested using an AAR 3-mode test cycle. With B20, a 13–19% decrease in CO, 7-8% increase in NOx and a 13–19% decrease in PM was noted.

Another study evaluated regulated emissions from a Tier 2 GE ES44DC line-haul locomotive with 3,280 kW rated traction power (Osborne, 2010). The locomotive was tested with a baseline LSD fuel of 400 ppm sulfur, followed by tests with soybean derived B2, B10, B20 and B100 biodiesel. Regulated emissions were sampled according to the 40 CFR Part 92 certification test procedures specified by EPA. PM emission reductions occurred over the line-haul and switch test cycles for each biodiesel blend tested. The bulk of the PM reduction benefit was present with B10, with small additional amounts of PM reductions found with increased blend levels. The change in cycle weighted NOx for B2, B10, and B20 were not greater than the expected test measurement variation; however, B100 increased NOx by nearly 15% over the line-haul cycle. Changes in HC emissions were within the test measurement variation except for B100, where HC was reduced by 21% and 24% over the line-haul and switch cycles. CO emission reductions of 17% and 24% over the line-haul cycle were measured for B20 and B100, respectively. Volumetric fuel consumption increased about 1% for both B2 and B10 blends. Just over 2% increase in fuel consumption was observed at B20 and nearly 7% increase at B100.

In a recent study, emission tests were conducted on two locomotive models, a Tier 2 EMD SD70ACe and a Tier 1+ GE Dash9-44CW (Fritz, 2013). A matrix of six fuels was used, including EPA No. 2 certification diesel fuel (max. 15 ppm S), CARB diesel (max. 15 ppm S), and B5 and B20 blends with both the EPA and CARB diesel fuels. The emission difference between B0 and B5 was generally not statistically significant, while the B20 blends often produced statistically significant differences. The findings of the study include:

- For some of the cycle and locomotive combinations, the B20 fuels produced significantly higher NOx than their respective base fuels, while NOx with the B5 blends was not significantly different from the base fuel case for either locomotive and for either base fuel.
- CARB B0 fuel had significantly lower NOx emissions compared to EPA B0 for the line haul and switch cycle, due to the relatively high cetane number and lower aromatics in the CARB fuel.
- In the GE locomotive (4-stroke engine), the B20 blends yielded significantly lower CO emissions than the B5 and B0 fuels. The EMD locomotive (2-stroke engine) produced comparable CO emissions using all test fuels.
- PM emissions from the EMD locomotive (2-stroke engine, PM dominated by lube oil) were essentially insensitive to fuel type.

Trials outside of North America have also been carried out. UK's Virgin Trains launched Europe's first biodiesel train in June 2007, supported by a cross-industry research program representing members of the British rail industry, known as the Biodiesel Working Group (Hayat, 2007). In the UK, where many passenger rail applications use multiple small diesel power plants such as Cummins' NT855 and QSX-19 and MTU's 6R-183, tests with a Cummins NT855, while showing trends consistent with Figure D8 up to B20, showed a poor response from the engine at blend levels above B20. Significant increases in PM and HC emissions were measured at B50 and B100 levels (Skinner, 2007). Tests by the French railway operator SNCF with B20 showed some reduction in smoke number but increases in all other emissions (Skinner, 2007).

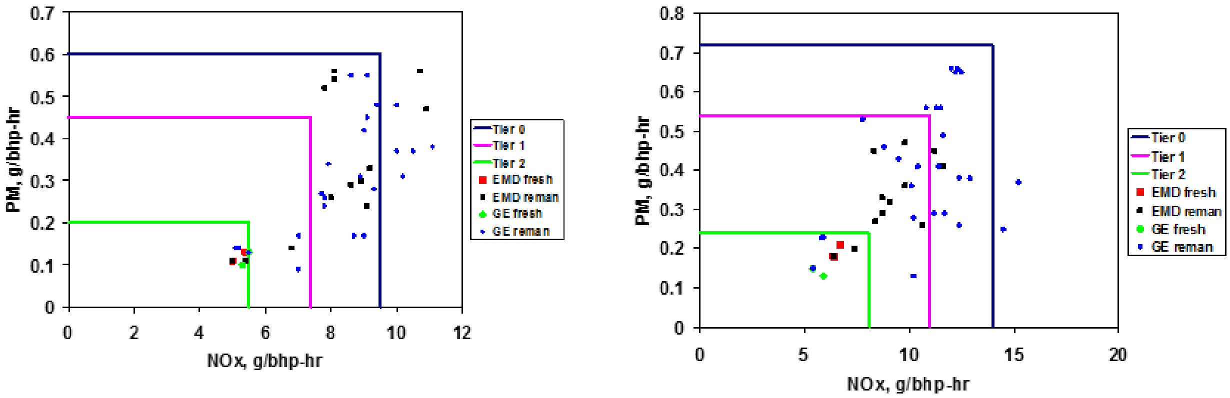
The results from the European tests also point to the fact that assumptions about emission reductions, especially for higher level blends, should not be taken as a given. Some level of testing is required to verify that locomotive operation and emissions performance will not be adversely affected.

3.3.2 NOx Increases

The increases in NOx with biodiesel blends may be a concern. A number of studies measured NOx increases that were comparable to or, in some cases, higher than those shown in Figure D9 (Fritz, 2004) (Su, 2005) (Osborne, 2010). Depending on the particular engine and the operating environment, these NOx increases could pose a significant challenge to using higher level blends of biodiesel, above B5. On the other hand, some studies have suggested that the use of B5 blends in locomotives would not produce a significant increase in NOx emissions (Fritz, 2013).

NOx increases were a particular concern for BNSF and UP railroads that operated under a "South Coast Locomotive Fleet Average Emissions Program" MOU with the California Air Resources Board (CARB, 1998). NOx was also the key issues for Canadian railroads that operated under an MOU with the Canadian government that capped NOx emissions. Estimated NOx emissions were near the capped limit and increases could not be tolerated (Dunn, 2003).

In-use NOx emissions higher than those achieved with certification fuel may also be a concern for EPA certified locomotives. Data from the 2007 EPA certification data base shows that little increase in NOx from locomotives meeting EPA Tier 1 and Tier 2 PM and NOx levels can be tolerated before NOx emissions exceed the line haul certification limit (Figure D11, left).



EPA line haul duty cycle

EPA switch duty cycle

Figure D11. EPA Certification Results for NOx and PM for Fresh and Remanufactured EMD and GE Locomotives

In switch mode however, there is a greater margin between the certification level and the certification limit for NOx. A larger increase in NOx could be tolerated before exceeding the certification limit. However, EPA certification rules state that locomotives over 2,300 hp must meet emissions over both cycles.

4 Compatibility with Existing Engines

4.1 Introduction

A number of concerns exist regarding the use of biodiesel blends, especially higher level blends (above B5) or B100, in existing diesel engines not designed for biodiesel fuels. The major potential issues are:

- *Material compatibility*—Depending on the engine make model and model year, the engine components that come in contact with the fuel can be made from incompatible materials.
- *Oil dilution*—A possibility exists with all engines that some fuel will make its way into the engine's crankcase and dilute the lubricating oil. Over time, the accumulated fuel can amount to a significant proportion of the engine's oil capacity. What happens to the lubricating oil and engine components that come into contact with the oil/fuel mixture can have an impact on engine durability and longevity.
- *Fuel injection equipment*—Impacts on fuel injectors, filters and other fuel system components can cause a significant deterioration in engine performance.
- *Emission control system*—Emission aftertreatment systems, including catalysts and particulate filters, can be negatively affected by biodiesel fuels. Increased engine emissions or shortened durability of emission components can result.

Experience with high-speed diesel engines indicates that low level blends—up to B5—can be used in most existing engines with no engine modifications. Almost all heavy-duty highway and non-road engine manufacturers allow up to B5 with no changes.

With blend levels higher than B5, compatibility depends on the manufacturer and specific engine model being considered. Some engines tolerate up to B20 with no changes. Other manufacturers have taken deliberate design steps to ensure their engines are compatible with higher level blends. Others offer OEM retrofit kits to make some engine models compatible.

4.2 Material Compatibility

Changes in fuel composition and the introduction of alternative fuels often create unforeseen problems in seals, gaskets, O-rings, as well as metallic components in the fuel system. An experimental laboratory study concluded that the physical properties of nitrile rubber, nylon 6/6, and high density polypropylene were affected by biodiesel and its blends while Teflon, Viton 401-C and Viton GFLT appeared to have good resistance to biodiesel, Table D7 (Besee, 1997).

Table D7. Biodiesel Compatibility with Elastomer Materials

Material	Effect of Biodiesel Relative to Diesel Fuel
Fluorosilicone	Hardness little change, swell +7%
Nitrile rubber	Hardness -20%, swell +18%, reduced tensile strength
Nylon 6/6	Decreased elongation, reduced tensile strength
High density polypropylene	Hardness -10%, swell +8 to 15%

Teflon	Little change
Viton 401-C	Little Change
Viton GFLT	Little change
Polyurethane	Hardness little change, swell +6%
Polyvinyl	Much worse
Tygon	Worse

Metals evaluated in the study included copper, steel, brass, aluminum, and bronze (Besee, 1997). Samples of metals were stored in the biodiesel and its blends for 6 months at 51.6°C. The samples were rated visually and the total acid number (TAN) of the fuels was determined. Copper containing metals (this included brass and bronze) exhibited severe corrosion when exposed to biodiesel and its blends. They also formed large amounts of gum when stored at elevated temperatures. It should be noted that copper is commonly used in locomotive engine fuel systems, for example in fuel heaters.

The steel and aluminum samples did not exhibit gum formation, but did exhibit exceptionally high total acid numbers which could corrode various parts of the fuel system. Zinc is also incompatible with biodiesel.

4.3 Fuel System Compatibility

In addition to the already mentioned fuel filter plugging, other potential compatibility issues with fuel systems have been investigated. Some fuel injection pumps lubricated by engine oil can introduce small amounts of lubricating oil into the fuel. It has been suggested that the polar nature of biodiesel may destabilize over-based detergents found in lubricating oil that enters the fuel system, leading to excessive deposits in the fuel filter and pre-mature fuel filter plugging (Fang, 2003).

Excessive deposit formation and wear in fuel injectors and pumps are also important considerations. According to some studies, biodiesel can have a negative impact on deposit formation in fuel injectors, especially if insufficient detergent additives are used (Caprotti, 2007). The deposits with biodiesel can include hard, carbonaceous coke materials, as well as compounds of calcium, phosphorus and magnesium (the latter study was performed with straight vegetable oil rather than methyl ester biodiesel) (Sem, 2004) (Li, 2009). Injector coking with biodiesel blends may lead to injector blockage. High pressure injection systems (e.g., those used for applications meeting more stringent emission standards) appear to be more vulnerable to this kind of problems.

Fuel system issues can be also caused by the presence of impurities (free methanol, water, glycerin, solid impurities…) and aging products (organic acids, polymerization products).

4.4 Engine Oil Dilution

Engine oil can be diluted by fuel, such as by fuel exiting the fuel injectors that did not fully vaporize and impinge on the cylinder liner. The differences in fuel properties of biodiesel (decreased volatility, higher surface tension and higher density) can lead to larger fuel droplets leaving the injector that travel farther and take longer to evaporate. These droplets are more likely to impinge on the cylinder wall and be scraped into the crankcase by the piston rings. Once in the crankcase, the higher boiling point biodiesel components are less likely to evaporate than the lower boiling point diesel fuel components.

Engine oil dilution issues using biodiesel can be aggravated by late injection and/or post-injection strategies, such as those commonly used in light-duty diesel engine for particulate filter regeneration. EU automobile manufacturers disallow the use of higher biodiesel blends or B100 in vehicles with particulate filters, presumably due to oil dilution during filter regeneration (performed via in-cylinder post-injection) and/or catalyst deactivation issues.

While it is still uncertain whether US Tier 4 locomotives will use particulate filters and, if they do, what regeneration strategies will be utilized, it can be noted that commercially available MTU locomotives for EU Stage IIIB applications (MTU 16V4000 R84 engine) utilize a DPF system with active regeneration strategy based on *retarded fuel injection* combined with intake air measures (without exhaust HC injection or a fuel burner) (Zitzler, 2014).

4.5 Aftertreatment Effects

Additional issues may exist with new engines fitted with catalytic exhaust aftertreatment, for instance particulate filters. While the issues are still not fully understood, potential problems may be caused by high ash levels in biodiesel PM due to the metal content (P, Na, K, Ca, Mg,…) in the fuel. In tests with B20 blends with metals at the maximum ASTM specification levels, the amount of ash in the DPF was doubled (Williams, 2011).

The presence of metals in biodiesel blends also carries the risk of catalyst deactivation. For instance, the 10 mg/kg level of phosphorus allowed in biodiesel by most standard specifications—considered sufficiently protective for low level blends—has been shown to cause catalyst deactivation with B100 (Krahl, 2006). Out-of-spec samples with even higher phosphorus content were reported by US biodiesel quality surveys (McCormick, 2005).

Potassium (K), sodium (Na) and calcium (Ca) from biodiesel blends can also deactivate catalysts, including SCR catalysts as well as DOCs and catalyzed DPFs (Krocher, 2007) (Williams, 2012) (Williams, 2013). In the latter study, tests with catalysts aged using B20 blends with metals at the maximum ASTM D6751 specification levels showed catalyst deactivation and loss of ammonia storage capacity in SCR washcoats in the aged samples. Alkaline metals that may be found in biodiesel (K, Na,…) are also known to corrode cordierite—a common material used for catalytic converter and particulate filter substrates.

4.6 FIE Manufacturer's Position

Faced with the increasing usage of biodiesel and with incidents of related engine problems, the major manufacturers of diesel fuel injection equipment (FIE) issued a common position statement on the use of biodiesel in 2000 which was later updated on several occasions (FIE, 2000) (FIE, 2004) (FIE, 2009).

Until 2007, the FIE manufacturers stated that blends of up to 5% of biodiesel in mineral diesel fuel should not create any serious engine problems if the final blend meets the European diesel fuel specification EN 590 at the point of sale, provided the biodiesel fuel used in the blend meets EN 14214. In 2009 they changed their position to allow up to 7% provided the biodiesel component meets EN 14214:2009 and the final blend meets EN590:2009. The inclusion of an oxidation stability requirement of 20 h (EN15751) in EN590:2009 assuaged FIE manufacturers concern over the oxidation stability of the finished blend. Resistance to oxidation has been a key biodiesel issue for the FIE manufacturers. Aged or poor quality biodiesel fuel may contain organic acids, free water, peroxides, and products of polymerization which can attack many components reducing the service life of fuel injection equipment.

In the North American market, an increasing number of new diesel models can be fueled with B20 blends. GM has approved B20 for use on all of their diesel vehicles starting with the 2011 model year (Lopes, 2013). This includes the 2014 Chevrolet Cruze diesel and the Duramax pick-up truck engines (the maximum blend is limited to B5 at temperatures below 0°C). Many diesel pick-ups utilize exhaust fuel injection for DPF regeneration (rather than in-cylinder post-injection) which makes them less sensitive to crankcase fuel dilution problems. Diesel cars of European brands (e.g., Volkswagen) sold in North America are typically compatible with blends up to B5 only. Many nonroad diesel engines can also be fueled with blends up to B20. For example, John Deere allows B20 in all new engine models. Blends up to B100 are allowed in John Deere engines *without diesel particulate filters*, provided the biodiesel is permitted by law and meets the EN 14214 specification.

The use of blends above B5 may come with special maintenance requirements, such as shortened oil change intervals or the use of manufacturer-approved fuel conditioners. Volvo Truck North America, for instance, allows the use of biodiesel blends up to B20, but customers need to utilize oil sampling to establish appropriate drain intervals for their application (Volvo, 2011). In the case of John Deere nonroad engines, all Tier 3 models can be used with blends up to B20 with no additional requirements, while Tier 4i models require the use of fuel conditioners containing detergent/dispersant additives when fueled with B10 and higher blends. This precaution is intended to prevent possible fuel injector coking/blocking with B10 and higher blends. Fuel systems used in the Tier 4i engines have higher injection pressures than those in Tier 3 engines, which makes them more vulnerable to injector deposits.

4.7 Locomotive Manufacturer’s Position

Positions on the use of biodiesel have been also issued by manufacturers of locomotives and locomotive engines. Since the late 2000s, when B5 blends were introduced into commercial No. 2 diesel fuels, manufacturers generally allow B5 biodiesel blends.

- GE—Blends of up to B5, which can be sold as No 2 diesel, have been approved by GE for use in their locomotive engines (CP, 2010) (Nelson, 2012). Under the express terms of GE’s warranty, the failure of the railroad to use the prescribed fuel (i.e., No 2 diesel) voids the contractual warranty obligations (GE, 2006).
- EMD—Blends up to B5 meeting ASTM D975 have been approved for use in EMD engines (Nelson, 2012). With higher blends, if an engine failure arises as a result of using biodiesel, it will be not covered by the engine warranty (EMD, 2005). EMD also noted that fuel system components may require modification to accommodate the lower energy content of biodiesel fuels.
- MotivePower allows the use of biodiesel blends up to B20 in the Head End Power engine, in consultation with Caterpillar, the engine manufacturer. Caterpillar allows the use of B20 biodiesel in most of their products if the fuel meets the applicable specifications and is sourced from BQ-9000 certified suppliers.

5 Railway Experience

5.1 Fuel Supply

5.1.1 Overview

There are a number of possible fueling pathways that can affect where and how the biofuel component is blended into diesel fuel that can potentially impact the quality of the biodiesel blend used to fuel a locomotive.

There are two main methods used by fueling railway locomotives:

- Wayside fueling, conducted from fuel tanks at the railyard facility, and
- Direct-to-locomotive (DTL) or direct truck to locomotive fueling performed at the side of the tracks, directly from a fuel supply truck.

DTL fueling allows for better utilization of locomotives and has been gaining importance compared to the historically predominant wayside fueling. At Canadian National Railway (CN), for example, DTL fueling is believed to account for more than 20% of the total fuel volume used by locomotives (Dunn, 2013).

The biodiesel blending levels and blending methods have undergone an evolution since the initial biodiesel trials. During the biodiesel demonstrations conducted by railways in the late 1990s and early 2000s, B20 was used in most of the trials and splash blending was employed, usually performed by smaller size, independent fuel suppliers. The overall biodiesel volumes were small, as the usage was limited to isolated demonstration programs and trials.

Since the introduction of the RFS-2 renewable fuel requirements, biodiesel has been blended into a significant proportion of the nationwide No. 2 diesel supply. The overall biodiesel volumes have increased and most of the blending is performed at fuel terminals operated by fuel manufacturers or large distributors. B5—allowed by ASTM D975 (without labeling)—is the most common biodiesel blend. The state of Illinois appears to be the most significant exception, where quantities of B11 have been introduced with sales driven by state tax incentives.

5.1.2 Biodiesel Blending at the Fuel Terminal

Under the RFS-2 rule (and the renewable fuels regulations in Canada), fuel suppliers must blend certain minimum quantities of renewables into gasoline and diesel fuels. Biodiesel remains the only renewable diesel fuel of practical significance that can be blended into diesel fuel.

In colder climates, biodiesel is blended into diesel fuel only during spring and summer months. In the Canadian prairies, for example, commercial diesel fuel sold by Shell can contain 5% of biodiesel from April 1st until September 30th, while no biodiesel is added from October through March (Mitchel, 2013).

Most of biodiesel blending to comply with RFS-2 and Canadian renewable fuels requirements is performed at fuel terminals (Mitchel, 2013). As most pipeline operators prohibit the transportation of biodiesel in pipelines, the B100 is brought into the fuel terminal by trucks or rail. The B100 blending stock is stored in small, heated and insulated tanks. The heating is typically accomplished by circulating the biodiesel through a liquid-to-liquid heat exchanger. The temperature of the B100 is maintained at least 6°C above the cloud point, to avoid precipitation and to enhance blending. In some fuel terminals biodiesel tanks are fitted with filters for the incoming B100, while others do not filter the biodiesel blending stock (Mitchel, 2013) .

Biodiesel blending is performed via side-stream blending directly into diesel fuel delivery trucks. Splash blending is no longer used by any of the major US or Canadian fuel suppliers (Mitchel, 2013) .

Shell in the US and Canada has been using exclusively biodiesel ASTM D6751-12 Grade 1-B (with specifications on monoglycerides and CSFT, see Section 2.2.1) as the blending stock. Even prior to the adoption of ASTM D6751-12, Shell required that the B100 met concentration limits for monoglycerides. It is believed that most other fuel suppliers, especially large manufacturers and distributors, also use biodiesel Grade 1-B for blending into No. 2 diesel.

While the issue has not been well documented, there appears to be more incidents of filter blockage in fuel dispensing pumps at Shell Canada fuel stations (serving trucks and light-duty vehicles) since the introduction of biofuel mandates (Mitchel, 2013) .

5.1.3 Biodiesel Blending by Independent Suppliers and Railroads

In addition to purchases from a fuel terminal, railroads may be supplied with biodiesel blends by smaller size contractors and blenders. There are a number of possible scenarios, including:

- DTL fueling with No. 2 diesel (often including up to 5% biodiesel) that is supplied by tank trucks operated by independent contractors. In this case, the fuel would be typically acquired by the contractor from a fuel terminal.
- Fueling locomotives with biodiesel blends above B5 for biodiesel demonstrations/trials and when financial incentives exist to buy biodiesel (e.g., B11 in Illinois). In this case, there are a number of logistic pathways usually including smaller size fuel blenders, as higher biodiesel blends are not available from diesel fuel manufacturers. In several demonstration programs, biodiesel from a local blender was supplied by trucks for DTL fueling. In cases where biodiesel purchases are driven by economics, the higher blends may be diluted before use. For example, one railway company took delivery of B2 and B11 tank trucks in the Chicago area and splash blended the biodiesel in their main tanks to a B5 concentration (McAndrew, 2013).
- In some cases, railways can buy No. 2 diesel (B0) and blend it with B100 on their own. This practice has been occasionally used by CN (Dunn, 2013) who bought biodiesel-free diesel fuel in the US (RFS-2 requirements do not apply for fuels exported from the US), brought it into Canada and splash blended with B100 in the rail tank cars to satisfy the Canadian renewable fuel requirements.

A number of quality issues are possible with biodiesel blends sourced from suppliers of uncertain quality record. For instance, splash blending which is often used does not ensure thorough mixing of the biodiesel, potentially leading to fueling of locomotives with blends higher than anticipated. Whenever possible, railway should also insist that suppliers use the higher quality grade 1-B biodiesel rather than grade 2-B.

In the US, No. 2 diesel can include up to 5% biodiesel without labeling. Biodiesel blenders produce higher blends, for instance B20, by blending 80% of commercial No. 2 diesel with 20% of B100. If the commercial No. 2 diesel already contains 5% biodiesel, the final blend will be closer to B24 than to the nominal B20.

5.1.4 Fuel Quality

The quality of the biodiesel used for blending depends entirely on the biodiesel supplier. Only very basic tests are conducted on receipt of the biodiesel blending stock at the terminal, including visual appearance and density. These tests ensure that received fluids are correctly identified and unloaded from the rail car or truck into the right tank at the terminal. Compliance with specifications (including ASTM D6751 and any additional requirements specified by the buyer) is determined based on the certificate of analysis (COA) provided by the biodiesel supplier. Example COAs for B100 blending stocks intended for commercial diesel fuel are included in Attachment A. These COAs, obtained from Shell Canada, include certificates from both actual and prospective suppliers of B100 blending stock to Shell.

During the storage of B100 at fuel terminals, periodic analyses must be performed to ensure biodiesel stability. At Shell Canada terminals, B100 samples are taken monthly and tested for oxidation stability, microbiological growth and flash point (Mitchel, 2013).

Fuel quality—diesel fuel and biodiesel blends—is tested by some railroads, according to responses to the LMOA biofuel survey (Mitchel, 2013). Common tests conducted by one railway include visual analysis, API gravity, thermal stability, biodiesel, sulfur, lubricity (wear scar), and cetane. Water and sediment is tested if sample is noted to have visual particulates or cloudiness. Winter testing includes cloud point, pour point, and a proprietary cold soak filter plugging test (CSFPT). There are also railroads that do not conduct their own routine quality testing, or conduct only a limited set of tests, and rely on the quality assurance system and the COAs provided by the fuel supplier (Dunn, 2013).

5.2 Wayside Storage

Railways store diesel fuel at the railyards in large fuel tanks, with capacities often on the order of millions of gallons (Dunn, 2013). The tanks are filled with fuel and the locomotives are fueled from the tanks via connections at the bottom part of the tank. At their lowest point, the tanks are typically fitted with drains to remove the accumulated water and sludge.

Since the wayside tanks were not designed for biodiesel, they are typically not insulated, not heated and there are no provisions for mixing of the stored fuel. One of the consequences is that biodiesel blends supplied to the tank in summer may persist, with poor mixing, long into the winter months. In theory, a number of issues are possible with biodiesel blends, including deposits at cold temperatures, microbial growth, or corrosion due to increased likelihood of water presence. Several incidents of problems apparently related to biodiesel have been reported. However, due to the relatively short period of biodiesel usage, as well as the limited number and incidental character of the existing reports, it remains unclear if biodiesel blends are indeed responsible for operational problems at wayside storage facilities. There has been no quantitative assessment of the issues and there is no ‘control group’ of tanks for making comparisons. With good housekeeping programs, it appears that blends up to B5 can be stored in most of the existing facilities.

The issue of corrosion of the tanks and tank equipment (pumps, etc.) has been further obscured by the so far unexplained phenomenon of increased corrosion in ULSD tanks. Since 2007, rapid corrosion has been observed in some systems storing and dispensing ULSD fuel in the United States. In the affected systems, corrosion was coating the majority of metallic equipment in ULSD underground storage tanks (UST), such as submersible turbine pumps, drop tubes, sensor probes and dispenser components. While initially linked to the 2006 launch of ULSD, later work suggested contamination of diesel USTs by ethanol may also be a contributing factor. Mandatory blending of ethanol in gasoline in the US market started a few months later, in 2007. A study by the Battelle Memorial Institute suggested that the corrosion was likely caused by the dispersal of acetic acid throughout USTs (Battelle, 2012). The acetic acid was thought to be produced by Acetobacter bacteria feeding on low levels of ethanol contamination. The report went on to speculate that acetic acid, dispersed into the humid vapor space by its higher vapor pressure and by disturbances during fuel deliveries, was deposited throughout both the wetted and unwetted portions of the system where it corroded metallic equipment. Plausible sources of ethanol contamination of diesel USTs could include tanker truck switch-loading practices and manifolding problems in retail fuel station storage tanks. However, it should be noted that the appearance of corrosion issues that coincide with the introduction of ULSD have also been reported in Canada, where ethanol use has not been as ubiquitous as in the United States. In addition to microbial contamination, other potential contributors commonly cited include salt contamination, corrosion inhibitor depletion and poor housekeeping.

Incidents of increased sludge and microbial contamination of wayside tanks have been reported (McAndrew, 2013). One railway reported that out of 7 locations, 3 were contaminated with water and microorganisms in connection with biodiesel. However, the affected tanks could not be drained in winter resulting in accumulation of water and debris. The same railway company initially reported no issues, when tanks were drained from water on a weekly basis.

Incidents of leaking wayside fueling systems seals were also linked to biodiesel (McAndrew, 2013).

Removing water from the fuel storage tanks is critical. Bulk wayside tanks (as well as locomotive fuel tanks) are provided with the capabilities to remove water and this should be done regularly. Additives can also be used to control water content.

If the tank becomes contaminated through microbial growth, remediation techniques must be applied to return the fuel and the fuel system to acceptable conditions. The choice of remediation techniques may include fuel polishing (primarily involving filtration), the use of biocides to control microbial growth, and tank cleaning (Passman, 2003). Therefore, wayside facilities should have procedures in place for cleaning the tanks when contaminated.

5.3 Rail Operational Experience

5.3.1 Introduction of Biodiesel in Rail

The patterns of biodiesel usage by US railway companies have evolved over time, following the evolution of the general driving forces that were responsible for the commercialization of biodiesel. In the initial years—from the late 1990s to the late 2000s—biodiesel use was largely limited to local trials and demonstration projects. The drivers behind these projects included the perceived environmental and fuel security benefits, which positively reflected on the company PR image. Several early projects were also driven by economics—several biodiesel demonstrations received state or federal grants to offset the cost of fuel. There was also a period in 2008, when the prices of biodiesel matched those of petroleum diesel, creating hopes that biodiesel may become a cost-competitive fuel option. These hopes quickly faded away, and several biodiesel demonstration projects were terminated due to the high cost of biodiesel.

Since the adoption of RFS-2 renewable fuel requirements, volumes of biodiesel must be blended into commercial diesel fuel, with B5 being the maximum blend level that has been used nationwide. The biodiesel blending requirements started around 2009 and a sharp increase of biodiesel consumption was recorded in 2011 (compare Figure D2). The RFS-2 quotas are currently the major driver of biodiesel consumption, with most of biodiesel consumed in the United States being blended into the general pool of diesel fuel, including fuel used by railways.

In spite of the growing exposure to biodiesel, the operational experience of railways remains poorly documented. While a number of engine incidents have been linked to biodiesel, the impacts of biodiesel blends on locomotive engines are still not well understood. This is especially true in regards to long term effects—none of the biodiesel trials conducted so far had a sufficient duration and/or were properly designed to shed more light on the long term biodiesel effects. A protocol for such locomotive durability test has been proposed by the Locomotive Maintenance Officers Association (LMOA) (McAndrew, 2012).

5.3.2 Potential Sources of Operational Issues with Biodiesel

A number of locomotive engine components can be potentially affected by biodiesel, including (McAndrew, 2012):

- *Pre-combustion system*: fuel tank, volume (reduction of onboard fuel energy), low pressure suction pump, fuel heater, pipes and hoses, fuel filters, high pressure pumps.
- *Combustion*: injection and combustion process (needle list timing, injection spray, injection delay, kinetics of pre-mixed and diffusion controlled combustion stages); ring groove deposits; cylinder liner (increased rates of varnish/lacquer deposits); the ability to maintain full power with high biodiesel blends; fuel consumption penalty.
- *Post-combustion*: exhaust temperature, emissions, turbo speed, blow-by gases (lube oil dilution and oxidation).

The existing operational experience seems to indicate that the most common issues with biodiesel include plugged fuel filters and damaged fuel injectors. Several examples can be found in responses to the biodiesel survey conducted by LMOA (McAndrew, 2013). An SD40 locomotive was found to have stuck/damaged injectors due to a B20 test in 2010-2011. Several switch locomotives with HPCR injectors were found to have stuck injector pilot valves. Analysis revealed a coating of carboxylate ‘soap’, an issue known in the industry as a reaction between corrosion inhibitor and excess sodium in the fuel, potentially coming from biodiesel.

In Minnesota, fuel pump and injector failures in several locomotives were reportedly caused by B5 biodiesel delivered by mistake to the Minnesota Commercial Railway (Hennessy, 2013). The reported extent of damage, however, seems inconsistent with B5 fueling. It may be possible that the problems were caused by out-of-spec biodiesel or that a blend higher than B5 was used.

5.3.3 Biodiesel Demonstration Projects

A survey of railway biodiesel projects conducted in the United States and Canada over 1996–2011 has been commissioned by the national Biodiesel Board (Nelson, 2012). Twenty biodiesel projects were identified, Table D8.

Table D8. Summary of Biodiesel Demonstrations (1996–2011)

Railroad	Location	Duration (months)	Blend	# of Units & hp	Engine	Tier
Passenger Train / Commuter						
Amtrak Heartland Flyer	OK - TX	12	B20	1 3200	GE P32-8	1
New Jersey Transit	New Jersey	19	B20	2	645E3B 710GB	
South Florida Tri Rail	Miami/WPB, FL	96	B20	16 2000 2800	EMD 645 CAT 3412 Detroit 3406	0
Santa Fe Southern	Santa Fe, NM	54	B20	2 1500	EMD GP-7	n/r
NM Rail Runner	NM	12	B20	5 3600	EMD rblt.	1
Indiana State Fair RR	IN	0.5	B10	2 1500	EMD 6P-7 EMD 6P-9	n/r
Line Haul Freight						
Iowa Interstate RR	Council Bluffs, IA	6	B20	1 2000	GM EMD GP 38-645E	0
Canadian Pacific	Calgary - Edmonton	5	B5	4 4400	GE AC 4400	1
Eastern Washington Gateway RR	WA	3	B25	1 3600	GM EMD	n/r
Genesee Wyoming GWI RR	Provo – Ogden, UT	3	B20	1 3000	GM EMD 16-645E3	0

MN Prairie Line RR	St. Paul, MN	42	B5	2 2000	Caterpillar GP20, GP15	n/r
Short Line / Switching						
Alabama State Port Authority RR Yard	Mobile, AL	3	B20	8	Older switching	0
BNSF Railway / Montana State University	MT	9	B20	1	SD-40-2	0
GWI	Kingsboro, TN	48	B20	5 1500 1800	GM EMD	1
US Navy Crane Naval Base	Crane, IN	60	B20	7	EMD-1200 Rblt QSK19	n/r
US Steel Switching Yard	Gary, IN	48	B10	22	EMD rblt. 1950s era	n/r
San Francisco Bay LB RR	San Francisco, CA	36	B50	1 1000	Alco S-2	n/r
Richmond Pacific Switching Yard	Richmond, CA	12	B5	3 1200	EMD 1200	n/r
Specialty Locomotives						
Sierra Railroad Powertrain Electricity Generation	Davis, CA	6	B100	6 3000	GE B30-7A	n/r
Mt. Washington Cog Railway summer tourist train	Conway, NH	12	B10	1 600	J. Deere 6125H	2

In the survey, a total of 91 engines were operated on biodiesel. Thirty-four locomotives were operated using B5–B10 blends, fifty on B20-B30, one on B50, and six on B100. A significant number of engines were non-regulated.

While a useful inventory of biodiesel trials, the NBB survey provides little insight into the operational experience with biodiesel. The projects descriptions include brief, subjective summaries indicating that “no problems were reported” in some projects, while “some low temperature problems were experienced” in others. In either case, no test particulars or analytical data is offered, suggesting that most of the demonstrations did not include a rigorous testing program. Four railroads cited improved engine performance with B20 while two other railroads cited an improvement in fuel efficiency with B20 and B50, without providing any supporting data or discussion of the rather surprising observation.

One of the studies from Table D8 that included a rigorous evaluation and published a final report was the cold weather trial conducted by Canadian Pacific in cooperation with GE (CP, 2010). The CP biodiesel test was conducted under cold weather conditions in Alberta, in the winter of 2009/2010. The project was conducted as part of the National Renewable Diesel Demonstration by Natural Resources Canada—a feasibility demonstration initiative in support of the then proposed (now final) provisions of the Canadian Renewable Fuels Regulations that require an average 2% renewable fuel content in diesel fuel based on annual volumes.

The focus of the CP study was to assess the feasibility of using B5 biodiesel blends in freight locomotives operating in cold weather service. Due to the relatively short duration of the trial—about 150 days—long term biodiesel effects were not investigated. Four GE AC4400CW diesel-electric locomotives, including three Tier 1 and one Tier 0 unit, were held in captive service on the CP mainline between Calgary and Edmonton for the period of November 2009 to March 2010. Ultra-low sulfur diesel was splash blended with soy-based biodiesel to produce the resulting B5 biodiesel. All fueling was conducted by way of DTL. Despite temperatures below -40°C, CP experienced no temperature-related interruption of service. GE’s engine inspections further demonstrated no negative mechanical effects from the use of B5 biodiesel.

It should be noted that the CP study has not investigated the effects of cold weather on the storage requirements of biodiesel, and the fuel was never allowed to reach ambient temperatures. Product was transferred directly from supplier heated storage tanks to fuel trucks, and fueling of the locomotives took place on the trucks’ arrival.

In Brazil, GE has conducted a number of tests to enable the operation of locomotives on biodiesel. The projects have been apparently driven by Brazilian renewable energy regulations. According to unpublished reports from some of the earlier tests, GE locomotives (presumably unmodified) operated on biodiesel blends in Brazil experienced compatibility issues with fuel injection hoses, leading to leaks from fuel supply and jumper lines. The most recent project, conducted in cooperation with Brazilian partners including Vale and completed in 2013, involved operating GE locomotives using blends up to B25.

In B20 trials using Bombardier Class 220 and Class 221 locomotives equipped with Cummins QSK19-R engines by Virgin Cross Country in the UK, modifications were made to the fuel feed and return lines, fuel filter and fuel fill adapter (Edwards, 2007).

6 Conclusion

The use of biodiesel in the United States has been increasing, driven by the RFS-2 and by mandatory requirements introduced by some States. Under the ASTM D975 standard, up to 5% biodiesel can be blended in No 2 diesel without disclosing it to the customer. The railway industry must ensure that locomotives can be operated with at least B5 blends.

The literature search suggests that recent science and the US energy security situation provide little justification for the continued use or expansion of crop based biofuels. The future of biofuels seems to be a political issue that will depend to a large degree on the agricultural subsidy policy at the federal and state levels. The outcomes of the political debate are difficult to predict—one possibility is that that future biodiesel mandates may increase. Blend levels up to B20 have been already considered by some states.

Testing biodiesel blends in medium speed diesel engines to date in North America has been limited. The data available suggests that biodiesel impacts on medium-speed engines may not necessarily mirror those in high-speed diesel engines. Additional work is needed to characterize the effects of biodiesel blends, especially blends above 5%, up to 20%. The areas that require further research include:

- Effect on emissions and performance on EPA regulated Tier 0–Tier 4 locomotives. The effects on NOx emissions from existing locomotives is especially of concern as even a small increase in NOx from these engines may cause emissions to exceed the certification limits and/or the NOx emission caps under MOUs with railroads that are in place in parts of California and in Canada.
- Effects on combustion and fuel injection system behavior. Impact on the long term performance of the fuel injection system, with a focus on newer, Tier 3+ locomotives that utilize high pressure fuel injection systems believed to be more sensitive to injection deposit formation and blocking with biodiesel.
- Oil dilution in medium speed engines and the effect on engine durability.
- Low temperature operability issues.
- Effect on aftertreatment devices that may see use in Tier 4 locomotives, including SCR catalyst systems and diesel particulate filters.
- Compatibility with the current lubricating oil specifications.

Wayside storage of biodiesel blends is another area of concern. Existing experience seems to indicate that blends of up to B5 can be stored in wayside facilities—with good housekeeping—with no problems. Storage of higher blends may lead to such problems as precipitate formation in cold weather, at temperatures above those for diesel fuel, and microbial growth. Guidelines should be developed that would cover the feasibility and the relevant procedures for wayside storage of higher biodiesel blends. Considering the wayside storage concerns, direct-to-locomotive (DTL) fueling with B5 blends from commercial fuel terminals presents a less risky fueling option in terms of potential biodiesel related issues.

Still another source of uncertainty with biodiesel fuels is related to the feedstock. While most of US biodiesel is made from soybeans, some of the larger scale biodiesel plants can process the more cost-effective, imported palm oil feedstock. It is known that palm oil biodiesel has poorer low temperature operability properties than most other biodiesels. In the future, biodiesel can be also made from algae, with a yet unknown impact for the fuel properties.

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Abbreviations and Acronyms

B5	5 Percent Biodiesel
B20	20 Percent Biodiesel
B100	100 Percent Biodiesel
ARB	Air Resources Board
API	American Petroleum Institute
AAR	Association of American Railroads
ASTM	ASTM International
Bxx	Blend of xx Volume Percent Biodiesel in Petroleum Diesel
CO2	Carbon Dioxide
COA	Certificate of Analysis
CFR	Code of Federal Regulations
CSFPT	Cold Filter Plugging Test
CSFT	Cold Soak Filtration Test (or time)
DOE	Department of Energy
DGE	Diesel Gallon Equivalent
DOC	Diesel Oxidation Catalyst
DPF	Diesel Particulate Filter
DTL	Direct-To-Locomotive
EMD	Electro Motive Diesel
EDS	Energy Dispersive Spectroscopy
EISA	Energy Independence and Security Act of 2007
EPAct	Energy Policy Act of 2005
EROI	Energy Return on Investment
EPA	Environmental Protection Agency
EN	European Standard
FAME	Fatty Acid Methyl Ester
FRA	Federal Railroad Administration
FTP	Federal Test Procedure
FTC	Federal Trade Commission
FTIR	Fourier Transform Infrared
FIE	Fuel Injection Equipment

FL&E	Fuel, Lubes, and Environment Committee
GE	General Electric
GHG	Greenhouse Gases
GREET	Greenhouse Gases, Regulated Emissions, and Energy Use
HPCR	High-Pressure Common-Rail
HC	Hydrocarbons
HDRD	Hydrogenation Derived Renewable Diesel
IPCC	Intergovernmental Panel on Climate Change
CIMAC	International Council on Combustion Engines
IDID	Internal Diesel Injector Deposits
IEA	International Energy Agency
LEM	Life Cycle Analysis
LMOA	Locomotive Maintenance Officers Association
LCFS	Low Carbon Fuel Standard
MOC	Management of Change
MOU	Memorandum of Understanding
NBB	National Biodiesel Board
NRDDI	National Renewable Diesel Demonstration Initiative
NREL	National Renewable Energy Laboratory
NRC	National Research Council
B100	Neat Biodiesel
N_2O	Nitrous Oxide
NOx	Nitrogen Oxides
PME	Palm Oil Methyl Ester
RME	Rape Seed Oil Methyl Ester
RFS	Renewable Fuel Standard
RFS-2	Renewable Fuel Standards: Final Rule
SEM	Scanning Electron Microscope
SCR	Selective Catalytic Reduction
SwRI®	Southwest Research Institute
SME	Soy Methyl Ester
TFLRF	TARDEC Fuels and Lubricants Research Facility

TARDEC	Tank Automotive Research Development and Engineering Center
TAN	Total Acid Number
UST	Underground Storage Tank
UP	Union Pacific Railroad
EIA	U.S. Energy Information Administration
XRD	X-Ray Diffraction