CRC Report No. DP-04-17

CRC INTERNAL DIESEL INJECTOR DEPOSIT (IDID) TEST: HARDWARE, FUEL, AND ADDITIVE EVALUATIONS

September 2019

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

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CRC Internal Diesel Injector Deposit (IDID) Test: Hardware, Fuel, and Additive Evaluations

CRC Project No. DP-04-17

FINAL REPORT

Prepared for:

Coordinating Research Council, Inc.
5755 North Point Parkway, Suite 265
Alpharetta, GA 30022

Prepared by:

G.R. Wilson
D.M. Yost
J.E. Gomez
S.R. Westbrook

Southwest Research Institute® (SwRI®)
San Antonio, TX

September 2019

Reviewed by:

Kevin Shannon, Manager
Fuels & Lubricants Technology Department

Approved by:

Scott A. Hutzler, Director
Fuels & Lubricants Technology Department

EXECUTIVE SUMMARY

The objective of this project was to establish and demonstrate a new test system to evaluate internal diesel injector deposits. This methodology is a combination of an injector deposit test rig and a novel, spectroscopic technique to measure deposit thickness. The project was not designed to be a comprehensive study of the factors that affect injector deposit formation.

- A new IDID test system, based on previously published work, was assembled.
- Thirteen tests were performed to demonstrate that the assembled test rig could rank fuels similarly to results from previous rig and engine tests. Results from these tests were:
  1) Test rig capability to discriminate between fuels with and without contaminants/additives.
  2) Capability to discriminate between high and normal additive levels.
  3) Discrimination was demonstrated using both visual rating and VASE deposit thickness measurement methods.
  4) Longer rig run time (21 hr vs. 7 hr) produced thicker deposits for fuel with normal additive/contaminant treat rates, as expected.
  5) Discrimination between additive/contaminant levels was demonstrated at both 21 hr and 7 hr run times.
- Seventy tests were conducted using fuels blended to a designed experimental plan. The fuels were blends of a base diesel fuel (clay-treated to remove additives) and combinations of eight different contaminants and/or fuel additives.
- Using the Variable Angle Spectroscopic Ellipsometer (VASE), pintle deposits as thin as 10 nanometers were measurable. Deposits of this thickness are not discernable to the unaided eye.
- Statistical analysis of the VASE/deposit results showed:
  - There were no statistical outliers.
  - Regarding deposit by location on the injector pintles:
    - No significant axial location differences.
    - No significant radial location differences.
  - Sodium increases deposit thickness.
  - No significant corrosion inhibitor and cetane number improver differences.
  - Detergent additive reduces deposit thickness in fuels without biodiesel.
  - Sodium increases deposit thickness in fuels without:
    - Detergent additive.
    - Glycerin.
    - Mono-acid lubricity additive.
  - Conductivity additive increases deposit thickness in fuel without:
    - Biodiesel.
    - Glycerin.
  - Conductivity additive increases deposit thickness in fuel with mono-acid lubricity additive.

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ACKNOWLEDGEMENTS

The authors wish to acknowledge the support of the Coordinating Research Council for this work. We also greatly appreciate the statistical analyses performed by Jo Martinez of Chevron. Special acknowledgement is also given to Delphi Technologies Ltd for providing the test method that was the basis for the test rig and test conditions.

ACRONYMS & ABBREVIATIONS

°	degree
%	percent
µm(b)	micron (b)
F	Fahrenheit
g	grams
GPM	gallons per minute
kPa	kilopascals
L/sec	liters per second
mg/L	milligrams per liter
psi	pounds per square inch
psid	pounds per square inch, differential
AFLRF	Army Fuels and Lubricants Research Facility (SwRI)
ATR	Attenuated Total Reflectance
CARB	California Air Resources Board
CLyy-xxxx	SwRI Chemistry Lab Sample ID (yy = year, xxxx = sample number)
CRC	Coordinating Research Council
DDSA	Dodecyl Succinic Acid
DPG	Diesel Performance Group (CRC)
EMRE	ExxonMobil Research and Engineering
EPA	Environmental Protection Agency
FTIR	Fourier Transform Infrared Spectrometry
HDD	Heavy Duty Diesel
IDID	Internal Diesel Injector Deposit
MTxx	Matrix Test (xx = test number)
ND	Non-Destructive
PTxx	Proof Test (xx = test number)
RFP	Request for Proposal
SwRI	Southwest Research Institute
VASE	Variable Angle Spectroscopic Ellipsometer

1.0 INTRODUCTION AND OBJECTIVE

Since 2012 three studies related to diesel internal injector deposits/sticking have been conducted under the Diesel Performance Group of the Coordinating Research Council (CRC).[1,2,3] The work done under the 2016 project established a reasonable correlation between the Delphi-designed Internal Diesel Injector Deposit (IDID) rig and an actual commercial heavy-duty engine. This correlation showed that the Delphi rig had the ability to discriminate between fuels that result in internal injector sticking and those that do not. The 2016 project was designed to evaluate the rig capability only, it did not investigate the specific effects of fuels, additives, or impurities.

In addition to the work on the IDID approach, CRC organized a small proof of concept program with ExxonMobil Research and Engineering (EMRE) to evaluate the potential use of ellipsometry to provide a more sensitive measurement of internal deposits than can be done visually. This program showed it was possible to map the deposits that form on the fuel injector pintle, a key capability that allows more precise and sensitive quantitation of fuel deposits.

Since the 2016 IDID rig work demonstrated a meaningful correlation, between the rig and the engine, and the EMRE tests showed a promise of a breakthrough analysis technique, the CRC Diesel Performance Group (DPG) agreed that both avenues should be pursued under a single project. Therefore, the CRC issued a request for proposal (RFP) for a project to 1) set up the IDID rig at a U.S. research facility and 2) develop a novel injector deposit evaluation system for evaluation of fuels and additives, and impurities.

The objective of CRC project DP-04-17 was to establish and demonstrate this combination of capabilities to generate and measure IDID. It was not designed to be a comprehensive study of the factors that affect IDID.

2.0 TEST RIG

2.1 Test Rig

The CRC Request for Proposal (RFP) directed that the contractor should set up the test rig according to the description provided in the "Test Methodology for IDID Apparatus" that was attached to the RFP. According to the RFP, the rig was designed to accelerate formation of internal injector deposits. The operating parameters of the rig simulate severe engine operating conditions for light duty vehicle, high pressure, common rail systems. It was anticipated that test results would be useful for HDD, heavy duty diesel, engines as well.

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[1] "Scoping Study to Evaluate Two Rig Tests for Internal Injector Sticking," CRC Project DP-04, July 2012.
[2] "Internal Injector Deposits; A Scoping Study to Evaluate the Delphi Test Rig," CRC Project DP-04-13b, August 2013.
[3] "Internal Injector Deposits; Correlation of the Delphi Test Rig with Production Engines," CRC Project DP-04-10, March 2016.

The rig was mounted on an electric motor-driven test stand. Injected fuel was not recirculated. The operating conditions were selected to continuously reproduce conditions that mimicked the severe thermal soak back conditions similar to that which would briefly occur during idle, immediately following extended operations at full power on an engine or vehicle. To achieve this, elevated temperatures were maintained using an electrical heater to replicate combustion heat combined with high injection pressures. A slow injection rate was used, similar to that observed during engine idle operation, which gave time for fuel deposit-forming reactions to occur and also minimized fuel consumption. It was a continuous replication of transient shut down condition. Injection pressure and temperature were high. Injected volume was low. This resulted in providing maximum stress to the fuel with minimum fuel flow.

Although Delphi injectors were used in the current study, the rig is not specific to any fuel injection equipment (FIE) design or brand. Neither the test program nor the apparatus were intended for evaluation of FIE design or construction. Electric heaters were used to replicate combustion temperature.

Figure 1 is a schematic diagram of the test rig and Figure 2 is a photograph of the rig constructed under this project.

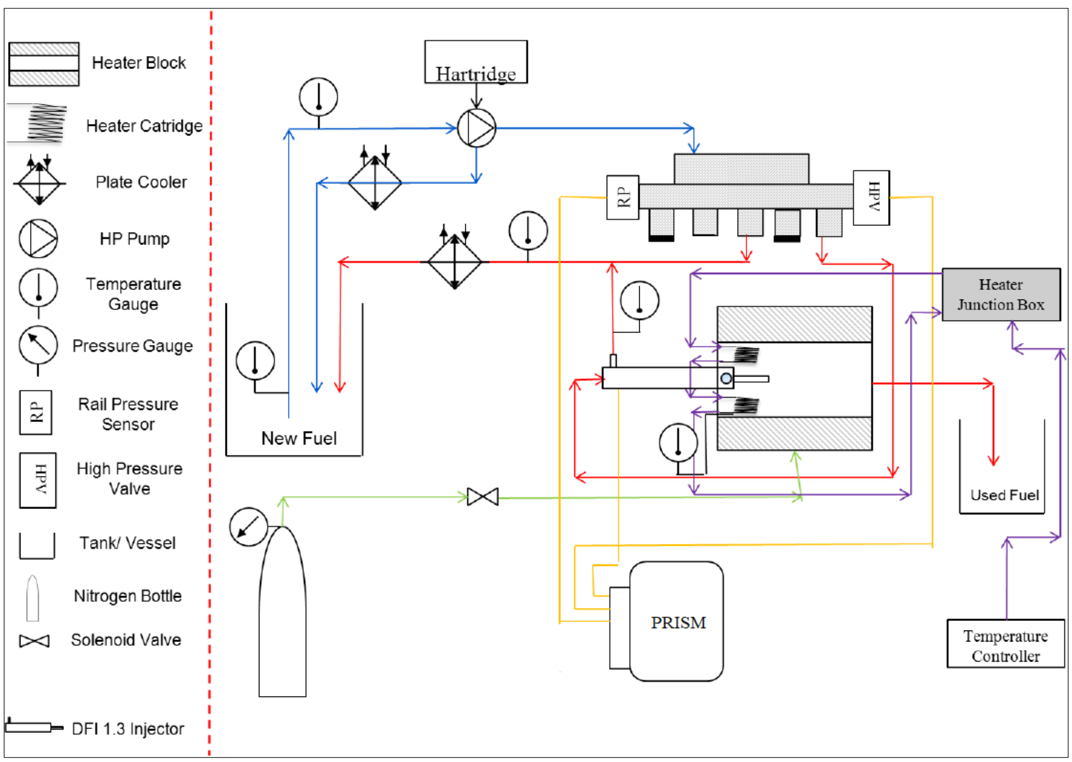


Figure 1. Test Rig Schematic

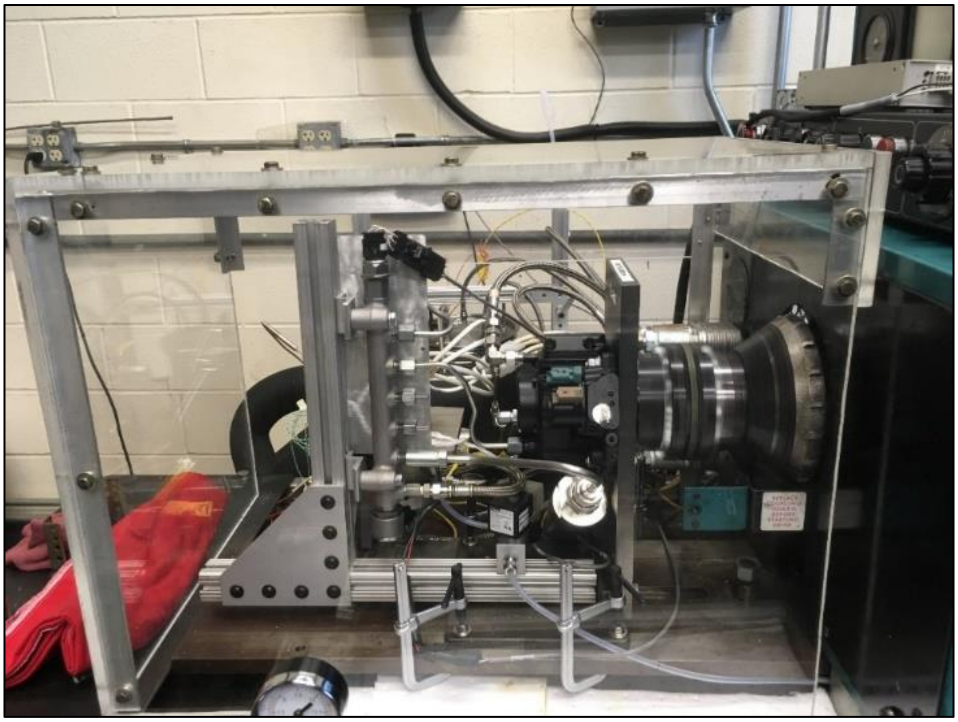


Figure 2. IDID Test Rig

2.2 Test Fuels, Additives, Contaminants, and Treat Rates

The CRC, Diesel Performance Group, Deposit Panel provided specific instructions regarding all the test fuels, additives, contaminants, and treat rates to be used in this project. The two base fuels and the B100 were all provided through the deposit panel. All fuel additives were likewise provided to the project through the deposit panel. Additives were provided by several additive companies, through the American Chemistry Council, and final selection was made by an American Chemistry Council representative. SwRI agreed not to identify the specific additives that were used nor to do any analysis of the additives. This additive policy is in keeping with the intent of the project to demonstrate the capability and not perform an in-depth study of fuel or additive effects. The sodium and glycerin were purchased from chemical supply companies as reagents.

The first 13 tests conducted were Proof Tests (PT01 through PT13). These tests were intended to demonstrate that the SwRI test rig would discriminate the deposit-forming tendencies of fuels similarly to the Delphi test rig. The test fuels used in the Proof Tests used the same fuels, additives, and contaminants used in the Delphi rig testing (see Section 2.3 for additional information). Below is a list of base fuels, additives, contaminants, and treat rates used in these Proof Tests.

- CARB No. 2 ULSD (donated by a major oil company)
- EPA No. 2 ULSD (donated by a major oil company)
- DDSA provided through CRC Deposit Panel (Normal Use Rate: 1 mg/kg) (Higher Concentration: 44.0 mg/kg)

- Sodium as sodium naphthenate (Reagent Grade, TCI America) (3.55 mg/kg mass)

Following the Proof Tests, 64 Matrix Tests were conducted using a specific test plan provided by CRC. Below is a list of the test fuels, additive types, and contaminants used in the matrix tests. The test fuels were clay-filtered, to remove additives, prior to preparation of test blends.

- CARB No. 2 ULSD (donated by a major oil company)
- EPA No. 2 ULSD (donated by a major oil company)
- B100 biodiesel (meets D6751, Rancimat induction period 7.5 hours) (20 volume %, i.e. used to prepare a B20 blend)
- Sodium as sodium naphthenate (Reagent Grade, TCI America) (1 ppm mass)
- Glycerin (Reagent Grade, LabChem, Fisher Scientific Catalogue No. LC148502) (0.004 mass %)
- Corrosion inhibitor additive (supplied by major additive manufacturer) (20 ppm mass)
- Diesel fuel lubricity additive (supplied by major additive manufacturer) (200 ppm mass)
- Detergent additive (supplied by major additive manufacturer) (425 ppm mass)
- Cetane improver additive (supplied by major additive manufacturer) (4000 ppm mass)
- Static dissipator (conductivity improver) additive (supplied by major additive manufacturer) (3 ppm mass)

2.3 Test Rig Proof Testing

Once the rig was assembled and ready for testing, the next phase, per the CRC statement of work, was to conduct a small matrix of tests called the proof tests. The proof tests were intended to demonstrate that the rig would be able to discriminate between various test fuel blends and would also rank fuels similarly to testing conducted previously,[4] as well as explore some other aspects of the test method. A total of 13 proof tests were conducted and the results are presented in Tables 1 and 2. Table 1 presents the visual rating results for the pintles. Table 2 presents the deposit thickness on the pintles, as measured with the VASE instrument (the VASE instrument is discussed later in this report). The first six proof tests (PT01-PT06) were conducted to evaluate the precision of the test rig and its ability to discriminate fuels. The visual rating scale is:

1 = very little deposit
2 = some deposit
3 = heavy deposit, stiff
4 = heavy deposit, stuck

It is noted at this point that the previously reported CRC work used visual assessments of the level of deposit, along with reporting when the pintle was stiff or stuck. No deposit thickness measurements were conducted during that testing. The purpose of the proof tests was to confirm

[4] "Internal Injector Deposits; Correlation of the Delphi Test Rig with Production Engines," CRC Project DP-04-10, March 2016.

that testing with the same test fuels and test conditions would result in the same visual rating as reported in CRC DP-04-10. After reviewing the results, the deposit panel concluded that the results were comparable and that the work should continue with the matrix tests.

SwRI operated the rig proof tests following the procedures previously outlined by Delphi, performing each 21-hour test over three consecutive 7-hour test days. Approximately 12.6 L of EPA test fuel was utilized for each 21-hour procedure without the fuel filters. For operating the filtered test the fuel quantity was increased to 15 L, to allow for more flush fuel and the filter canister volume.

Proof tests PT07 and PT08 were the same as PT03 and PT04 with the addition of an inline fuel filter (CAT 1R-0750, 2 micron rating, advanced efficiency). The fuel filter was added to aid CRC in determining if the discrepancy between the Cummins and the John Deere engine correlation in the 2016 CRC program (CRC Project DP-04-10) was due to one of the engines running on filtered fuel. During the 2016 work, both engine participants reported having difficulty keeping the contaminants in solution. One of the engines used an inline fuel filter to remove the particles ahead of the engine and one did not. When differences in pintle ratings were seen, the use of the filter was thought to be the source of the differences by removing contaminants ahead of the engine. Under the current project, SwRI found that the visual rating results both with and without a filter, were equivalent. It should also be noted that we saw no visible evidence of contaminant insolubility in any of the test fuels. The deposit thickness for PT04, 07, and 08 were also of similar magnitude. The deposit thickness for PT03 was somewhat lower than the other three. We believe this is due to accidentally switching pintles PT03 and PT05 in the time between taking the visual rating and the VASE analysis.

The first filter run, Proof Test 7, terminated at 20-hours and 18-minutes due to a fuel shortage. During testing the test rig shut down 3-times due to power outages. The re-establishment of test conditions after the shutdowns utilized excess fuel. The injector pintle at the conclusion of Proof Test 7 was stuck, a rating of 4. The second filter run, Proof Test 8 completed 21-hours of testing. The injector pintle at the conclusion of Proof Test 8 was stuck, a rating of 4.

Proof tests PT09-PT12 were the same as PT02-PT05 with one exception. These tests were run for only 7 hours rather than the 21 hours used for the other PT tests. These four tests were conducted to confirm that the test rig, combined with the VASE method of measuring deposits, is able to differentiate fuels with a 7-hour test as opposed to a 21-hour test. The original rig-test method, as developed by Delphi, was seven hours long. The test duration was lengthened to 21 hours for the CRC correlation study.[5] The additional test time was added in order to develop sufficient deposits on the injector pintles to allow visual rating of the deposits with the test fuels that were used. CRC approved the SwRI recommendation to do only two 21-hour tests with filters and to devote the other four proof tests to exploring 7-hr tests. Both of the tests (PT10 & PT11) with the elevated DDSA + Na resulted in stuck pintles. The tests with normal DDSA (PT09 & PT12) had light

[5] "Internal Injector Deposits; Correlation of the Delphi Test Rig with Production Engines," CRC Project DP-04-10, March 2016.

deposits. At the end of these tests, the deposit panel concluded that 7-hour tests, combined with VASE analysis, would give acceptable results and the matrix tests were conducted as 7-hour tests.

Proof test PT13 was a repeat of PT05 because the average deposit depth result for PT05 appeared to be unusually high. The average deposit depth for PT13 was more in line with expected results. It appears that the average deposit depth for PT05 was incorrect or that two pintles (PT03 and PT05) had been accidentally switched prior to VASE analysis. Unfortunately, there was no means to confirm if the pintles had been switched. In order to keep this from happening again, SwRI etched each pintle with a unique number at the completion of the rig test and before any additional analysis of the pintle (see Figure 3Figure 3).

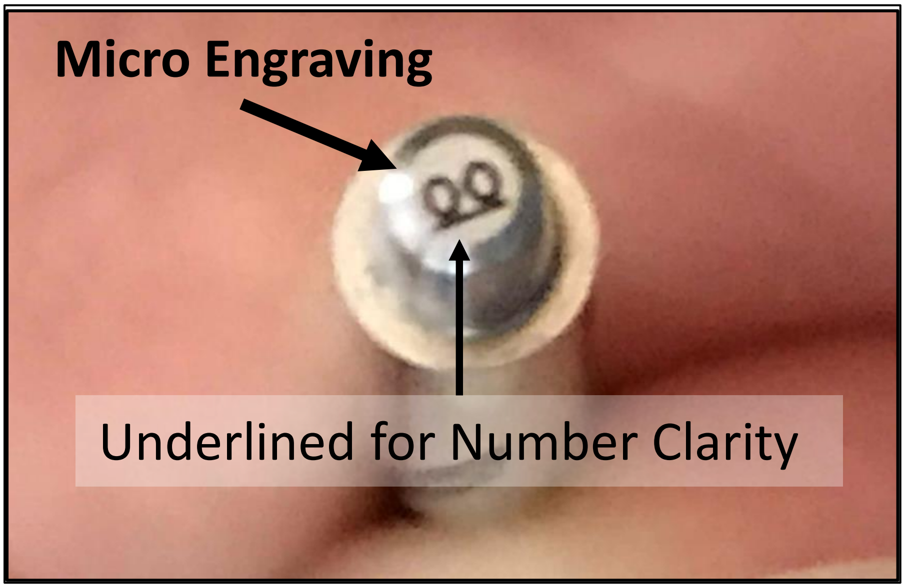


Figure 3. Engraved Identification Number on Pintle

Table 1. Proof Tests -- Rating of Injector Pintles Using CRC Guidelines

Test	Fuel (see Sec 2.2 for details)	Rating* (1:clean to 4:stuck)
PT01 (21-hour)	CARB	1.5
PT02 (21-hour)	EPA + Normal Use Rate DDSA + Na	2
PT03 (21-hour)	EPA + Higher Concentration DDSA + Na	3, sticky, sluggish
PT04 (21-hour)	EPA + Higher Concentration DDSA + Na	4, stuck
PT05 (21-hour)	EPA + Normal Use Rate DDSA + Na	2
PT06 (21-hour)	CARB	1.75
PT07 (21-hour)	EPA + Higher Concentration DDSA + Na with In-Line Fuel Filter	4, stuck
PT08 (21-hour)	EPA + Higher Concentration DDSA + Na with In-Line Fuel Filter	4, stuck
PT09 (7-hour)	EPA + Normal Use Rate DDSA + Na	2
PT10 (7-hour)	EPA + Higher Concentration DDSA + Na	4, stuck
PT11 (7-hour)	EPA + Higher Concentration DDSA + Na	4, stuck
PT12 (7-hour)	EPA + Normal Use Rate DDSA + Na	2
PT13 (21-hour)	EPA + Normal Use Rate DDSA + Na (PT05 repeat)	2
* Non-integer ratings indicate a rating judged to fall between two integer ratings.		

Table 2. Proof Tests -- Average Pintle Deposit Thickness per VASE (Pintle Region 1-B)

Test No.	Base Fuel	Additive/Contaminant (see Sec 2.2 for details)	Notes	Avg. Deposit Thickness, nm
PT01	CARB	None	21-hr. no filter	64.2
PT02	EPA	Normal use rate DDSA + Na	21-hr. no filter	169.8
PT03	EPA	Higher concentration DDSA + Na	21-hr. no filter	180.5
PT04	EPA	Higher concentration DDSA + Na	21-hr. no filter	456.3
PT05	EPA	Normal use rate DDSA + Na	21-hr. no filter	355.8
PT06	CARB	None	21-hr. no filter	23.8
PT07	EPA	Higher concentration DDSA + Na	21-hr. with filter	592.0
PT08	EPA	Higher concentration DDSA + Na	21-hr. with filter	395.1
PT09	EPA	Normal use rate DDSA + Na	7-hr. no filter	25.4
PT10	EPA	Higher concentration DDSA + Na	7-hr. no filter	478.7
PT11	EPA	Higher concentration DDSA + Na	7-hr. no filter	573.4
PT12	EPA	Normal use rate DDSA + Na	7-hr. no filter	37.0
PT13	EPA	Normal use rate DDSA +Na (rerun of #5)	21-hr. no filter	140

The results of the proof tests were statistically analyzed during a panel meeting held at SwRI to review the proof tests. Below is a summary of that statistical analysis:

7-hr no filter – 4 runs

There's significant difference between the two fuels.

Summary of Fit

RSquare	0.989312
RSquare Adj	0.983968
Root Mean Square Error	0.208618
Mean of Response	4.842081
Observations (or Sum Wgts)	4

Analysis of Variance

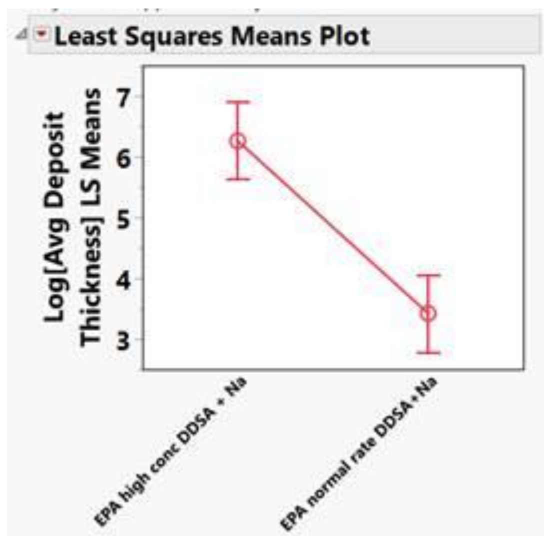
Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	8.0570555	8.05706	185.1275
Error	2	0.0870433	0.04352	Prob > F
C. Total	3	8.1440988		0.0054*

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	4.8420812	0.104309	46.42	0.0005*
Fuel[EPA high conc DDSA + Na]	1.4192476	0.104309	13.61	0.0054*

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Fuel	1	1	8.0570555	185.1275	0.0054*



21-hr no filter – 7 runs

There's significant difference between the CARB and the EPA fuels.

Summary of Fit

RSquare	0.76989
RSquare Adj	0.654834
Root Mean Square Error	0.593131
Mean of Response	4.943029
Observations (or Sum Wgts)	7

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	2	4.7081804	2.35409	6.6915
Error	4	1.4072160	0.35180	Prob > F
C. Total	6	6.1153964		0.0530

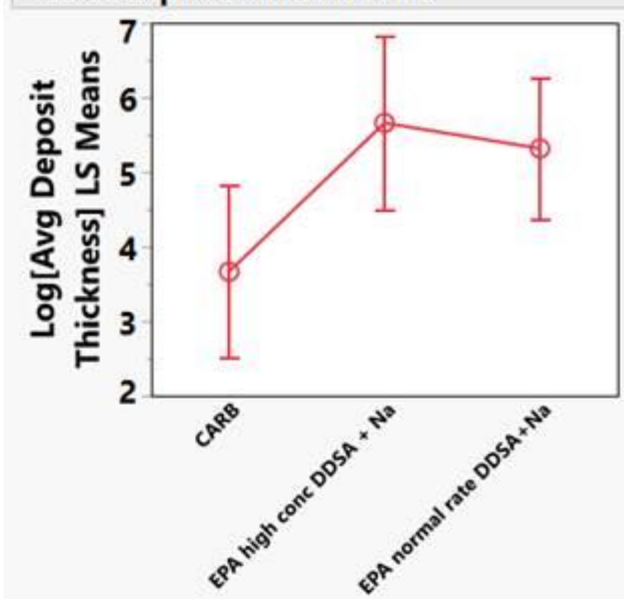
Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	4.8807208	0.228296	21.38	<.0001*
Fuel[CARB]	-1.214876	0.332796	-3.65	0.0218*
Fuel[EPA high conc DDSA + Na]	0.7787198	0.332796	2.34	0.0794

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Fuel	2	2	4.7081804	6.6915	0.0530

Least Squares Means Plot



EPA high conc DDSA + Na – 4 runs

There's no significant difference between with or without filter

Summary of Fit

RSquare	0.592089
RSquare Adj	0.388133
Root Mean Square Error	135.4304
Mean of Response	378.175
Observations (or Sum Wgts)	4

Analysis of Variance

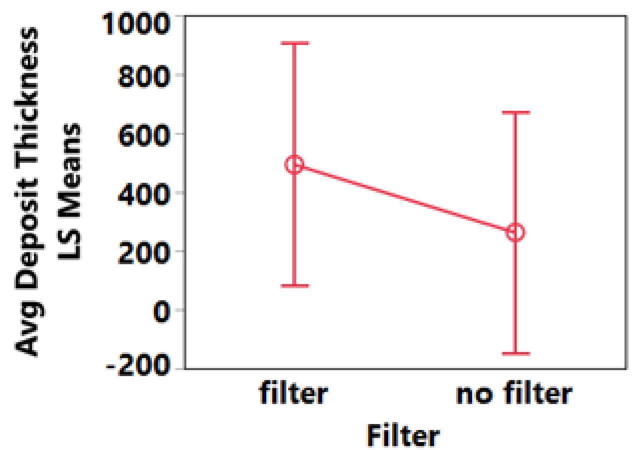
Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	53245.563	53245.6	2.9030
Error	2	36682.805	18341.4	Prob > F
C. Total	3	89928.368		0.2305

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	378.175	67.71522	5.58	0.0306*
Filter[filter]	115.375	67.71522	1.70	0.2305

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Filter	1	1	53245.563	2.9030	0.2305



The proof tests demonstrated:

1) Test rig capability to discriminate between fuels with and without contaminants/additives.
2) Capability to discriminate between high and normal additive levels.
3) Discrimination was demonstrated using both visual rating and VASE deposit thickness measurement methods.
4) Longer rig run time (21 hr vs. 7 hr) produced thicker deposits for fuel with normal additive/contaminant treat rates, as expected.
5) Discrimination between additive/contaminant levels was demonstrated at both 21 hr and 7 hr run times.

3.0 MATRIX TESTS

Based on the results of the proof tests, the CRC panel authorized SwRI to conduct the 64-test matrix as laid out in the RFP/Statement of Work. Additionally, the CRC panel gave permission to conduct 7-hour tests rather than 21-hour tests. Prior to the start of the test matrix, all heaters in the heating block were replaced. Additionally, the safety valve cracking pressure was adjusted and the jam nut wire tied. These adjustments were made because the cracking pressure of the safety valve had lowered due to vibration. In turn that caused variation in the rail pressure control which was witnessed towards the end of the proof testing.

The sixty four (64) test matrix, 7-hour, rig tests were completed without any operational issues. The matrix tests completed were numbered MT01 through MT64 as shown in Appendix B. Also shown in Appendix B are six additional matrix tests, MT65-MT70. These final six tests were selected by the CRC panel following completion of the first 64 matrix tests. These six tests are repeats of three previous matrix tests, run in duplicate. They were conducted as an evaluation of the precision of the test method. For all matrix tests the injector pintles and control valves were freely moving when the injectors were disassembled. The deposit thickness results from the matrix tests are discussed in Section 4 of this report.

Operating data are given in Appendix A. The data are the averages and standard deviations of the 1-Hz sampling for each of the 7-hour runs. They include rail pressure, fuel supply temperature, fuel inlet temperature, nozzle temperature, pump return temperature, system return temperature, injector return temperature, and pump speed. Also included is the weight of fuel utilized for each test. Appendix B gives the blend composition for each of the matrix test fuel blends.

Because each test fuel was blended individually, we used a specific protocol and work instruction for each blend in an attempt to maintain consistency. Also, each blend was prepared within 2 days of running and kept in cold storage until used. The test fuel was allowed to come to room temperature before it was used. This appears to have worked because there were no instances of particulate and/or crystalline pintle deposits in this test program, including the initial very high additive concentration runs

4.0 DEPOSIT THICKNESS MEASUREMENT AND MATRIX TEST INJECTOR DEPOSIT RESULTS

The most technically challenging part of the program had the least amount of definition. The RFP (request for proposal) simply stated:

> "Contracting laboratory will work closely with an expert in Variable Angle Spectroscopic Ellipsometry (VASE) analysis to apply this technique to the injector parts. Photos and FTIR also are required."

Referencing the available documents from CRC, the project final report of March 2016 and a follow up review of deposit evaluation technology of September 2016, provides some information. The former primarily defined the nature of the problem and documented the methods used, leading to justification of relying on the Delphi approach for the generation of deposits. Also mentioned are issues surrounding being able to visually judge the depth of the deposit acurately.

A presentation at the September 2016 meeting of the DPG[6] detailed the work of the group to outline the objectives that led to the RFP for this project. Included in that presentation was a presentation made by ExxonMobil Research and Engineering (EMRE), explaining their work on measuring injector deposits with ellipsometry.

The EMRE presentation showed how they used a VASE system to quantify deposits on components from a selection of injectors from multiple sources. The presentation was not detailed in regard to how it was done (other than it was done with the VASE system). SwRI personnel discussed the process with EMRE. While they were willing to provide some overview thoughts and discuss their results and concerns, they were not able to share specific EMRE techniques. They did provide a complete listing of the VASE system used for their work, which allowed SwRI to replicate the capability at SwRI.

SwRI asked CRC, as part of the RFP question and answer period, if there was a written method for VASE analysis of injector parts. EMRE stated, through CRC, that there was no formal method. They had been working on applying VASE techniques to fuel deposition for several years and applied that knowledge to make a simple proof of concept, no more. During subsequent consultations with EMRE, they reiterated some of the issues that would be important in developing an actual method, in particular they were concerned about potential deposits that were not amenable to the VASE process.

SwRI also sought clarification regarding exactly which parts, or areas of parts, should be measured. The implication of the RFP, and the associated committee documents, was that the injector pintle was the intended target of analysis. The reply from the deposit panel also clarified that this program is aimed at internal deposits, as would be found on the injector pintle. Based on this information,

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[6] Joan Axelrod and Manuch Nikanjam, "CRC Diesel Performance Group Deposit Panel," Tuesday 27 September 2016, Las Vegas, NV.

SwRI proposed the following analysis effort. It covered VASE ellipsometry, FTIR and visual analysis along with an intent to consider other surface analysis techniques that could be useful.

<u>VASE Ellipsometry:</u> VASE is a registered trademark of the J.A. Woollam Co (Woollam), Lincoln, NE. Dr. Woollam is the acknowledged industry leader in understanding the use of spectroscopic ellipsometry. The EMRE pro bono effort with the VASE system showed it was potentially the best solution for the work intended in this program. Upon receipt of the project, SwRI initiated the acquisition of a system identical to that used by EMRE.

The VASE was a long lead time item, 120 calendar days, however that did not put the project on hold. During that time SwRI worked with an expert in this technology from Woollam. SwRI negotiated a proposal with them that allowed initial elements of the program to be developed with their equipment while the SwRI unit was being built.

While Woollam was building the actual instrument, SwRI was constructing the needed fixture to ensure accurate reproduction of test data. Woollam supplied the requisite technical information on how to place specimens in their system and that was used to prepare a fixture. Building the fixture required the disassembly of a new injector of the specified type from which to extract the pintle. While that removed an injector from the inventory, it was still useful as a "clean" reference.

The Woollam system is highly automated and standardized so the process developed using their in-house equipment transferred directly to the SwRI unit. An SwRI researcher was trained in the system during build up period and collaborated with Woollam on the method development. This part of the program used the new pintle (this pintle was used during the construction of the fixture) to collect baseline properties for the pintle itself.

CRC provided two (2) used injector pintles of the designated type at this point. Since the actual analysis program had to be developed with deposited injector pintles, these pintles were very useful for developing the initial analysis program in conjunction with Woollam. Once the main evaluation program was commenced, SwRI, relying on advice from Woollam, considered the potential ways to scan the surface of the pintle.

SwRI initially scanned all of the areas shown in Figure 4. We then processed all of the scans in order to develop a protocol for subsequent analysis of the test pintles. SwRI determined that the last 4 mm of the main pintle body (area "B" in Figure 4, below) provided the most consistent results. Results from the scans outside of Area B tended to be far more varied and provided little to no additional information. During the program, it was noted that twenty one (21) data points over 4 mm resulted in some data overlap. That is true but this issue was covered in the development discussions with the Woollam technical support representative. Woollam's stated that using the overlapping data provides a better picture of the structure of the deposit formation. Discreet data is still contained by simply skipping bridging data cells.

<u>FTIR:</u> The RFP requested that each pintle be scanned using Fourier Transform Infrared (FTIR) spectroscopy. These analyses were conducted using an attenuated total reflectance (ATR) method. This technique allows samples to be analyzed without removing the deposit from the pintle. During the analysis of the test pintles, it was determined that several had deposits that were too thin to be detected with our FTIR instrument (a Bruker Tensor 27 with an ATR cell). FTIR results are presented in Appendix C. All of the FTIR spectra are presented but several of them are not useful spectra. No analysis of the FTIR results was conducted because, presumably, at least some of the deposits could be caused by the presence or absence of certain additives in the fuel; and, we had agreed not to analyze any of the additives used in the project. Analysis of the spectra is left to the reader.

Photographic Record: While SwRI has experience with this type of documentation from nearly six decades of documenting engine tests, developing a good method for this effort was a challenge. The primary benefit of the test rig and methodology developed under this project was being able to run a 7-hour test and still measure deposits that were often unseen with the unaided eye. As such, photography of the pintles often failed to document the deposit thickness differences that were recorded with the VASE.

SwRI reviewed several approaches to photographing the pintles, ranging from photomicrographs to group pictures. After considering options, we decided to use individual pictures for system record and group pictures for comparison purposes in this report.

Visual Rating vs. VASE Analysis: In some of the earlier CRC projects there was evidence that some deposits could occur that would be too heavy for analysis by ellipsometry. There were photographic examples from previous studies that showed particulate and crystalline deposits on the injector pintle surface, substantiating this concern. As discussed earlier in this report, lacking another suitable method of deposit analysis/rating, visual rating was used. This meant that deposits needed to be sufficiently thick to be visible. That requirement leads to longer test times and also typically means higher than normal additive/contaminant treat rates, reducing the relevance of the results and potentially causing handling problems with the test fuel. Use of the VASE technique to measure deposits allows shorter test times and more realistic levels of additives and contaminants.

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4.1 Variable Angle Spectroscopic Ellipsometry (VASE) Analyses

The VASE is a non-destructive technique that uses polarized light to pass through and refract in a film or deposit at a specified angle of incidence. As the polarized light interacts with the film, the light depolarizes creating an ellipse. The information from the ellipse is then used to graph the experimental data in the form of ψ (amplitude component) and Δ (phase change) each plotted against multiple wavelengths (370 nm – 1687 nm). A data model is then generated to fit the experimental data to calculate the film thickness. Some of the variables utilized in the modeling are refractive index, UV contribution, and IR contribution.

The pintle deposit thickness data was measured as four radial readings at each of 21 axial measurement points over a 4-mm section of the pintle. Figure 4 is a photograph of a pintle showing the regions we scanned on each pintle. The scan data were recorded for each pintle but deposit thickness measurements/reporting were limited to a smaller region. As discussed earlier in this report, deposit thicknesses shown in Figures 5-12 are measurements in Region B.

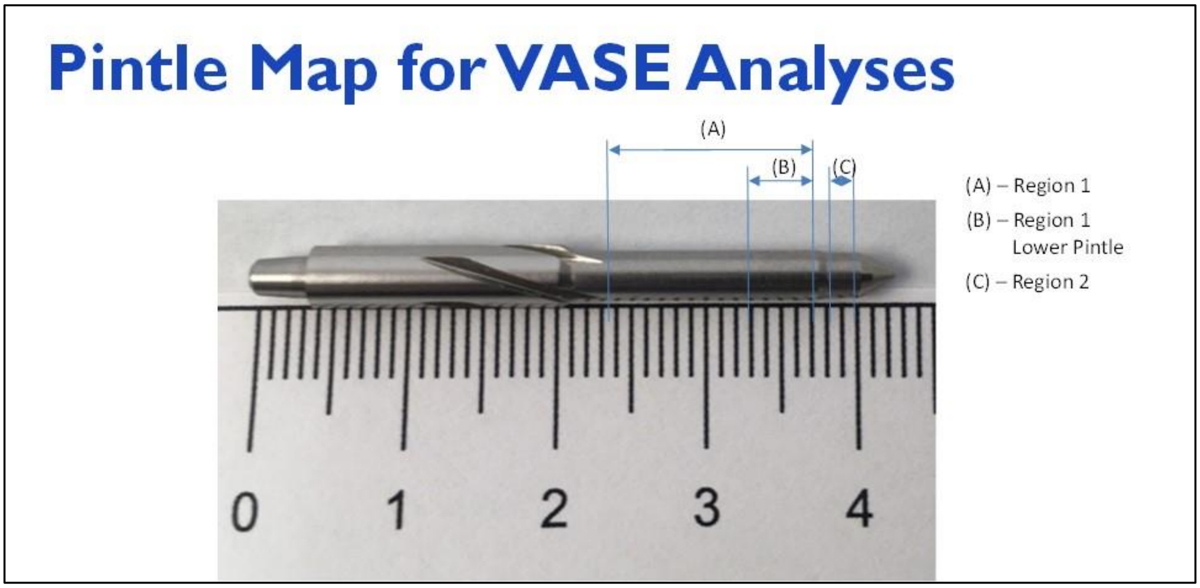

Figure 4. Injector Needle Showing Regions of Analysis (scale is millimeter/centimeter)

4.2 Deposit Measurement Results for Proof Tests

A total of 13 injector rig proof tests were completed, as described in Section 3. The pintles from each of the proof tests were analyzed using the VASE. Figure 5 and Figure 6 are plots of the deposit thickness measurement results.

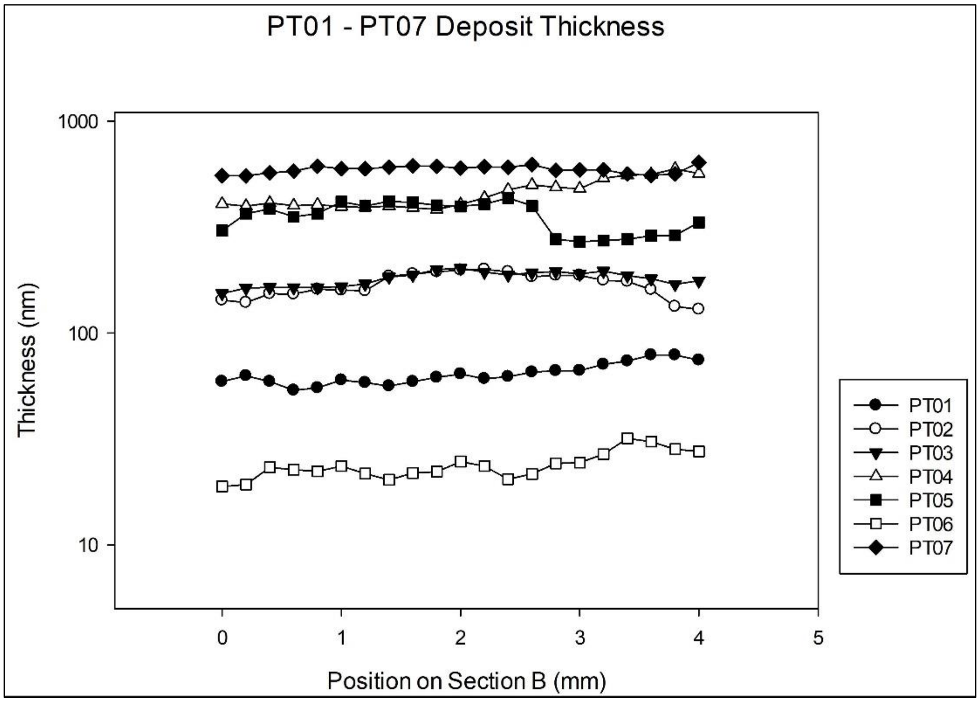

Figure 5. PT01 – PT07 Deposit Thickness Plots

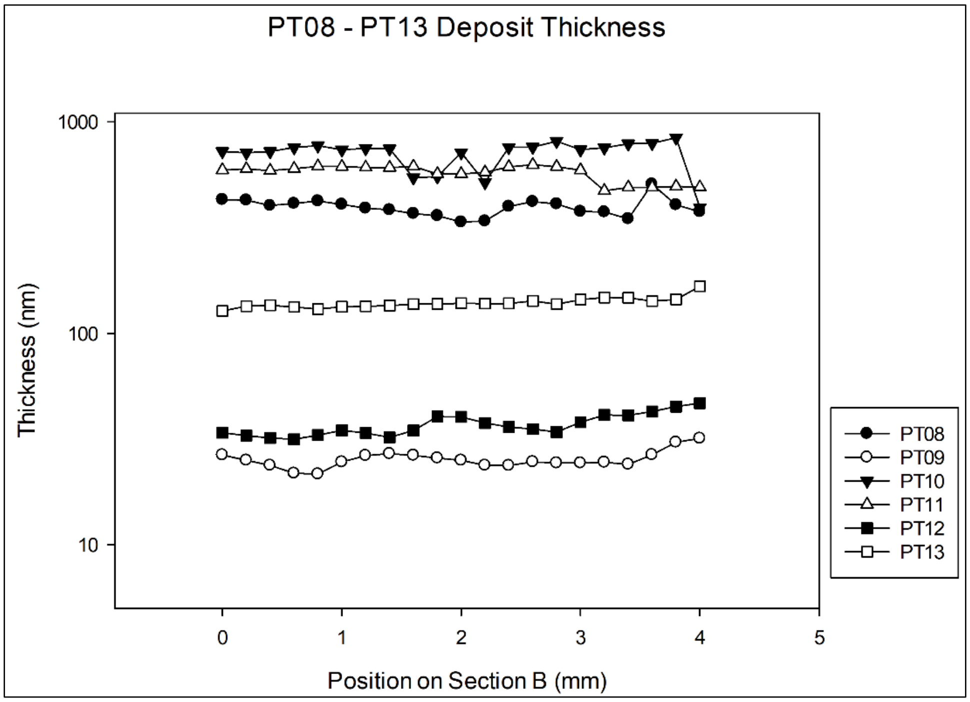

Figure 6. PT08 – PT13 Deposit Thickness Plots

4.3 Deposit Measurement Results for Matrix Tests

Figures 7 – Figure 13 are plots of the deposit thickness measurement results for the matrix tests. Data is presented on a log scale and limited to ten (10) pintles per graph for clarity.

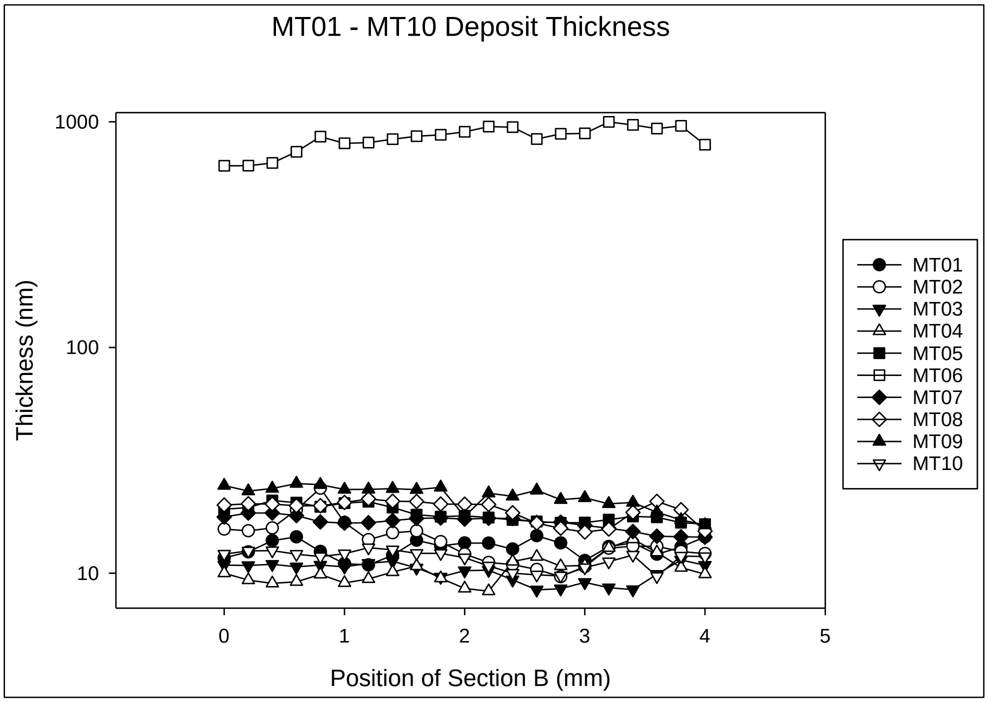

Figure 7. MT01 – MT10 Deposit Thickness Plots

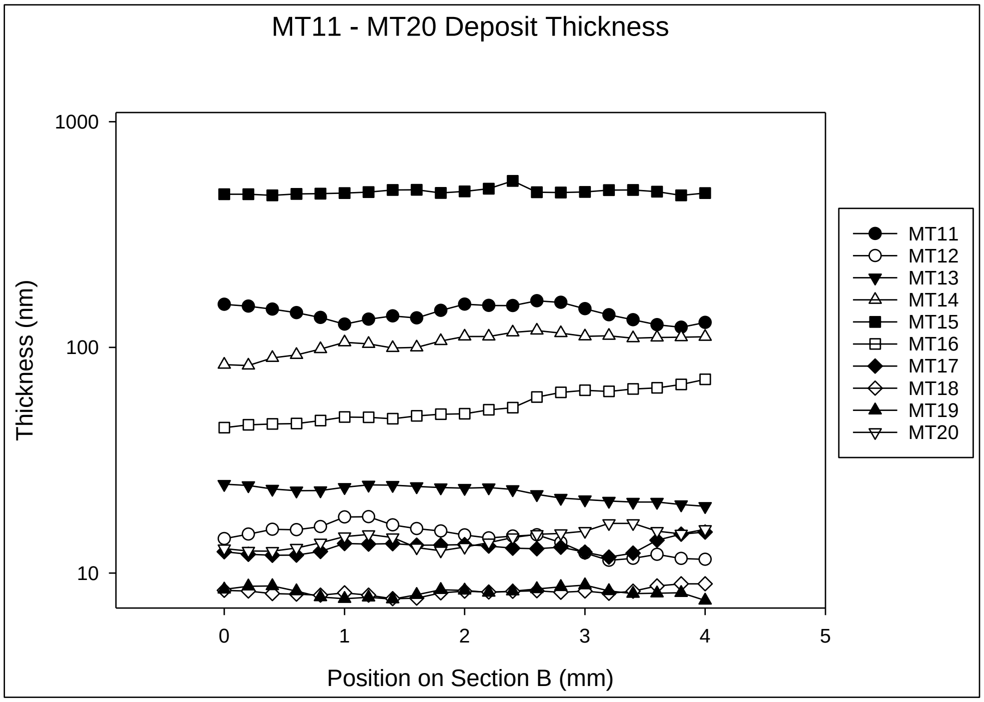

Figure 8. MT11 – MT20 Deposit Thickness Plots

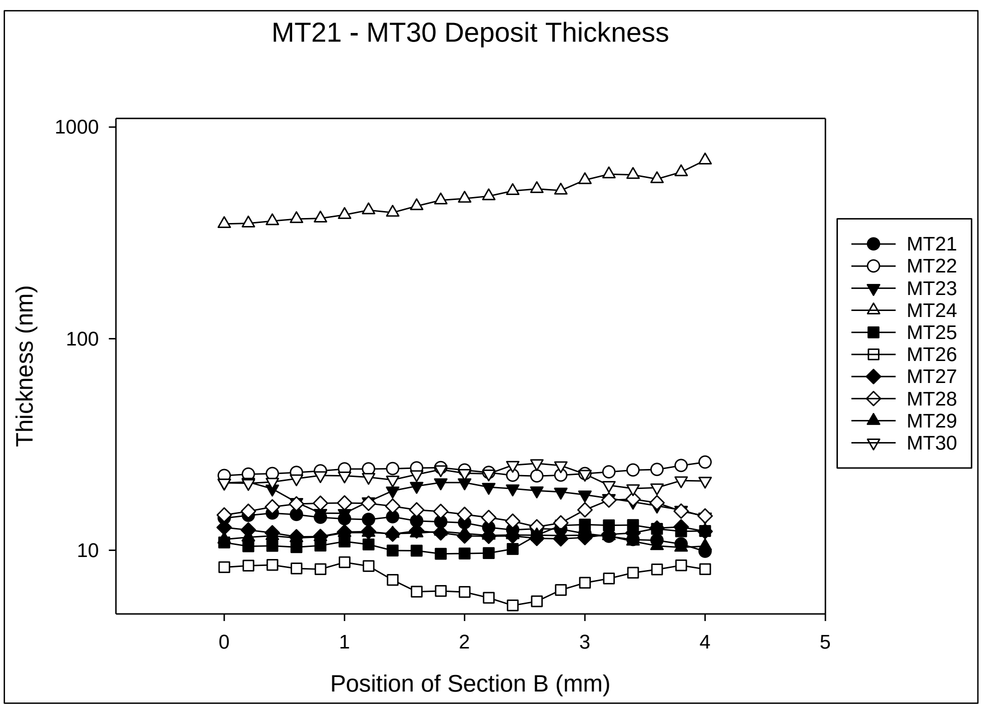

Figure 9. MT21 – MT30 Deposit Thickness Plots

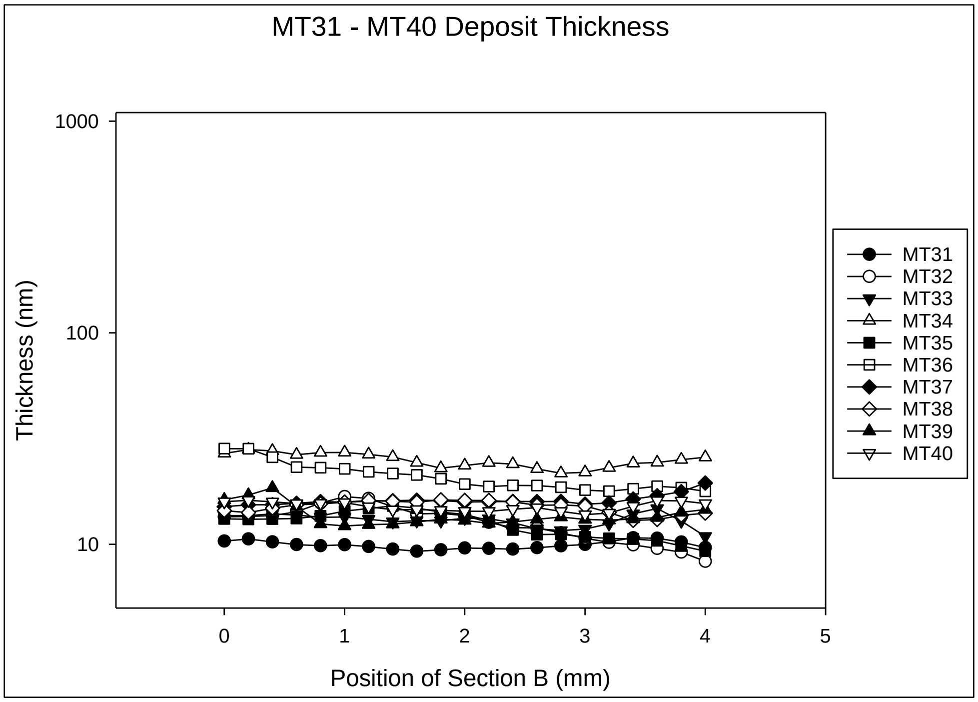

Figure 10. MT31 – MT40 Deposit Thickness Plots

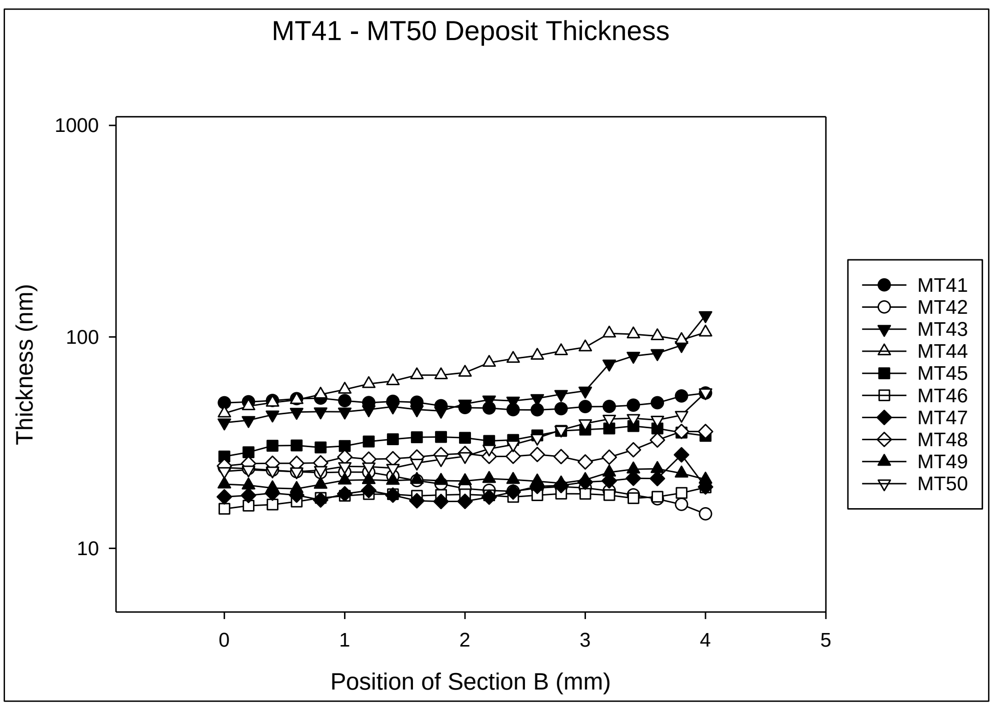

Figure 11. MT41 – MT50 Deposit Thickness Plots

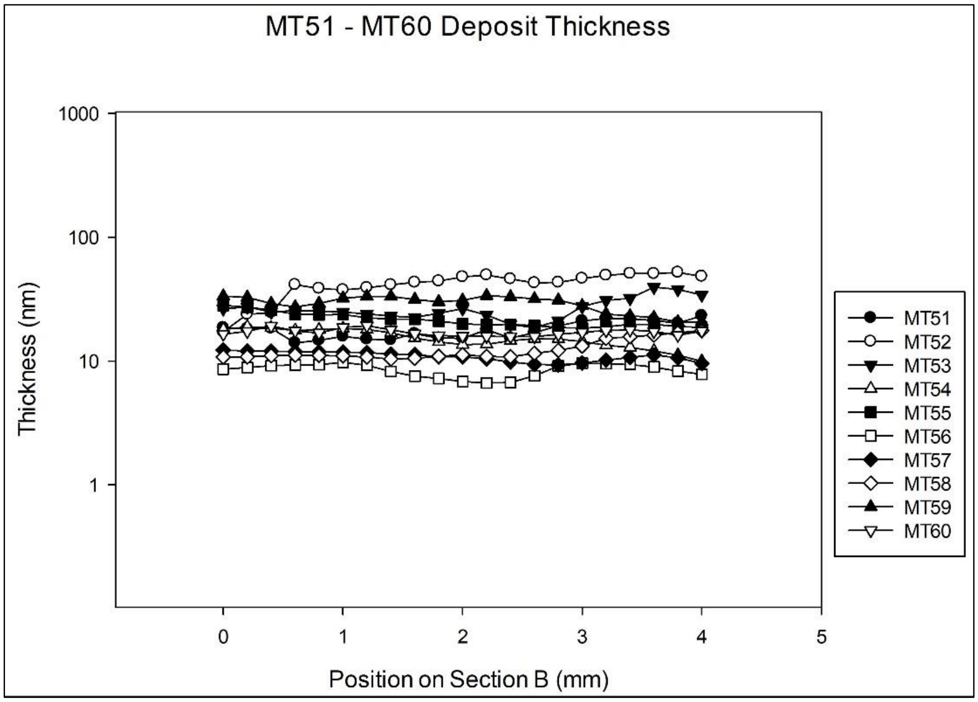

Figure 12. MT51 – MT60 Deposit Thickness Plots

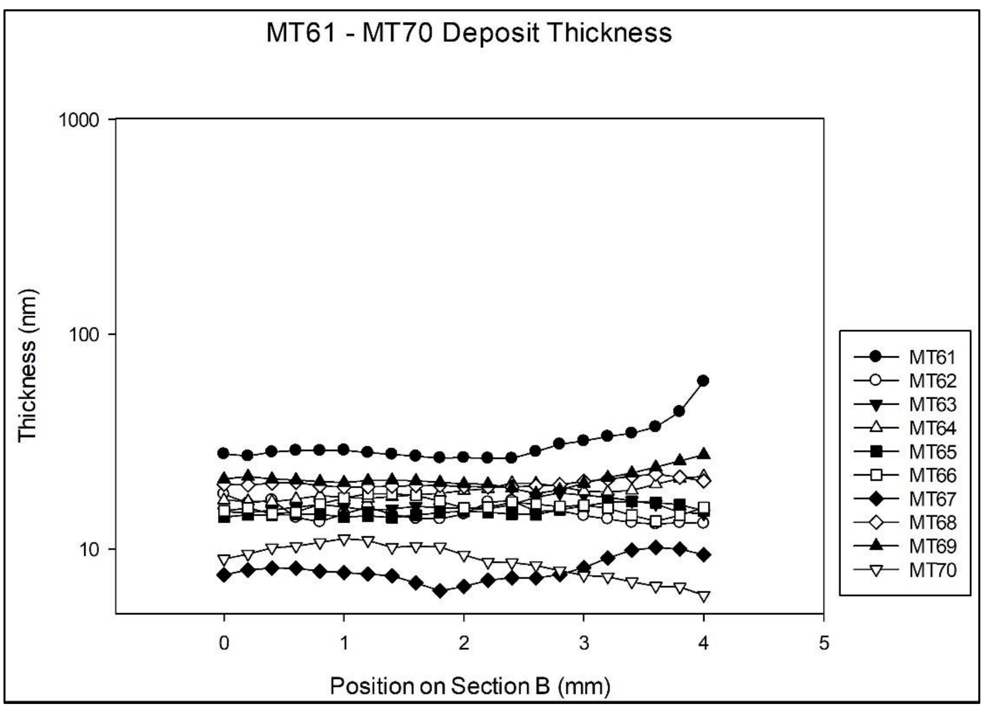

Figure 13. MT61 – MT70 Deposit Thickness Plots

4.4 Statistical Analysis of Deposit Results

4.4.1 Matrix Tests MT01 – MT64

The deposit depth data, for all of the matrix tests, were sent to Chevron for statistical analysis. The report of results for the first 64 tests in provided in Appendix E. In summary, the analysis showed:

- There were no statistical outliers.
- Regarding deposit by location on the injector pintle.
    - No significant axial location differences
    - No significant radial location differences
- Sodium increases deposit thickness
- No significant corrosion inhibitor and cetane number improver differences
- Detergent additive reduces deposit thickness in fuels without biodiesel
- Sodium increases deposit thickness in fuels without
    - Detergent additive
    - Glycerin
    - Mono-acid lubricity additive
- Conductivity additive increases deposit thickness in fuel without
    - Biodiesel
    - Glycerin
- Conductivity additive increases deposit thickness in fuel with mono-acid lubricity additive

4.4.2 Matrix Tests MT65 – MT70

These six tests were conducted as a measure of the test method repeatability. The tests fuels used in these analyses were chosen by the deposit panel. The results from these six tests were included in a separate statistical analysis conducted by Chevron statistician J. Martinez. The full presentation of the results is in Appendix E.

The results of the statistical analysis are summarized as follows (see presentation in Appendix E for full report):

"Based upon the estimated standard deviation (RMSE) and repeatability (r), there is no significant difference between deposit thickness results of

5nm and 14nm, or

10nm and 50nm, or

15nm and 140nm"

4.5 Matrix Deposit FTIR Results

Each pintle was scanned using an attenuated total reflectance (ATR) cell on a Bruker Fourier transform infrared spectrometer (FTIR). The FTIR spectra for the deposits on each pintle are given in Appendix C. As shown earlier in this report, the levels of deposits on the pintles varied greatly. For this reason, the FTIR spectra also vary widely. Some of the spectra give very little useful information. SwRI agreed not to analyze the additives used in this project and therefore conducted no analysis of the FTIR spectra. Any analysis of the FTIR spectra is left to the reader.

5.0 SUMMARY AND CONCLUSIONS

The objective of this CRC project was to establish and demonstrate a new system to evaluate internal diesel injector deposits. This system is a combination of an injector deposit test rig and a novel, spectroscopic technique to measure deposit thickness. The project was not designed to be a comprehensive study of the factors that affect injector deposit formation. The following is a summary of the results of CRC project DP-04-17.

- A new IDID test system, based on previously published work, was assembled.
- Thirteen tests were conducted to demonstrate that the test methodology could rank fuels similarly to results from previous rig and engine tests. The proof tests demonstrated: 1) Test rig capability to discriminate between fuels with and without contaminants/additives. 2) Capability to discriminate between high and normal additive levels. 3) Discrimination was demonstrated using both visual rating and VASE deposit thickness measurement methods. 4) Longer rig run time (21 hr vs. 7 hr) produced thicker deposits for fuel with normal additive/contaminant treat rates, as expected. 5) Discrimination between additive/contaminant levels was demonstrated at both 21 hr and 7 hr run times.
- Seventy tests were conducted using fuels blended to a designed experimental plan. The fuels were blends of a base diesel fuel (clay-treated to remove additives) and combinations of eight different contaminants and/or fuel additives.
- Using the Variable Angle Spectroscopic Ellipsometer (VASE), pintle deposits as thin as 10 nanometers were measurable. Deposits of this thickness are not discernable to the eye.
- Statistical analysis of the VASE/deposit results showed:
    - There were no statistical outliers.
    - Regarding deposit by location on the injector pintle
        - No significant axial location differences
        - No significant radial location differences
    - Sodium increases deposit thickness
    - No significant corrosion inhibitor and cetane number improver differences
    - Detergent additive reduces deposit thickness in fuels without biodiesel

- Sodium increases deposit thickness in fuels without
  - Detergent additive
  - Glycerin
  - Mono-acid lubricity additive
- Conductivity additive increases deposit thickness in fuel without
  - Biodiesel
  - Glycerin
- Conductivity additive increases deposit thickness in fuel with mono-acid lubricity additive

- Statistical analysis of the results of the final six tests showed:
  - Based upon the estimated standard deviation (RMSE) and repeatability (r), there is no significant difference between deposit thickness results of

    5nm and 14nm, or

    10nm and 50nm, or

    15nm and 140nm.
  - This is a measure of the repeatability based on the 9 data points (3 repeats of 3 fuels). The deposits are transformed since the variability of deposits increase as deposits increase. So different levels of deposits will have a different magnitude of differences as you increase the deposits. This is an initial measure of test precision (repeatability) and more data is needed to really define this.