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Suitability of Leak Detection Technology for Use In Ethanol-Blended Fuel Service

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Suitability of Leak Detection Technology for Use In Ethanol-Blended Fuel Service

By

Battelle
505 King Avenue
Columbus, OH 43201

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1.0 TABLE OF CONTENTS

1.0 TABLE OF CONTENTS 3

2.0 LIST OF ABBREVIATIONS/ACRONYMS 5

3.0 INTRODUCTION 8
- 3.1 Ethanol and Gasoline Blends 9
- 3.2 Fuel Properties that Affect the Suitability of Leak Detection Technologies 10

4.0 FUEL PROPERTIES 12
- 4.1 Ethanol Content 13
- 4.2 Ethanol/Water Solubility in Fuel – Phase Separation 14
- 4.3 Conductivity 16
- 4.4 Dielectric Constant 18
- 4.5 Density (or Specific Gravity) 19
- 4.6 Viscosity 21
- 4.7 Acidity 23
- 4.8 Coefficient of Thermal Expansion 23
- 4.9 Non-additive Volume Changes (Degree of Accommodation) 24

5.0 LEAK DETECTION TECHNOLOGY OPERATING PRINCIPLES 25
- 5.1 Volumetric versus Non-volumetric-Based Testing Technology Categories 25
- 5.2 Automatic Tank Gauging System Technologies 26
- 5.3 Statistical Inventory Reconciliation Technologies 29
- 5.4 Pipeline Leak Detection Technologies 29
- 5.5 Non-volumetric Leak Detection Methods 29

6.0 SUITABILITY ASSESSMENT OF LEAK DETECTION TECHNOLOGIES IN ETHANOL-BLENDED FUEL 32

7.0 REFERENCES 36

APPENDICES

Appendix A Environmental Technology Verification Fuel Property and Technology Testing
Appendix B Fuel Property Testing Methods and Data Results
Appendix C UST LD Operating Principle Testing Methods and Data Results
Appendix D Pressure Decay Testing Methods and Results
Appendix E ETV Automatic Tank Gauging Verification Test Summary
Appendix F ATG Simulated Leak Results

FIGURES

Figure 1. Phase Separation Plot of UV-V Measurements 16
Figure 2. Conductivity Plot by Test Blend and Water Content 17
Figure 3. Density Plot by Test Blend and Water Content 20
Figure 4. Viscosity Plot by Test Blend and Water Content 22
Figure 5. Thermal Expansion Plot by Test Blend 24

TABLES

Table 1. Summary of Fuel Property Data Collected* 14
Table 2. Biofuel-Water Mixture (BFW) Phase Separation 14
Table 3. F-Test Results of Fuel Blend Comparison for Conductivity 18
Table 4. Summary of Density Results for the BFWs (g/mL) 19
Table 5. F-Test Results of Fuel Blend Comparison for Density 21
Table 6. F-Test Results of Fuel Blend Comparison for Viscosity 22
Table 7. F-Test Results of Fuel Blend Comparison for Acidity 23
Table 8. Degree of Accommodation Summary for all Test Blends 25
Table 9. Leak Detection Technologies and Principles of Operation 27
Table 10. Suitability of Existing Leak Detection Technology for Ethanol-Blended Fuel 34

2.0 LIST OF ABBREVIATIONS/ACRONYMS

ANOVA	analysis of variance
ASTM	ASTM (American Society for Testing and Materials) International
ATG	automatic tank gauge
BFW	biofuel water mixture
°C	degree Celsius
E0	gasoline
E10	gasoline with up to10% ethanol
E15	gasoline with up to 15% ethanol
E30	gasoline with 30% ethanol
E50	gasoline with 50% ethanol
E85	gasoline with 51 to 83% ethanol
EPA	Environmental Protection Agency
ETV	Environmental Technology Verification
gal/hr	gallon per hour
I16	gasoline with 16% isobutanol
kg/L	kilogram per liter
L	liter
LD	leak detection
mL	milliliter
mm^2/s	millimeter squared per second
NWGLDE	National Work Group on Leak Detection Evaluations
OUST	Office of Underground Storage Tanks
%	percent
pS/cm	picosieman per centimeter
QAPP	Quality Assurance Project Plan
QA/QC	quality assurance/quality control
SIR	statistical inventory reconciliation
µL	microliter
UST	underground storage tank
UV-Vis	ultraviolet visible

EXECUTIVE SUMMARY

Suitability of Leak Detection Technology for Use In Ethanol-Blended Fuel Service

As the use of biofuels has increased in the last decade, there has been a level of concern over the effect that ethanol blends have on the material compatibility and operability of existing infrastructure. The focus of this research is to determine whether leak detection (LD) technologies are functioning properly in ethanol fuel blends. Fuels with different concentrations of ethanol have different intrinsic properties. As new fuels with varying blends of ethanol emerge, the resulting variations in fuel properties might affect the functionality of LD technologies. Technology to detect leaks has been required since late 1989 when UST operators were required to implement procedures to prevent and detect leaks in existing and new USTs under Title 40 of the Code of Federal Regulations Part 280 (40 CFR 280) Technical Standards and Corrective Action Requirements for Owners and Operators of Underground Storage Tanks (Subpart D).

When first employed, test procedures used to determine LD technology performance were commonly performed on USTs containing diesel fuel, in which the technologies tested generally behave in a similar manner as they do in gasoline. LD technologies tested with one of these procedures were then "listed" by the National Work Group on Leak Detection Evaluations (NWGLDE) as having been evaluated by a third party in accordance with an approved leak detection protocol. Currently, the increasing desire to use motor fuels containing ethanol, such as E15 and Flex Fuel (also referred to as E85), has led EPA, NWGLDE, and others to question the appropriateness of use of these LD technologies with fuels that have different properties than the fuel on which they were originally tested and for which the test methods were designed.

Fuel property research was conducted in order to better understand how ethanol blended into fuels in different concentrations can affect the properties of those blends. The objective of examining fuel properties was to identify when various blends are significantly different with respect to a fuel property. The fuel blends included E0, E10, E15, E30, E50, E85 and an isobutanol blend at 16 percent (I16).

Subsequently, various LD technology categories were described with respect to operating principle and how the change in fuel property may affect the operability of the technologies in that category. For the purpose of this technology review, ethanol blends are categorized as low-ethanol (i.e., E10, and E15) and high-ethanol blends (51 to 83 percent ethanol) and categorized as:

- Technology is expected to be suitable for indicated use (GREEN).
- Technology has limitations with the indicated use (YELLOW).

- Technology is expected to not be suitable for indicated use (RED).

As all technologies are different, have different algorithms, and are influenced by human inputs and installation, these conclusions may not be appropriate for every technology in a category. This paper discusses the relationship between fuel properties and operating principles against the performance standards established in the federal LD requirements. The potential negative impacts are highlighted in the following sections for consideration. In some cases, the technology may need to be modified to recognize these changes at the regulatory level with adjustments of threshold values and monitoring data processing.

3.0 INTRODUCTION

Biofuels are an increasing portion of the fuel supply in the United States (US) due partially to enactment of the Renewable Fuel Standard established by the Energy Policy Act of 2005 and amended by the Energy Independence and Security Act of 2007. As the use of biofuels has increased in the last decade, there has been a level of concern over the effect that ethanol blends have on the material compatibility and operability of existing infrastructure. The focus of this research is to determine whether leak detection (LD) technologies are functioning properly in low and high ethanol fuel blends. Fuels with different concentrations of ethanol have different intrinsic properties. As new fuels with varying blends of ethanol emerge, the resulting variations in fuel properties might affect the functionality of LD technologies.

Approximately 571,000[1] underground storage tanks (USTs) currently in service in the US have the potential for contaminating groundwater and subsequently drinking water should they fail. UST LD regulations were therefore created to specify monitoring requirements for detecting leaks. Technology to detect leaks has been required since late 1989 when UST operators were required to implement procedures to prevent and detect leaks in existing and new USTs. As a result of regulations adopted at that time [Title 40 of the Code of Federal Regulations Part 280 (40 CFR 280) Technical Standards and Corrective Action Requirements for Owners and Operators of Underground Storage Tanks], LD technology was to be applied not only to the USTs themselves, but also to the piping network that connected storage tanks and delivered fuel to dispensers. LD requirements are defined in 40 CFR 280 Subpart D.

To assist the regulated community when evaluating LD options, US Environmental Protection Agency (EPA) developed a series of standard test procedures that cover most of the technologies commonly used for UST LD monitoring and testing. Over the years there have been numerous additional test procedures and adaptations of these standard EPA test procedures. The procedures are publicly available through the National Work Group on Leak Detection Evaluations (NWGLDE) (www.nwglde.org) and are organized according to general LD technology categories.

These test procedures have been used by technology vendors or third party evaluators to provide information needed by tank owners and operators to determine if a LD technology meets the regulatory requirements. Concerns regarding LD operability arise from the trend of using legacy LD technologies in new fuel applications. When first employed, these procedures were commonly performed on USTs containing diesel fuel, in which the technologies tested generally behave in a similar manner as they do in gasoline. LD technologies tested with one of these procedures were then “listed” by the NWGLDE as

having been evaluated by a third party in accordance with an approved LD test procedures. Currently, the increasing desire to use motor fuels containing ethanol, such as E15 and Flex Fuel (also referred to as E85), has led EPA, NWGLDE, and others to question the appropriateness of use of these LD technologies with fuels that have different properties than the fuel on which they were originally tested and for which the technologies were designed.

This suitability assessment presents an analysis of the available information on characteristics of ethanol-blended fuels and on LD technology operating principles to assess potential LD technology performance functionality in ethanol-blended fuels. This assessment and related testing were performed under the EPA Environmental Technology Verification (ETV) program Advanced Monitoring Systems Center (www.epa.gov/etv). ETV involves a rigorous quality assurance/quality control (QA/QC) program, engagement with stakeholders in the industry, and a peer review process. Data were collected in multiple phases of testing following two ETV-approved Quality Assurance Project Plans (QAPPs): Biofuels Properties and Behavior Relevant to Underground Storage Tank Leak Detection System Performance[2] and Addendum[3] and QAPP for Verification of Underground Storage Tanks Automatic Tank Gauging Leak Detection Systems.[4] The data are presented in Appendices A – E. Appendix F presents supplemental data of simulated leak tests performed in the field by a reputable testing company and have not been independently generated through ETV.

3.1 Ethanol and Gasoline Blends

Several ethanol-gasoline blends are currently in use or being considered for use as motor fuels. E10, which represents a mixture of up to 10 percent (%) by volume ethanol with the remaining percent gasoline, has been distributed throughout the US for several years and is the most widely used gasoline blend in the US. E85 or Flex Fuel (between 51 and 83 % ethanol) has also emerged as a motor fuel, although its use is much less prevalent compared to E10. A waiver under the Clean Air Act to allow distribution of fuel containing 10 to 15 % ethanol (E15) was partially approved by EPA in 2010 and 2011 and has appeared minimally on the market. EPA has stated that E15 is suitable for 2001 and newer model year vehicles (FR 68093 November 4, 2010 and 76 FR 4662 January 26, 2011). Other blends being evaluated by Oak Ridge National Laboratory for material compatibility issues include various mixtures of ethanol and gasoline up to 30 % ethanol by volume[5].

For the purpose of this technology review, ethanol blends are categorized as low-ethanol (i.e., E10, and E15) and high-ethanol blends (51 to 83 % ethanol). Although mid-ethanol blend levels (i.e., E30, and E50) are included in the fuel property discussion, conclusions with respect to the technologies are categorized as low and high blends. There are limited data on the performance of the technologies

with the mid-level blends; therefore, this review is evaluating blends that are currently in use. It should also be noted, that if mid-level ethanol blends are offered on the market in the future, they may be blended at the dispenser from E10 and E85 instead of having dedicated tanks for the specific blends. Different grades (i.e., regular, mid-grade, and premium) are not considered separately in the current review. Seasonal differences in fuel properties (mainly related to vapor pressure) and detergents or additives are also not being considered.

In addition, an isobutanol-blended gasoline is another option that potentially will enter the market. Isobutanol blended at 16% is an anticipated level of one of the manufacturers and the higher of two levels attempting to be brought to market. Isobutanol can function within the current infrastructure and ethanol production plants have the potential to be retrofitted for its production. Although not ethanol, this alcohol may potentially enter the market and therefore is included in this discussion.

When reviewing the suitability of LD technology in ethanol-blended fuel service a challenge is accounting for the uncertainty of knowing the actual ethanol percentage in each blend of fuel, because fuel quality specifications allow for ethanol content variation in the blends. This uncertainty can best be illustrated by looking at the ASTM International (ASTM) specification for E85. Pursuant to ASTM D5798[6], E85 must contain between 51 and 83 % alcohol by volume. Similarly, low ethanol blends may be subject to the same variability in ethanol content of the fuel. For example, E10 may technically contain any ethanol percentage up to 10 % volume (although most often blended close to 10%), while E15 contains greater than 10 volume % by volume ethanol and up to 15 % volume ethanol (http://www.epa.gov/otaq/regs/fuels/additive/e15/). As discussed below, in addition to the physical characteristics of ethanol-blended fuel, this allowable variation of ethanol content may produce an unwanted impact on functionality or accuracy of the technologies.

3.2 Fuel Properties that Affect the Suitability of Leak Detection Technologies

Parties interested in LD technologies usually discuss two topics when evaluating the suitability of a particular LD technology to be used in ethanol-blended fuel service: (1) material compatibility, and (2) operability. The first topic, compatibility, relates to corrosiveness of ethanol and ethanol/water mixtures on metal and plastic components of the detection system in contact with fuel or fuel vapor. Increased microbial growth induced by ethanol is also a concern. Since this has been the subject of significant research by Oak Ridge National Laboratory[5] and others, the material compatibility aspect of technology used in ethanol-blended fuel service will not be discussed herein. The second topic, operability, relates to the ability of LD technology to properly function in ethanol-blended fuel service as a result of different product characteristics than were used to originally design the equipment. Technology evaluators

generally consider two properties to be most important on the ability of existing LD technologies to properly operate while in ethanol-blended fuel service: (1) water solubility in ethanol, and (2) temperature. Depending on the technology operating principles, other properties that may also be important include ethanol concentration, density, viscosity, and conductivity.

The data generated is presented in the summary of the fuel properties in Section 4 and the operating principles of the various LD technologies categories are discussed in Section 5. Finally in Section 6 is the suitability assessment of the various technology categories which utilized the data presented in Appendices A - E and summarized in the main document.

4.0 FUEL PROPERTIES

The primary fuel properties that are suspected of affecting LD system operability include:

- Ethanol content (or isobutanol content)
- Alcohol/water solubility in gasoline
- Dielectric constant
- Electrical conductivity
- Viscosity
- Coefficient of thermal expansion

Each of these properties is affected by the ethanol content in the blend, and as ethanol content increases, other properties are affected. For example, the density of pure (neat) ethanol is greater than the density of neat gasoline, and therefore, as the ethanol content of a blend increases, so does the density of the blend. In a similar fashion, water solubility is greater in ethanol than in gasoline (water is essentially insoluble in gasoline), and therefore, a blend with a greater ethanol content is able to absorb a greater amount of water. Viscosity, conductivity, and coefficient of thermal expansion are also all greater for neat ethanol than for neat gasoline, thereby producing higher values for each parameter as ethanol content increases. Several other combinations of properties are also related to one another. For example, addition of water to an ethanol-blended fuel also increases the density, viscosity, dielectric constant, and (usually) conductivity of the blend. These interrelationships can make exact identification of property effects complicated and difficult.

In addition to the difficulty noted above, ethanol-blended fuel may not consistently contain the same amount of ethanol. This may be due to blending differences, volatilization, water ingress, or phase separation. Thus, the actual value of the physical property of interest may be unknown. Furthermore, while values for these properties are readily available for neat materials such as gasoline, ethanol, and water, they are much less available for different mixtures of ethanol, gasoline, and water. Fuels also have proprietary additives and detergents that have the potential to affect all of these fuel properties. All of these uncertainties in fuel composition could contribute to potential errors during system operation.

EPA utilized the ETV program to conduct fuel property research in order to better understand how ethanol blended into fuels in different concentrations can affect the properties of those blends. The objective of examining the fuel properties was to identify when various blends are significantly different with respect to a fuel property. For example, is the conductivity of E15 significantly different from E30 or is the viscosity of E10 significantly different from E85? Table 1 summarizes the fuel blends and fuel properties data gathered from samples measured in triplicate. Fuel blends included E0, E10, E15, E30,

E50, E85 and an isobutanol blend at 16 % (I16) and were prepared using the same gasoline throughout the project. The variability of gasoline and unknown proprietary differences are common at fueling stations; however, for the purposes of lab testing, these variables were limited by the use of one fuel for preparing the mixtures. Detailed methods, QA/QC procedures, and results are presented in the Appendices A and B.

4.1 Ethanol Content

As mentioned in the previous paragraph, each of the properties listed above are impacted by ethanol content in the blended fuel. Other than compatibility, however, which is not the subject of this suitability assessment, ethanol content does not directly impact LD technology operability. Instead, its effect is manifested by altering listed fuel properties that impact one or more operating principles of specific technologies. As a result of the variability of ethanol content mentioned previously, one cannot estimate how other physical properties of the blended fuel are altered by the addition of ethanol. Without some independent means of knowing the exact ethanol content of the blend, the true correction that may need to be made to readings from the various technologies will not be known. Because ethanol affects each of the physical properties noted above, this situation may impact LD technology by limiting the ability of a technology to accurately quantify leak rates, even when a technology may still be able to qualitatively identify that a leak is present. The regulations require technologies to identify a 0.2 gallon/hour (gal/hr) leak rate for monthly testing and a 0.1 gal/hr leak rate for tank tightness testing, establishing a target leak detection performance level that may be influenced by these unknown changes. For example, when ethanol content increases, so does the density of the fuel blend. The LD technology software may not be set for the actual fuel blend density because the ethanol content of the fuel blend may vary with each delivery. Qualitative leak determination will still be possible; however, when comparing calculated product volumes at different periods, the volumes change with time and the true leak rate will have the potential for more error since it is based on the assumed ethanol content (entered into the software program) or assumed density.

Table 1. Summary of Fuel Property Data Collected*

Property	Gasoline (E0)	E10	E15	I16	E30	E50	E85
Specific Gravity (Dimensionless)	0.722	0.761	0.764	0.765	0.770	0.776	0.790
Density (g/mL) (15.6 ^{O}C)	0.722	0.762	0.764	0.766	0.770	0.776	0.788
Coefficient of Thermal Expansion (5–30 $^{O}C^{-1}$)	0.0010	0.0012	0.0011	0.0012	0.0013	0.0009	0.0010
Viscosity 25 °C (mm^2/S)	0.555	0.557	0.582	0.659	0.698	0.863	1.085
Conductivity (pS/cm)	192	12233	104722	5163	4321111	9204444	8304444
Acidity (% mass)	0.00053	0.0012	0.00093	0.0011	0.0012	0.0016	0.0015

*Triplicate samples were measured in triplicate for all properties and blends.

4.2 Ethanol/Water Solubility in Fuel – Phase Separation

The solubility of water in fuel increases dramatically as ethanol content increases. This increase has an effect on the physical properties of the blended fuel and will have an effect on many operating responses of LD technologies. Water is absorbed into the ethanol fraction of the blended fuel, and as water is absorbed, density, viscosity, and conductivity increase while the coefficient of thermal expansion remains relatively similar for the blended fuels. Tests were performed using the above test blends with multiple levels of water content, 0%, 0.25%, 0.5%, 2.5%, and 5.0%. Test results show that some of these mixtures became two distinct phases (S), some were semi-separated with the separation not clearly distinguished (SS), and others were composite single-phased mixtures (C). Table 2 presents the biofuel-water-mixtures (BFW) and the observed separation, if any. When samples were separated, analytical results were acquired for the bulk fuel phase (top). If the dense phase (bottom) sample volume was large enough to sample, a sample was archived for analysis, if deemed necessary. E0 and I16 had clearly separated phases (S) as they have the lowest miscibility with water.

Table 2. Biofuel-Water Mixture (BFW) Phase Separation

% Water	E0	E10	E15	I16	E30	E50	E85
0.0	C	C	C	C	C	C	C
0.25	S	SS	C	S	C	C	C
0.5	S	SS	C	S	C	C	C
2.5	S	S	S	S	SS	C	C
5.0	S	S	S	S	S	C	C

C = Composite, SS = Semi-Separated, S = Separated Clearly; All at 25°C

Because water is essentially immiscible in gasoline, a very small addition of water to a UST storing gasoline will cause a water phase to settle in the bottom of the tank. This makes it relatively simple to determine the presence of water in USTs storing gasoline. However, E10 and E15 blends can hold approximately 0.5% of water with mixing before phase separation occurs. As fuel temperature is lowered, the amount of water needed before phase separation occurs is also lowered. Because water alters the solubility of ethanol in gasoline, when phase separation occurs in E10, the separated phase consists of an ethanol/water mixture with a density greater than ethanol but less than water. If water entering a UST does not mix into a low ethanol-blended fuel, it will collect at the bottom of the UST, similarly to E0. However, once the UST receives a fuel drop (that is not saturated with water), substantially mixing the contents, the water bottom is absorbed into the fuel. With continued water ingress, water will collect at the bottom and be detected, then disappear with each fuel delivery. This phenomenon has been shown to render traditional water detection floats unreliable unless the float composition density is adjusted in comparison with the density of the separated phase[7, 8]. Another alternative would be for the technology console to be programed to recognize this reoccurring pattern of detected water followed by no detectable water.

As mentioned previously, water absorbed into the blended fuel will also increase the density of the blend (as well as other physical parameters), thus making proper selection of volumetric correction factors difficult. In addition, a certain amount of water can be absorbed in ethanol without an increase in volume. In a large volume of stored fuel, the amount of water absorbed into the ethanol fraction of an ethanol-blended fuel could be appreciable and could exceed the required sensitivity of the regulation [e.g., 40 CFR280.43(a)(6) requires the measurement of any water level in the bottom of tank be made to the nearest 1/8" at least once a month]. Therefore, an automatic tank gauging (ATG) system or other level-based technology may be unreliable in detecting water at the bottom of a tank, because the product volume will not accurately reflect the total volume of water that has entered a tank. Liquid level readings may also be unreliable if a tank has multiple leak points and fuel is leaking out while water is leaking in.

As a method to characterize phase separation and define the vertical position of the interface of various fuel blends, an experiment was conducted measuring the absorbance of fuel blend-water mixtures. Figure 1 represents the Ultraviolet Visible (UV-Vis) measurements recorded on the 50-50 mixture of fuel blend and water (mixed with a dye). The UV-Vis measurements were recorded on a 10 milliliter (mL) aliquot that was drawn from the bottom of the sample vial holding the 50-50 fuel-water mixture (See Appendix B for more detail). The plateau on the top left hand side of Figure 1 represents the dyed water while the one on the bottom right hand side represents fuel (where dye did not reside and therefore no absorbance was measured). For gasoline (E0) with no ethanol content it can be observed that there are

only two distinct features to the curve, plateaus on the left and right hand sides with no intermediate peaks. This infers that the E0 fuel had no transition zone or phase mixed with water. However, with the increase in ethanol content the measurements became more complicated and the phase separation more apparent. The following observations of the transition zone can be made from the data presented in Figure 1.

1. A drop in absorbance value (y-axis) indicates the ethanol is absorbing into the water. With the increase in ethanol content, more ethanol was available for absorption into the water, which led to lower initial absorbance values.
2. For E0 and I16, the fuel phase was detected at draw 8 (approximately midway up the sample vial), as ethanol content increased in the fuel blends, the fuel phase was detected at higher draw levels (up to 12). In other words, with the increase in ethanol content the water-ethanol mixture was more dominant.
3. The appearance and augmentation of intermediate peaks indicates formation of a transition phase and its broadening as ethanol content increases.

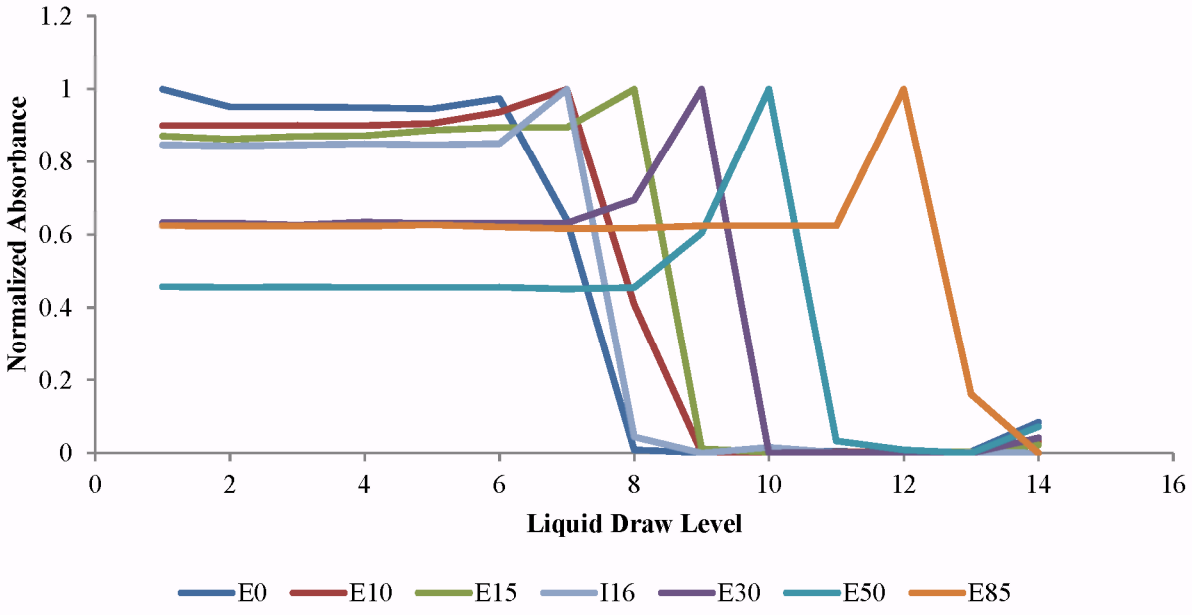

Figure 1. Phase Separation Plot of UV-V Measurements

4.3 Conductivity

From the conductivity plot (Figure 2) it can be observed that with the increase in ethanol content, conductivity of the fuel increased exponentially. Also, conductivities of fuels E30, E50, and E85 were

found to be in the same range. The change in water content did not appear to have an effect on conductivities of the fuels E30, E50 and E85, however, increase in water content beyond 0.5% lead to drop in conductivity by two orders of magnitude for the fuels E15 and E10 and beyond 2.5% lead to a similar trend for E30. This was due to the bulk fuel being measured since the BFW mixtures had phase separated at these water concentrations. Similarly, E0 and I16 had distinct water-fuel separation and the bulk fuel conductivity measurements were not influenced by the water. The wide range of conductivity readings between the test blends (with or without water) indicates that a technology operating principle based on this property would need to operate over a large range or specify the range of operability by fuel blend.

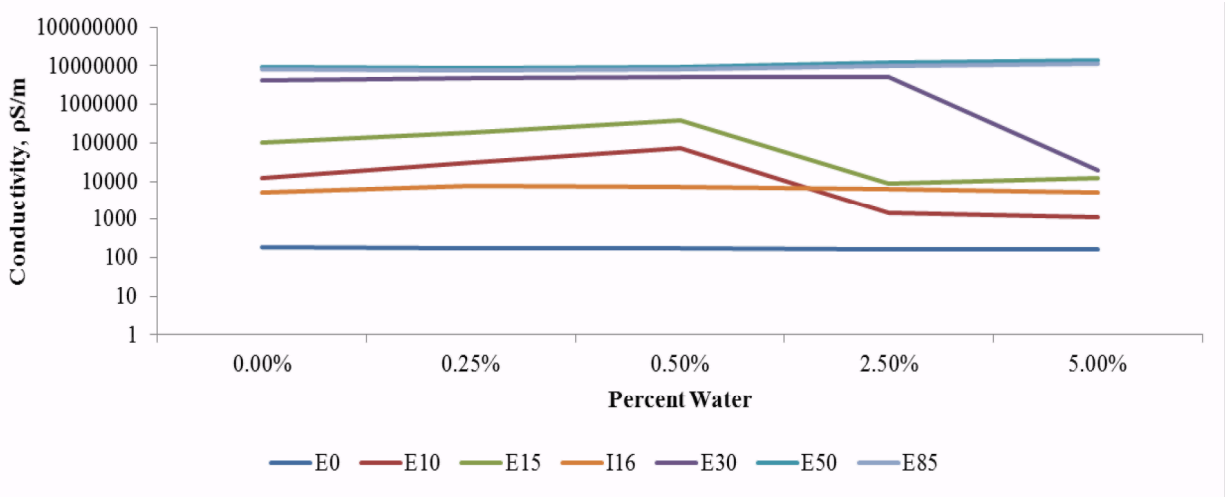

Figure 2. Conductivity Plot by Test Blend and Water Content

To determine if the differences between conductivities of the fuel blends were significant, an analysis of variance (ANOVA) was performed on the dataset. The ANOVA found significant differences existed within the dataset of fuel blend conductivity measurements. To further understand the differences, an F-test was performed, which allowed for direct comparison between the different fuel blends. The null hypothesis of the F-test assumes that the means of each fuel blend are equal. Rejection of the null hypothesis of the equality of means was done at the 0.05 significance level. Rejection of the null hypothesis is an indication at least one mean among the different types of fuel blends is not equal. Table 3 presents the *p*-values obtained from the F-test along with "YES" and "NO" to indicate yes, there is a significant difference, or no, there is not a significant difference between the fuel blends being compared. These *p*-values take into account the fact that multiple comparisons are being performed by applying the Sidak adjustment to the reported significance level.

In Table 3, a p-value less than 0.05 indicates a significant difference, while any value 0.05 or greater (i.e., up to 1) indicates the difference is not significant. Almost all significant differences in conductivity were observed between the higher alcohol-blended fuels (i.e., E30, E50, and E85) and the lower alcohol-blended fuels (i.e., E0, E10, E15, and I16). The only exception was the comparison between E50 and E85. Given the effect of water in these blends on conductivity, without modification, technologies which operate on conductivity may function differently in low versus high ethanol-blends.

Table 3. F-Test Results of Fuel Blend Comparison for Conductivity*

Fuel Blend	E0	E10	E15	I16	E30	E50
E10	1 NO					
E15	1 NO	1 NO				
I16	1 NO	1 NO	1 NO			
E30	<0.0001 **YES**	<0.0001 **YES**	<0.0001 **YES**	<0.0001 **YES**		
E50	<0.0001 **YES**	<0.0001 **YES**	<0.0001 **YES**	<0.0001 **YES**	<0.0001 **YES**	
E85	<0.0001 **YES**	<0.0001 **YES**	<0.0001 **YES**	<0.0001 **YES**	<0.0001 **YES**	0.948 NO

$p < 0.05$ indicates a significant difference
*F-test performed after significant differences were identified using an ANOVA analysis of the dataset.

4.4 Dielectric Constant

Dielectric constant is the "measure of a substance's ability to insulate charges from each other. Taken as a measure of solvent polarity, the higher dielectric constant means higher polarity, and greater ability to stabilize charges."[9] When ethanol and water are added to gasoline the conductivity of the mixture substantially increases and this can affect certain capacitance probes (depending on the design). Several technology manufacturers and organizations have indicated that this change makes use of some capacitance probes in ethanol-blended fuel service unreliable. Furthermore, the presence of a separated phase at the bottom of a tank would produce a different dielectric constant in the separated phase than in the fuel phase and make it difficult to determine the proper response for a capacitance probe when used for leak detection. Legacy capacitance ATG probes are no longer offered by manufacturers; however, this operating principle is being applied to sensors for monitoring at various parts of UST systems.

4.5 Density (or Specific Gravity)

Density of a material is often defined in terms of specific gravity. Specific gravity is the ratio of the density of a material to the density of water (the density of water is 1 kg/L at 15ºC). A material with a specific gravity less than 1 is less dense than water, and a material with a specific gravity greater than 1 is more dense than water. Because gasoline is a mixture of hydrocarbons, the content of one batch of gasoline (and by extension, specific gravity) may be different than that of another batch. Density is a parameter of inherent importance for several mass-based or pressure-based LD technologies (e.g., buoyancy probe, piping flow meters). Until the density difference due to mixing of different batches comes to equilibrium, a response change in the LD technology could be interpreted as inconclusive. Achieving equilibrium is mainly driven by the rate of temperature change after a delivery and can vary substantially if the delivered fuel temperature is very different from the stored fuel temperature. Once equilibrium is achieved or the rate of change is within the technology's acceptable range, the test will complete. However, the LD technology may not be able to compensate for a density change when the change is due to phase separation or water absorption into ethanol. In these cases, the technology may not be able to detect a leak, or the calculated leak rate may not be accurate. Because density of a liquid varies with temperature, the highest precision in level measurement necessitates that density be compensated for or expressed with relation to the actual temperature of the measured liquid. Table 4 summarizes and Figure 3 plots the density values obtained during fuel property testing of the BFWs.

Table 4. Summary of Density Results for the BFWs (g/mL)

% Water	E0	E10	E15	I16	E30	E50	E85
0.0	0.7222	0.7617	0.7643	0.7656	0.7701	0.7758	0.7883
0.25	0.7228	0.7648	0.7650	0.7658	0.7708	0.7766	0.7927
0.5	0.7227	0.7649	0.7663	0.7669	0.7722	0.7779	0.7937
2.5	0.7224	0.7630	0.7629	0.7669	0.7753	0.7849	0.8014
5.0	0.7230	0.7624	0.7618	0.7684	0.7583	0.7951	0.8067

From the data it is evident that an increase in ethanol content leads to increase in the density of the fuel. Furthermore, the plot also reveals that the densities of the low alcohol-blended fuels (being dominated by the hydrocarbon portion) are fairly independent of low additions of water. However, as ethanol content dominates the blend, beyond 2.5% water content the density of E50 and E85 appear to be marginally increasing. While that of the fuel E30 decreases after the 2.5% water content level, this is due to the analysis of the bulk fuel after phase separation occurred.

To determine if the differences between the densities of the fuel blends were significant, an ANOVA was performed on the dataset. The results are presented and interpreted as above in Section 4.3. As shown in Table 5, the ANOVA found significant differences existed within the dataset of fuel blend density measurements. All differences in density between the fuel blends were found to be significant with the exceptions of low alcohol-blended fuels (E10 and E15, E10 and I16, and E15 and I16), again since they are dominated by hydrocarbons. The low alcohol-blended fuels were significantly different from the E0, so the alcohol does have an effect. With the significant differences in densities observed between most fuel blends, technologies which utilize this principal may not be transferable between blends.

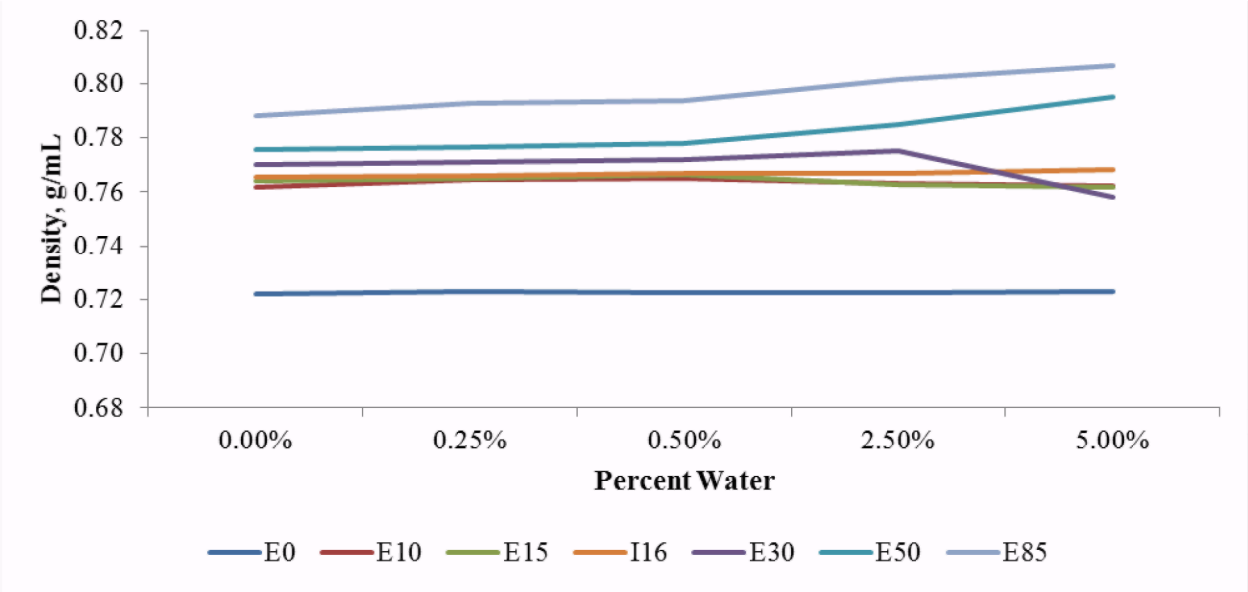

Figure 3. Density Plot by Test Blend and Water Content

Table 5. F-Test Results of Fuel Blend Comparison for Density*

Fuel Blend	E0	E10	E15	I16	E30	E50
E10	<0.0001 YES					
E15	<0.0001 YES	1 NO				
I16	<0.0001 YES	0.839 NO	0.821 NO			
E30	<0.0001 YES	<0.0001 YES	<0.0001 YES	<0.0001 YES		
E50	<0.0001 YES	<0.0001 YES	<0.0001 YES	<0.0001 YES	<0.0001 YES	
E85	<0.0001 YES	<0.0001 YES	<0.0001 YES	<0.0001 YES	<0.0001 YES	<0.0001 YES

$p < 0.05$ indicates a significant difference
*F-test performed after significant differences were identified using an ANOVA analysis of the dataset.

4.6 Viscosity

Measurement of flow through piping requires that pressure in the pipe section be monitored. Pressure monitoring systems require knowledge of several parameters of product in the piping, including density and viscosity. Addition of ethanol to gasoline increases the viscosity of the blend thus yielding higher differential pressures across the flow measurement device than obtained for neat gasoline (E0). Proper calculation of leak rate would require knowledge of the ethanol and water content of the blend or exact determination of density and viscosity. Once again, because these liquid properties vary with temperature and the rate of temperature change effects the ability for a technology to make a conclusive test, the highest precision in level measurement may necessitate that they be compensated for or expressed with relation to the actual temperature of the measured liquid.

From Figure 4 it is evident that an increase in ethanol content leads to increase in fuel viscosity and that E85 is the most viscous among the fuels. Furthermore, the plots also reveal that fuel viscosity measurements are fairly independent of low additions of water. However, beyond 2.50% water content, the viscosity of E50 and E85 appear to be marginally increasing, while that of the fuel E30 decreases. Again the E30 decrease is due to the analysis of the bulk fuel after phase separation occurred.

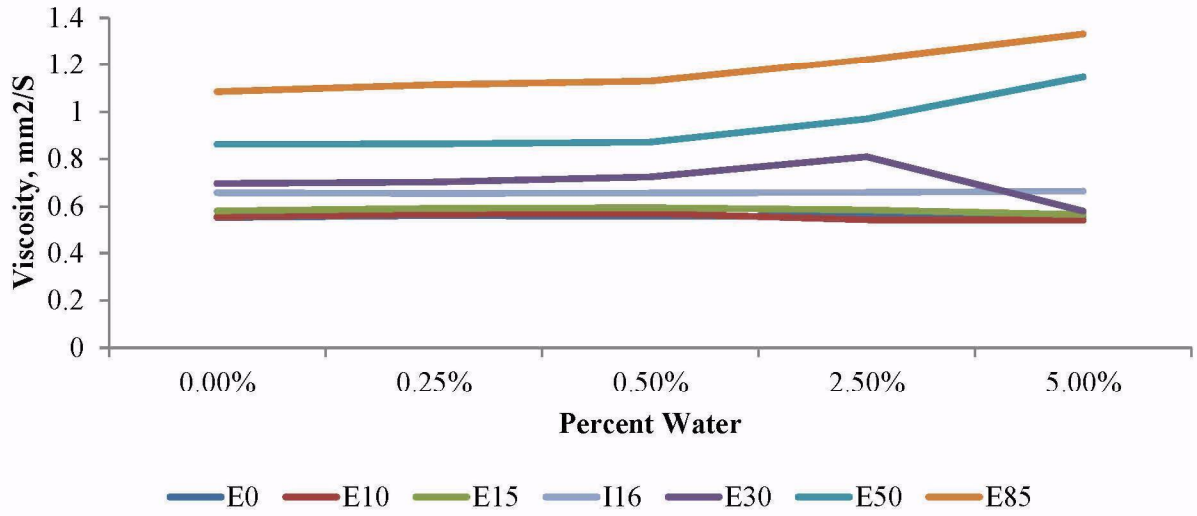

Figure 4. Viscosity Plot by Test Blend and Water Content

To determine if differences between viscosities of the fuel blends were significant, an ANOVA was performed on the dataset. The results are presented and interpreted as above in Section 4.3. As shown in Table 6, the ANOVA found significant differences existed within the dataset of fuel blend viscosity measurements. Every fuel blend comparison was found to be significantly different, except for the comparison between E0 and E10. Without modification, technologies which incorporate viscosity as an operating principle may not function appropriately across all the tested fuel blends.

Table 6. F-Test Results of Fuel Blend Comparison for Viscosity*

Fuel Blend	E0	E10	E15	I16	E30	E50
E10	1 NO					
E15	0.017 **YES**	0.037 **YES**				
I16	<0.0001 **YES**	<0.0001 **YES**	<0.0001 **YES**			
E30	<0.0001 **YES**	<0.0001 **YES**	<0.0001 **YES**	0.001 **YES**		
E50	<0.0001 **YES**	<0.0001 **YES**	<0.0001 **YES**	<0.0001 **YES**	<0.0001 **YES**	
E85	<0.0001 **YES**	<0.0001 **YES**	<0.0001 **YES**	<0.0001 **YES**	<0.0001 **YES**	<0.0001 **YES**

$p < 0.05$ indicates a significant difference
*F-test performed after significant differences were identified using an ANOVA analysis of the dataset.

4.7 Acidity

Acidity may not have a direct relation to the operating principles of LD technologies; however, it is included here as a measure of potential compatibility issues. Acidity of the fuel (expressed by the ASTM method as percent mass normalized to acetic acid) remained fairly independent of its water content, little to no change was observed with the increase in water. While E0 was least acidic among the fuels, E50 and E85 were found to be on the higher end.

To determine if the differences between acidity of fuel blends were significant, an ANOVA was performed on the dataset. The results were presented and interpreted as above in Section 4.3. As shown in Table 7, the ANOVA found significant differences existed within the dataset of fuel blend acidity measurements. Of 21 comparisons made between different blends for acidity, 12 were found to be significant and nine (9) were not, with no discernable pattern being observed between fuels blends. What can be said is that E0 is significantly different from all of the other blends tested.

Table 7. F-Test Results of Fuel Blend Comparison for Acidity*

Fuel Blend	E0	E10	E15	I16	E30	E50
E10	<0.0001 **YES**					
E15	0.029 **YES**	0.334 NO				
I16	0.001 **YES**	1 NO	0.932 NO			
E30	<0.0001 **YES**	1 NO	0.334 NO	1 NO		
E50	<0.0001 **YES**	0.029 **YES**	<0.0001 **YES**	0.004 **YES**	0.029 **YES**	
E85	<0.0001 **YES**	0.19 NO	0.001 **YES**	0.029 **YES**	0.19 NO	1 NO

$p < 0.05$ indicates a significant difference
*F-test performed after significant differences were identified using an ANOVA analysis of the dataset.

4.8 Coefficient of Thermal Expansion

All materials expand or contract when their temperature changes. The degree of this expansion or contraction is described by a material-specific coefficient of thermal expansion. Knowledge of this coefficient and its use as a correction factor is imperative in making accurate liquid level determinations. The storage temperature of fuels in USTs is constantly changing, albeit by relatively small amounts

compared to the average storage temperature. A measurement change can easily be produced by thermal expansion/contraction under typical fuel storage conditions. Therefore, the coefficient of thermal expansion must be known and used to make corrections to the measured fuel volume to allow accurate storage volume determinations. Accurate volume calculations can only be obtained if the ethanol content of a blend is known and used by a LD system. Figure 5 below presents the similar increasing trend of all of the test blends as temperature increases. Regardless of ethanol content, the volume of fuel increased with the increase in the temperature. The coefficient of thermal expansion for all fuels remained similar at 0.001 (as presented in Table 1); therefore, if necessary, LD technologies have been compensating for this magnitude of thermal expansion and most likely would not be affected by ethanol content.

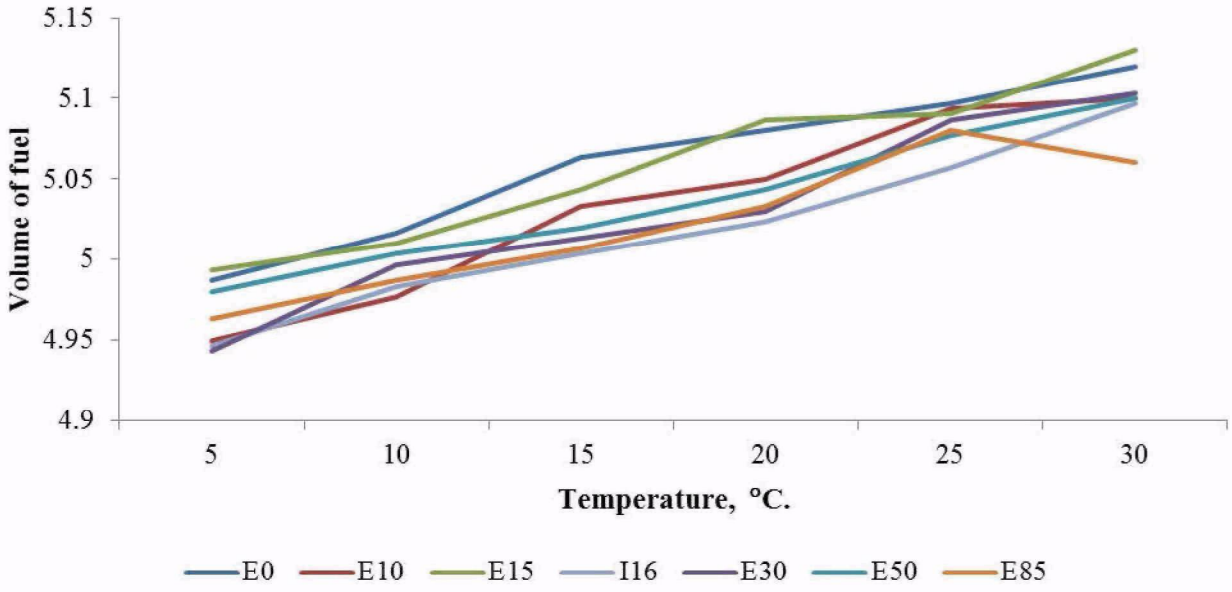

Figure 5. Thermal Expansion Plot by Test Blend

4.9 Non-additive Volume Changes (Degree of Accommodation)

Because of the varying miscibility of gasoline, water and ethanol, it is expected that as an aliquot of water is added to each of the test blends, the total volume change of the resulting BFW mixture was less than the volume of that aliquot, and the separated, dense phase grew disproportionately to the added volume of water. The relative total volume decrease is due to accommodation of polar water molecules into the structure formed by the polar ethanol molecules referred to as the degree of accommodation.

Table 8 shows as the test blends increase in ethanol content, the amount of ethanol accommodated within the polar water structure increases which results in a relative volume reduction

upon the addition of water. Results less than 1 show that the total volume is less than expected total volume and with the exception of I16, all of the fuel bends were less volume than expected.

Table 8. Degree of Accommodation Summary for the Test Blends

Test Blend	Growth of Total Volume (Slope of Δ measured total volume/ Δ expected total volume)
E0	0.9557
E10	0.9953
E15	0.9915
I16	1.0039
E30	0.9665
E50	0.9838
E85	0.9510

5.0 LEAK DETECTION TECHNOLOGY OPERATING PRINCIPLES

The standard test procedures are divided amongst five main categories of leak detection technologies. Evaluation of operability of these technologies when applied to alternative fuel service necessitates a basic understanding of the principles of operation of each technology category. Table 9 presents the categories and lists various technologies associated with each intended to represent the most common methods and their operating principles within each category. In addition, Table 9 presents a brief description of the operating principle of each technology category. More detailed descriptions of the test procedures and technologies associated with each are available on the EPA Office of Underground Storage Tank (OUST) website[1].

5.1 Volumetric versus Non-volumetric-Based Testing Technology Categories

The compendium of leak detection technologies can be delineated as being either volumetric or non-volumetric. Each specific technology falls into one of these two categories; in some cases a technology may apply to both categories. Table 9 shows the relationships between leak detection technology categories and these technology types. Either type may be used to satisfy requirements of 40 CFR 280. The primary distinction between the two categorical procedures is that volumetric technologies yield quantitative results (i.e. a reported leak rate) whereas non-volumetric technologies yield qualitative results (i.e. only whether there is evidence of a leak or not when compared to a threshold value).

Volumetric technologies quantitatively measure leak rate from a UST based on changes in liquid level in a tank. Various types of technology are available for measuring these changes, including floats, load cells, and ultrasonic devices. They can be further categorized into methods that meet 40 CFR 280

requirements for precision testing; 0.1 gal/hr leak rate (e.g., tank or pipeline tightness tests) or a 0.2 gal/hr leak rate (e.g., ATG systems or statistical inventory reconciliation [SIR] methods) respectively. Accurate use of each volumetric technology requires knowledge of certain storage conditions and fuel properties so that adjustments can be made to compensate for other factors that might produce a change in liquid level. For example, the coefficient of thermal expansion must be known in order to allow volume corrections to be made based on changes in the temperature of the stored product. Without this correction a volume change that occurs as the storage temperature drops could be interpreted as a fuel leak or the actual calculated leak rate may be inaccurate. Other corrections that may be necessary include fuel density (based on temperature and ethanol content), air density (based on temperature above the stored liquid), or the ground water level surrounding a tank.

Non-volumetric technologies make use of equipment that qualitatively identify when a leak is occurring in a UST. While these technologies cannot be used to determine an actual leak rate in a UST system, the signal from the technology can provide an indication that a tank might be leaking. Various types of non-volumetric technology include acoustic measurements, water sensing equipment, external tank monitoring systems, and interstitial sensors. These technologies can be used to detect sounds made by fuel leaks through an orifice (i.e., tank shell), water present at the bottom of a tank, or liquids in the interstitial space of a double-walled tank, respectively. A response from one of these technologies cannot be used to calculate an exact volume or leak rate, but observation of a response provides the tank operator with a clear indication that the integrity of the tank shell may have been compromised. Other non-volumetric technologies include vapor and liquid out-of-tank monitoring in the excavated soil area or ground water surrounding a UST. Tracers can also be used to detect the presence of a leak.

5.2 Automatic Tank Gauging System Technologies

Whereas manual tank gauging typically consists of "sticking" a UST with a long pole containing graduated length markings, an ATG system relies on various physical properties of the storage system to generate an electronic signal that can be converted into a value representing the volume in a tank. As such, ATG systems are volumetric leak detection technologies.

An ATG system consists of a probe or sensor that is located inside the UST and a controller (or console) that is mounted in an indoor location. The probe or sensor is used to generate the electronic signal that is subsequently processed in the console to calculate volume and/or leak rate. The electronic signal is generated in one of several ways, including:

- A float mounted to a probe (a liquid level method);

- A set of acoustic sensors to detect sound in the liquid or the air space above the liquid (a sound transmission/reception method similar to sonar or radar);
- A load cell suspended in the liquid product (a buoyancy method); or
- A set of sensors to determine the electrical properties of a liquid (an electric conductance/capacitance method).

Table 9. Leak Detection Technologies and Principles of Operation

Technology	Principle of Operation
VOLUMETRIC-BASED TECHNOLOGY CATEGORY	
Automatic Tank Gauge (ATG) Systems	
Magnetostrictive Probes	Wire sensor inside a shaft detects presence of magnetic field, which indicates height of float
Ultrasonic or Acoustic Methods (speed)	Sensor detects changes in fluid levels detecting a sound wave echo reflected from the interface of water/fuel or fuel/air and calculates level based on speed of sound in the product
Capacitance Probes	Detection is based on dielectric property of the stored liquid
Mass Buoyancy/ Measurement Systems	Buoyancy of probe is detected on a load cell and compared to tank geometry to calculate liquid level
Statistical Inventory Reconciliation (SIR) Methods	
Traditional SIR	A SIR vendor performs analysis of liquid level data for evidence of tank tightness. Data are collected using an ATG or by taking daily manual liquid level readings.
Continuous SIR	SIR vendor software performs temperature compensation and leak-test calculations on data collected from designated input devices during tank quiet times.
Pipeline Methods (Piping)	
Pressure Decay	Measures the change in pressure between the atmosphere and the pressurized product in the line over time.
Constant Pressure	Sensors monitor change in volume at constant pressure.
Mechanical Leak Detectors	Permanent installation on piping. Conducts leak tests every time the pump engages.
NON-VOLUMETRIC-BASED TECHNOLOGY CATEGORY	
Fuel Sensitive Polymers	Fiber optic cable is coated with a polymer that interacts with fuel. When fuel is present, the light or current passing through the cable will be affected
Tracers	Chemical markers (i.e., tracer) are added to the product and the surrounding soil is monitored for the tracer
Acoustic Precision Test	Detected sounds are used to identify potential leaks; an orifice is used to simulate the sound produced as liquid or air leaks out of a system. This is accomplished using acoustic sensors and microphones, and ultrasonic sensors and hydrophones.
Vacuum /Pressure Decay Test	Determine tank tightness by the decay rate of the vacuum or pressure established by the method.
Dry Interstitial Integrity Monitoring Technologies	
Vacuum /Pressure Decay Monitoring	Technology uses an integral vacuum pump or pressurized system to continuously maintain a partial vacuum or pressure within the interstitial space of double-walled tanks and double-walled piping. Method is capable of detecting breaches in both the inner and outer walls of double-walled tanks or double-walled piping
Wet Interstitial Integrity Monitoring Technologies	
Liquid Filled	A liquid solution is used to fill the tank or piping interstice. The dual-point level sensor system monitors the liquid level in the interstitial reservoir and sounds an alarm if the liquid level is either too high (ingress of liquid) or too low (egress of liquid)
Sensor – liquid ingress	Varies depending on the type of sensor and comes in multiple forms. Most examples include use of refractive index or float switch

Table 9. Leak Detection Technologies and Principles of Operation (Continued)

Technology	Principle of Operation
Water Detection Technologies (ATG, Non-volumetric, Sensors)	
Water Float	Buoyancy of float allows the signal generated (magnetic field or capacitance) to coincide with the top of the liquid layer based on the liquid density in comparison to the float density. These floats are specifically designed for water detection and the density difference between water and the fuel product.
Density Float	Buoyancy of a float signals changes in product that compares density data changes over time to assess the change in product quality due to water ingress. This float is sensitive to the aqueous phase detection found in ethanol-blended fuels.
Conductivity Water Probe	The probe detects water by measuring current flow when water contacts the probe. Used with certain acoustic methods

Regardless of the method employed, the signal generated by any of these technologies is combined with a specific set of other data (entered by the owner or operator) and processed to calculate a volume of liquid in in the UST. The console contains a processor that compares calculated volumes at different times (during which the UST is not dispensing or receiving fuel) to determine if any observed difference is due to a leak or some other factor.

Depending on the ATG system in use, the associated processor must "correct" the calculated volume for other tank conditions. For example, the volume derived from liquid height obtained using a float system, electrical property, or acoustic sensor must be adjusted for liquid expansion or contraction produced by changes in temperature of the stored liquid. Similarly, the result obtained from a pressure, buoyancy, or sound velocity reading must incorporate a liquid or air density factor (which also varies with temperature) to accurately calculate volume. Given the proper inputs, ATG systems will yield information on volume of stored fuel and on calculated leak rates during a leak tests.

Most probes used for ATG systems are also equipped with a water float. The water float is located on the bottom of the tank where water may collect as a denser phase than the fuel. As the water or water phase (water-ethanol mixture) height increases, the float rises and transmits an electronic signal proportional to the level of the denser phase in the bottom of the tank. The inventory measurement would also register an increase in volume given water ingress, although the quantified amount may not be accurate depending on the water solubility of the fuel and proportion of ethanol in the fuel.

5.3 Statistical Inventory Reconciliation Technologies

SIR technologies, which can be either volumetric (quantitative) or non-volumetric (qualitative), rely on the comparison of manually or automatically-collected liquid level data and fuel delivery and dispensing (sales) records. Statistical evaluation of the data and records is performed, usually by a vendor or with a vendor software program, to determine if the stored volume reconciles with deliveries into and out of a tank. A discrepancy in the volumes may then be reported as a leak or some other event. SIR is subject to potential sources of human and measurement error when collecting or recording the records. In addition to errors in metering the fuel delivery and dispensing volumes, storage tank volumes may change between readings due to temperature differences, fuel transfer between manifold tanks, fuel volatilization, or introduction of water into the UST. Traditional SIR does not "correct" for these variables; however continuous SIR has multiple input devices and can compensate for these variables.

5.4 Pipeline Leak Detection Technologies

Pipeline leak detection can be conducted using volumetric or non-volumetric methods. Volumetric methods use fluid flow instrumentation to monitor flow rate of a moving fluid through the underground piping of a UST system at one or more locations, or the static pressure in a sealed pipe system. Flow measurement devices are usually based on pressure; however, these devices could also use a displacement piston or graduated cylinder instead of a pressure-based measurement device. The liquid within the piping is non-compressible, and therefore, a single flow measurement or a comparison of the flows at different locations will indicate if a leak has occurred along the piping. By necessity, several properties of the conveyed fluid must be known to correctly convert the measurement into a flow rate. Critical parameters needed by most non-compressible flow monitoring systems include fluid density and viscosity. Even without these parameters comparison of the pressures at different monitoring points can indicate the presence of a leak. The rate cannot be accurately determined without product-specific data. Friction losses may also need to be calculated in high-volume or long piping sections before a leak can be confirmed. Static pressure devices installed on a non-leaking pipe section should show the pressure is maintained over the duration of the test. Temperature correction may be needed if the product temperature is susceptible to change during the test, as this will produce product expansion or contraction, which in turn will change the static pressure.

5.5 Non-volumetric Leak Detection Technologies

Vapor-phase out-of-tank product detectors are non-volumetric technologies that employ instruments designed to detect hydrocarbon product vapors in the vadose zone or backfill area around a

UST. The technology relies on the high volatility of some chemical components of gasoline and the ability to measure them at low concentrations. Thus, sampling the "soil gas" surrounding a UST or within the tank top sump, for example, for gasoline components such as benzene or toluene can be used to detect UST system leaks. The fuel leak rate, however, cannot be quantified using this method.

A variation of this technology is an external tracer. In this system a volatile tracer compound is added to the product stored in a UST, and the tank backfill around the UST is monitored for this tracer. The tracer must be able to become completely mixed into the product, yet be volatile enough to separate from the fuel after a release from the tank and migrate through the tank backfill to a monitoring location where it is collected and later analyzed in a laboratory by gas chromatography - mass spectrometry.

Liquid-phase out-of-tank product detectors are non-volumetric technologies that employ instruments designed to detect a free-product layer on the water table in an observation well near a UST or on water collected in a dispenser sump, for example. Free-product detectors are used commonly in site remediation monitoring wells and rely on the immiscibility of petroleum products and water. Gasoline that leaks from a UST and intercepts the water table will rise to the top of the water column in an observation well and be detectable as a layer of product on top of the water. Although leaks can be detected using these detectors, the leak rate cannot be determined.

Acoustical methods (not to be confused with the ultrasonic ATG technology) make use of an acoustic sensor to detect the sound of fuel leaking out of a UST or water or air leaking into a tank. If desired, a tank can be placed under a slight negative pressure test condition to induce air flow into the tank. Interfering sounds must be eliminated to use this technology, and only qualitative leak determinations are possible. In addition, if the ground water level is above the bottom of a UST, water may enter the tank without an audible sound. Therefore, these technologies include a water detection component. One kind is based on conductivity and referred to as a conductivity water probe. Current flow is measured by a gauge when water ingress contacts a probe while under vacuum. In ethanol-blended gasoline, it is difficult to determine water ingress due to minimal conductivity of the transition zone between low ethanol-blend gasoline and phase separation (as discussed in Section 4.2), and will not work in high ethanol-blends due to the high conductivity of the high ethanol blend.

Interstitial integrity monitoring is a technology used on secondarily contained tanks and piping. ***Dry interstitial monitoring*** is performed in one of two ways: (1) a vacuum or pressure is induced in the interstitial space, and the pressure differential is monitored in the space, or (2) a sump (or reservoir) is connected to the interstitial space to allow liquid leaking into the space to collect and be detected by liquid detection systems. ***Wet interstitial monitoring*** is performed with the interstice full of liquid (usually brine) with a change in liquid level indicating a release into or out of the interstice. These options

can be performed continuously or intermittently, and no other parameters must be monitored to make adjustments based on the observations.

Traditional ***water detection*** **technologies** make use of the insolubility of water in non-ethanol blend gasoline (immiscibility) and are specifically calibrated to detect the density of water. The unexplained presence of water in a tank is an indication of a potential leak and must be investigated. When water sinks to the bottom of a UST and forms a separate layer, a float where density is greater than gasoline but less than water can be used to generate and send a signal to an ATG console. Because these technologies are now needed to function in a wide range of fuel densities, a traditional water float will be too dense to float on the interface layer between the aqueous phase and ethanol-blended fuel.

Aqueous phase ***density floats***, water detection technologies that are calibrated for aqueous phase detection, are density-based technologies that address concerns with ethanol-blended fuel and its ability to absorb water. When enough water is absorbed, the ethanol and water separate from the hydrocarbon phase and settle to the tank bottom. The density of this water-ethanol bottom; however, is less than that of water alone, and as a result, traditional water floats do not consistently detect this aqueous phase. These newly developed technologies employ either a float with a density sensitive to ethanol-water mixtures, or a sensor to directly measure the density of the ethanol-water mixture at the bottom of a tank.

6.0 SUITABILITY ASSESSMENT OF LEAK DETECTION TECHNOLOGIES IN ETHANOL-BLENDED FUEL

Most LD technologies have not been evaluated when in ethanol-blended fuel service; however, many are used in E10 fuel service and if not relying on conventional water floats to detect water ingress, are performing appropriately in the field. As a result, observations on the suitability of LD technology with respect to its operability in ethanol-blended fuel service are based on stakeholder input, laboratory tests, and hypotheses involving critical fuel properties. Table 10 presents an assessment of the suitability of several LD technologies with respect to operability. Some technologies are expected to operate properly in ethanol blended fuels due to their somewhat simple operating principles. For example, a piping pressure decay system is expected to work properly with any non-compressible fluid provided that adequate temperature monitoring is also conducted. This is because the technology represents a static system that can only be affected by loss of fluid or expansion/contraction of the fluid. On the other hand, the interaction of some technologies with critical fuel parameters, or the interaction of the fuel parameters themselves, makes the operability of some technology uncertain. For example, while most parties believe that a fuel float-based technology should be able to detect changes in liquid levels, some questions exist as to whether the simultaneous loss of fuel and ingress of water will be adequately detected. Water absorption into ethanol may or may not produce a change in liquid volume, and if water does not drop to the bottom of the tank, ingress is not expected to be detected. As the ethanol content increases in the fuel blend, water-fuel interactions and water-ethanol detection becomes more problematic.

As discussed previously, Table 10 provides observations for low ethanol content (low-E, up to 15%) and high ethanol content (high-E, E51 - E85) fuel blends. The question being posed by technology category with respect to operating principle is:

- **Is the Technology Capable of Detecting a Leak at the Regulatory Level?** This criterion assesses whether the response generated by the technology is expected to allow the user to derive the correct conclusion regarding a leak or no-leak condition while operating in a UST at the regulatory level.

The three possible suitability assessments were developed to the above question based on input from stakeholders (NWGLDE, regulators, testing company representatives, and technology vendors). These assessments are identified in Table 10 according to color coding, include the following:

- **Technology is expected to be suitable for indicated use (GREEN).** The operating principle of the technology is such that no major limitations or interferences are expected to exist when employed in the listed service as compared to gasoline service.

- **Technology has limitations with the indicated use (YELLOW).** One or more of the principles upon which the technology operates is not expected to be suitable when employed in the listed service. Without modification, the technology may or may not operate properly. A series of tests could be conducted to demonstrate that the technology performs as expected in the listed service.
- **Technology is expected to not be suitable for indicated use (RED).** One or more principles upon which the technology operates is unsuitable when employed in the listed service.

As all technologies are different, have different algorithms, and are influenced by human inputs and installation, these conclusions may not be appropriate for every technology in a category. This paper discusses the relationship between fuel properties and operating principles against the performance standards established in the federal LD requirements. The potential negative impacts are highlighted in the previous sections for consideration; however, in most cases, a change in liquid level will be detected whether it decreases due to a leak or increases due to water intrusion. In some cases, the technology may need to be slightly modified to recognize these changes at the regulatory level with adjustments of threshold values and monitoring data processing.

Table 10. Suitability of Existing Leak Detection Technology for Ethanol-Blended Fuel

LD Category and Technology	Is the Technology Capable of Detecting a Leak/Water Ingress at the Regulatory Level?		Comments
	Low-E (up to 15%)	High-E (51 to 83%)	
VOLUMETRIC METHODS			
Automatic Tank Gauge (ATG) Systems^			
Magnetostrictive Probe*			Fuel properties are needed; liquid level changes will most likely be detected. Water ingress detection may have limitations when traditional water floats are used.
Ultrasonic or Acoustic Methods (speed)			Fuel properties are needed; liquid level changes will most likely be detected. Water ingress detection may have limitations when traditional water floats or conductivity water probes are used.
Capacitance Probe	Gasoline-ethanol-water has unknown properties and therefore may not be able to accurately diagnose the extent of a leak. In addition, multiple liquid phases in a storage tank will make it difficult to derive an accurate dielectric constant for each observed phase. Although capacitance is being used in other LD technology categories, the traditional capacitance ATG probes are not expected to operate properly.		No longer commercially available; rarely used.
Mass Buoyancy/ Measurement System			Fuel properties are needed; liquid level changes will most likely be detected. Water ingress detection may have limitations when traditional water floats are used.
Statistical Inventory Reconciliation (SIR) Methods			
SIR – Manual			Comparing a change in condition using regularly collected data; assumes no changes in data collection process. Fuel properties are needed; liquid level changes will most likely be detected.
SIR – Data from ATG			
Methods of Release Detection for Piping			
Pressure Decay			Dynamic methods require fuel properties (coefficient of thermal expansion, viscosity) to calculate or compare against a threshold; properties should remain constant in a given piping system, so if known, the methods should operate properly.
Constant Pressure			
Mechanical Leak Detector			

^Water detection is a requirement of ATG systems that was evaluated separately in this paper.
*See Appendices for testing methods and results (A, C, D, E, and F).

Technology is expected to be suitable for indicated use.
Technology has limitations with the indicated use.
Technology is expected to be not suitable for indicated use.

Table 10. Suitability of Existing Leak Detection Technology for Ethanol-Blended Fuel (Continued)

LD Category and Technology	Is the Technology Capable of Detecting a Leak/Water Ingress at the Regulatory Level?		Comments
	Low-E (up to 15%)	High-E (51 to 83%)	
NON-VOLUMETRIC METHODS			
Vapor Out-of-tank Methods			
Tracers			Tracer must be proven compatible with the product, not foreseen as an issue given the available tracer compounds.
Liquid Out-of-tank Methods			
Hydrocarbon (HC) layer			Reduced petroleum content of high-E blends may produce difficulty in forming a free phase for detection.
Fuel Sensitive Polymers*			When the product is not dominated by hydrocarbons, the polymers may not react.
Acoustic Methods			
Sound Detection (Tanks)	Multiple liquid phases in a UST or piping and potential interfering sounds will make it difficult to identify air, water, or leaked fuel entering the tank while under vacuum.		No reliable database of sounds expected during leakage. Relies on human interpretation of noises during tank tightness testing.
Sound Detection (Piping)			
Interstitial Methods			
Liquid Filled			Should not be affected if liquid (product, water, or mixture of the two) is sufficiently dense or in sufficient quantity to trigger a reading.
Sensors – liquid ingress*			
Vacuum			
Pressure			
Water/Aqueous Phase Detection Methods^			
Water Float*			Potential effect on operation due to miscibility of water and ethanol-blended fuels.
Density Float*			Developed for use with E-blended fuel at the bottom of the tank.. Will not float until phase separation occurs.
Conductivity Water Probe			Current flow increases very slowly when there is water ingress into a tank with Low-E. This will not work with High-E because it is conductive.
Methods for Release Detection in Piping			
Pressure Decay*			Static method does not require exact fuel properties.

*See Appendices for testing methods and results (A, C, D, E, and F).
^Water detection is a requirement of ATG systems that was evaluated separately in this paper.

	Technology is expected to be suitable for indicated use.
	Technology has limitations with the indicated use.
	Technology is expected to be not suitable for indicated use.

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Appendix A

Environmental Technology Verification

Fuel Property and Technology Testing

Appendix A

Environmental Technology Verification Fuel Property and Technology Testing

A1 BACKGROUND

The U.S. Environmental Protection Agency (EPA) supports the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized testing organizations; with stakeholder groups consisting of buyers, vendor organizations, and permitters; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance (QA) protocols to ensure that data of known and adequate quality are generated and that the results are defensible. The definition of ETV verification is to establish or prove the truth of the performance of a technology under specific, pre-determined criteria or protocols and a strong quality management system. The highest-quality data are assured through implementation of the ETV Quality Management Plan. ETV does not endorse, certify, or approve technologies.

The EPA's National Risk Management Research Laboratory (NRMRL) and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV.

A2 TEST DESIGN AND PROCEDURES

A2.1 Test Overview

This verification test was conducted according to procedures specified in the Quality Assurance Project Plan[1] and the Addendum[2] for Biofuel Properties and Behavior Relevant to Underground Storage Tank Leak Detection System Performance (QAPP) and adhered to the quality system defined in the ETV AMS Center Quality Management Plan (QMP)[3]. A

stakeholder committee was specifically assembled for the preparation of the QAPP. A list of participants in the stakeholder committee members is presented at the end of this appendix (Table 9). The committee included representatives from industry associations, state and federal governments, including representatives of the National Work Group on Leak Detection Evaluations (NWGLDE), and users. The responsibilities of verification test stakeholders and/or peer reviewers included:

- Participate in technical panel discussions (when available) to provide input to the test design;
- Review and provide input to the QAPP; and
- Review and provide input to the verification report(s)/verification statement(s).

Battelle conducted this verification test with funding support from the EPA's Office of Underground Storage Tanks (OUST).

Testing was conducted as three distinct sets of tests. Each test set was designed to acquire specific data with respect to fuel properties or leak detection technology performance. The three sets were:

1. Bench-scale studies for the determination of select physical and chemical properties of biofuels and biofuel- water (BFW) mixtures.
2. Laboratory-scale studies for the identification and quantification of specific biofuel and BFW mixture processes affecting performance of UST LD operating principles.
3. Pressure decay testing for the understanding of the effect of ethanol, if any, on a leak when pressurized.

The bench-scale testing aimed at determining several fundamental properties of alcohol-blended fuels and BFW mixtures under typical conditions encountered during operation of underground storage tank (UST) leak detection (LD) systems. The goal of the bench-scale testing was to differentiate whether the range of ethanol blends had properties that behaved significantly different from each other, thereby being the evidence that the technologies may or may not function properly when used in the different blends. Bench-scale testing was divided into four series of tests described below and the results are presented in Appendix B.

1. Intrinsic Properties of BFW Mixtures
2. Coefficient of Thermal Expansion
3. Non-additive Volume Changes
4. Interface Determination of Phase Separation

The laboratory-scale tests evaluated the performance of an optical sensor, a sensor with a float switch and fuel sensitive polymer and a capacitance/conductance sensor (that is not yet on

the market) in ethanol blended fuels. One of the goals of this test was to provide information on the performance of different operating principles when used with ethanol-blended fuel. To accomplish this goal, the experimental design included the following three options for testing:

1. Initial water/test blend detection
2. High liquid detection
3. Water ingress detection when submerged in a test blend

The technologies were tested according to their capabilities; therefore, only the appropriate tests in the QAPP were conducted. The testing and results for the verification testing of the sensor can be found in Appendix C.

The pressure decay testing aimed at determining the impact of different ethanol/isobutanol blended fuels on the functionality of pressure decay as a pipeline leak detection method. Pressure decay relies on the concept that a pipeline containing fuel is pressurized and sections isolate to show a loss of pressure overtime if a leak is present. This pressure decay test is focused on whether the different blends of fuel would affect the leak rate. The testing procedures and results for the pressure decay testing can be found in Appendix D.

A2.2 Test Site Description

The interior of existing research buildings (Building 9 and Building 1) at Battelle's Columbus, Ohio campus was used to conduct the bench- and laboratory-scale experiments. Building 9 contains a large, high-bay room (9-0-50) on the north end of the building. Within the room, there is a smaller ventilated room (9-0-50C) where experimentation took place. The ventilated room was modified and connected to building steel to provide bonding and grounding to eliminate risks of static build up. Fuel and waste storage areas were located outside on the northwest side of Building 9. All experimental work on the pressure decay testing was conducted in a fume hood in the Environmental Restoration laboratory in Building 1 (1-2-30). The fume hood was modified and connected to building steel to provide bonding and grounding for the pressure decay vessel. The testing occurred between May and November 2013. Analytical results were determined by a contracted laboratory, Iowa Central Fuel Testing Laboratory (ICFTL).

A2.3 Experimental Design-Preparation of Test Blends

All test blends were prepared in an identical manner for all portions of the testing. All petroleum products were sampled, mixed and handled according to ASTM D4057[4] and D5854[5]; volumetric blend stocks of ethanol (or isobutanol) and gasoline were prepared according to

ASTM D7717[6]. In addition to ethanol blends, an isobutanol blend containing 16% (v/v) isobutanol (I16) was included in the list of test blends. Test blends were prepared by mixing different concentrations of ethanol-free gasoline (E0) with either denatured ethyl alcohol (ethanol; >97% purity) in the case of ethanol blends or isobutyl alcohol (isobutanol; >98% purity) in the case of I16. E0 was purchased from Marble Cliff Oil (Columbus, OH) and was approved for sale as automotive fuel. Information such as Material Safety Data Sheets and Bills of Lading were collected and recorded during fuel delivery. Proposed test blend compositions have been selected based on those that are currently available on the market or are anticipated to be available on the market. Test blends for the bench-scale test sets included gasoline (E0) and was prepared to simulate low ethanol blends (E10, E15, and E30), flex fuels (E50, and E85) and an isobutanol blend (I16). Test blends for the laboratory-scale test sets were E0, E15, E30, E50, E85 and I16 (only one technology was tested using E30 and E50) and groundwater. An aliquot of E0, E15, E85, and I16 test blends for the laboratory-scale testing were used for the pressure decay testing, as well as deionized water. E85 for the laboratory-scale and pressure decay testing was purchased from a local Giant Eagle (Columbus, OH) gas station.

Before preparation of the test blends, the water and ethanol content of the E0 gasoline were determined by ASTM D203[7] and ASTM D4815[8], respectively. Table 1 indicates the mixing ratios of E0 and ethanol or isobutanol to achieve the desired test blend composition assuming E0 contains no ethanol or water. Table 2 and 3 indicates the data quality objectives (DQO) that had to be met for the test blends. Table 4 and Table 5 display the test blend results for ethanol/isobutanol content and water content for all three sets of testing. As presented in these tables, all of the bench scale test blends had ethanol content relative percent differences (RPDs) <15% and less than 0.1% water content and therefore met the acceptance criteria. As well as, all of the laboratory-scale and pressure testing test blends fell below the required 0.25% water content, except for the E85 test blend which was purchased. In addition, they all fell within 25% of the target alcohol value. Test blends were sampled and mixed in two 4-liter (L) batches and used as soon as possible for the bench-scale and laboratory-scale experiments. Test blends which were not used immediately will be capped and stored at room temperature for no more than 21 days before use.

Table 1. Mixing Ratios of E0 and Ethanol/Isobutanol for Preparation of Test Blends

Test Blend	Volume Fraction E0	Volume Fraction Ethanol/Isobutanol
E0	1.0	0.0
E10	0.90	0.10
E15	0.85	0.15
E30	0.70	0.30
E50	0.50	0.50
E85	0.15	0.85
I16	0.84	0.16

Table 2. Data Quality Objectives and Corrective Action for Bench-scale Testing

Test Blend	Analysis	Method	Data Quality Objective	Corrective Action
Purchased Gasoline (E0)	Water Content	ASTM E203[7]	Water Content < 0.1% (v/v)	Note discrepancy in project files
	Ethanol Content	ASTM D4815[8]	Ethanol Content < 1% (v/v)	Note discrepancy in project files
Prepared Ethanol Test Blends (E10, E15, E30, E50 and E85)	Water Content	ASTM E203[7]	Water Content < 0.1% (v/v)	Note discrepancy in project files
	Ethanol Content	ASTM D4815[8]	Ethanol Content <15% RPD	Remake and reanalyze test blend
	Ethanol Content	ASTM D5501[9]	Ethanol Content <15% RPD	Remake and reanalyze test blend
Prepared Isobutanol Test Blend (I16)	Water Content	ASTM E203[7]	Water Content < 0.1% (v/v)	Note discrepancy in project files
	Isobutanol Content	ASTM D5501[9]	Isobutanol Content <15% RPD	Remake and reanalyze test blend

Table 3. Data Quality Objectives and Corrective Action for Laboratory Scale and Pressure Decay Testing

Test Blend	Analysis	Method	Data Quality Objective	Corrective Action
Purchased Gasoline (E0)	Water Content	ASTM E203[7]	Water Content < 0.25% (v/v)	Note discrepancy in project files
	Ethanol Content	ASTM D4815[8]	Ethanol Content < 1% (v/v)	Note discrepancy in project files
Prepared Ethanol Test Blends (E15, E30, and E50)	Water Content	ASTM E203[7]	Water Content < 0.25% (v/v)	Note discrepancy in project files
	Ethanol Content	ASTM D4815[8]	Ethanol content 11.25-18.75% (v/v) for E15	Note discrepancy in project files
		ASTM D5501[9]	Ethanol Content 22.5-37.5 % (v/v) for E30. Ethanol Content 37.5-62.5% (v/v) for E50	Note discrepancy in project files
Purchased Ethanol Test Blend (E85)	Water Content	ASTM E203[7]	None	Note true value in project files
	Ethanol Content	ASTM D5501[9]	None	Note true value in project files
Prepared Isobutanol Test Blend (I16)	Water Content	ASTM E203[7]	Water Content < 0.25% (v/v)	Note discrepancy in project files
	Isobutanol Content	ASTM D5501[9]	Isobutanol Content 12.00-20.00% (v/v)	Note discrepancy in project files

Table 4. Test Blend Ethanol and Water Content for Bench-Scale Testing

Test Blend	Date Prepared	Measured Ethanol Content (% volume)	Measured Water Content (% volume)	Data Quality Objective For Ethanol (%RPD)
E0 #1	4/2/2013	0.495	0.008*	< 1% ethanol
E0 #2		0.495	0.008*	< 1% ethanol
E0 #1	8/14/2013	0.32	0.017	< 1% ethanol
E10 #1	4/22/2013	10.85	0.024*	8.50%
E10 #2		10.76	0.037*	7.60%
E15 #1	4/24/2013	14.84	0.034*	1.07%
E15 #2		15.02	0.032*	0.13%
I16 #1	8/14/2013	17.41	0.050	8.81%
I16#2		17.35	0.051	8.44%
E30 #1	4/30/2013	28.32	0.036	5.60%
E30 #2		28.34	0.030	5.53%
E30 #1	8/14/2013	29.03	0.066	3.23%
E30 #2	8/15/2013	28.82	0.054	3.93%
E50 #1	5/8/2013	45.62	0.040	8.76%
E50 #2		45.44	0.041	9.12%
E85 #1	5/15/2013	78.67	0.051	7.45%
E85 #2		78.47	0.053	7.68%

*Water content was measured as % mass, not % volume

Table 5. Test Blend Analytical Results for Laboratory-Scale and Pressure Decay Testing

Test Blend	Water Content		Alcohol Content		Viscosity[1]	Density[2]	Acidity	Sample Information	
	% Mass	% Volume	% Mass	% Volume	mm^2/sec	g/mL	% Mass	Date Prepared	Sample ID
E0	0.013	0.01	0.32	0.31	0.555	0.7601	0.0008	8/22/2013	54013-64-22
	0.011	0.008	0.33	0.32	0.5467	0.7608	0.0008	11/13/2013	54013-109-14
E15	0.038	0.029	18.05	17.48	0.5922	0.7659	0.0008	10/21/2013	54013-80-21
	0.041	0.032	18.04	17.47	0.6037	0.7681	0.0012	11/13/2013	54013-108-21
	0.038	0.029	18.20	17.61	0.6001	0.7672	0.0012	11/13/2013	54013-108-21 DUPLICATE
I16	0.029	0.022	17.85	17.00	0.648	0.7681	0.0008	10/21/2013	54013-81-21
	0.095	0.073	17.84	17.08	0.6576	0.7699	0.0008	11/13/2013	54013-107-21
E30	0.054	0.042	29.62	28.77	0.6947	0.7712	0.0012	11/15/2013	54013-111-21
E50	0.068	0.053	47.81	46.85	0.8345	0.7781	0.0012	11/15/2013	54013-114-21
E85	1.111	0.87	84.41	83.21	1.2206	0.7827	0.0031	10/21/2013	54013-82-2

1 Viscosity measurement was taken at 25°C

2 Density measurement was taken at 15.6°C

A3 QUALITY ASSURANCE/ QUALITY CONTROL

Quality assurance/quality control (QA/QC) procedures were performed in accordance with the QMP[3] for the AMS Center and the QAPP[1] for this verification test. QA/QC procedures and results are described in the following subsections.

A3.1 Data Collection Quality Control

The overall DQOs of this study measured physical and chemical properties of biofuels and identified and quantified the applicable processes (e.g., mixing) affecting the performance of UST LD systems on two scales: (1) bench-scale test set for the determination of select physical and chemical properties of biofuels and BFW mixtures (no technologies were studied at this scale); and (2) laboratory-scale test set for the identification and quantification of initial fuel and water detection as well as water ingress (where applicable) affecting performance of UST LD systems. Sample measurements followed standard analytical methods that have been published and accepted by ASTM International, American National Standards Institute (ANSI), National Association of Corrosion Engineers (NACE), or EPA. The QC procedures and measurement quality objectives (MQOs) for the methods utilized by ICFTL and Battelle Labs are described in Table 6.

Table 6. Data Collection Quality Control (QC) Procedures and Measurement Quality Objectives (MQO) for Analytical Methods

Method Designation: Method Title	QC Procedures	MQOs
ASTM D4815: Standard Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C_1 to C_4 Alcohols in Gasoline by Gas Chromatography[8]	Annual multi-point calibration curve and with newly installed column and continuing QC check samples every 10 samples*	Calibration curve $r^2 > 0.99$ **QC Check Samples:** **Good**: PR<4 & TPI >1.2; PR≥4 & TPI>2.4 **Fair**: PR<4 & TPI between 0.8-1.2; PR≥4 & TPI between 1.6-2.4 **Poor**: PR<4 & TPI <0.8; PR≥4 & TPI<1.6
ASTM D5501: Standard Test Method for Determination of Ethanol and Methanol Content in Fuels Containing Greater than 20% Ethanol by Gas Chromatography[9]	Annual multi-point calibration curve and with newly installed column and continuing QC check samples every 10 samples*	Calibration curve $r^2 > 0.99$ **QC Check Samples:** **Good**: PR<4 & TPI >1.2; PR≥4 & TPI>2.4 **Fair**: PR<4 & TPI between 0.8-1.2; PR≥4 & TPI between 1.6-2.4 **Poor**: PR<4 & TPI <0.8; PR≥4 & TPI<1.6
ASTM D5501: Modified to analyze Isobutanol	Annual multi-point calibration curve and with newly installed column and continuing QC check samples every 10 samples*	Calibration curve $r^2 > 0.99$ **QC Check Samples:** **Good**: PR<4 & TPI >1.2; PR≥4 & TPI>2.4 **Fair**: PR<4 & TPI between 0.8-1.2; PR≥4 & TPI between 1.6-2.4 **Poor**: PR<4 & TPI <0.8; PR≥4 & TPI<1.6
ASTM E203: Standard Test Method for Water Using Volumetric Karl Fischer Titration[7]	QC check samples every 10 samples*	**Good**: PR<4 & TPI >1.2; PR≥4 & TPI>2.4 **Fair**: PR<4 & TPI between 0.8-1.2; PR≥4 & TPI between 1.6-2.4 **Poor**: PR<4 & TPI <0.8; PR≥4 & TPI<1.6
ASTM D1613: Standard Test Method for Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer and Related Products[10]	QC check samples every 10 samples*	**Good**: PR<4 & TPI >1.2; PR≥4 & TPI>2.4 **Fair**: PR<4 & TPI between 0.8-1.2; PR≥4 & TPI between 1.6-2.4 **Poor**: PR<4 & TPI <0.8; PR≥4 & TPI<1.6
ASTM D4052: Standard Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter[11]	QC check samples every 10 samples*	**Good**: PR<4 & TPI >1.2; PR≥4 & TPI>2.4 **Fair**: PR<4 & TPI between 0.8-1.2; PR≥4 & TPI between 1.6-2.4 **Poor**: PR<4 & TPI <0.8; PR≥4 & TPI<1.6
ASTM D287: Standard Test Method for AP Gravity of Crude Petroleum, and Petroleum Products[12]	Daily Check	Two standards were used to check hygrometer. The standards ranged in densities from 0.7788 g/mL to 0.8083 g/mL.

Method Designation: Method Title	QC Procedures	MQOs
ASTM D2624: Electrical Conductivity[13]	Daily instrument check of probe	Probe was calibrated as per manufacturer's specifications
ASTM D445: Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)[14]	QC check samples every 10 samples*	**Good**: PR<4 & TPI >1.2; PR≥4 & TPI>2.4 **Fair**: PR<4 & TPI between 0.8-1.2; PR≥4 & TPI between 1.6-2.4 **Poor**: PR<4 & TPI <0.8; PR≥4 & TPI<1.6

*Assessment of QC data compared to repeatability and reproducibility outlined in ASTM Methods.
Precision Ration (PR) =test method reproducibility/ test method repeatability
Test Performance Index (TPI) =test method reproducibility/site precision
Site precision=2.77*standard deviation

A3.2 Audits

Three types of audits were performed during the verification test: a performance evaluation audit (PEA) of the analytical methods, a technical systems audit (TSA) of the verification test procedures, and a data quality audit (DQA). Audit procedures are described further below.

A3.2.1 Performance Evaluation Audits

The accuracy of the analytical methods performed by ICFTL was evaluated in the PEA by analyzing certified standards. For the low-level ethanol content determination method D4815[8], SRM 2287- Reformulated Gasoline (10% Ethanol) was used. The isobutanol method (ICFTL In-House Modified D5501) was verified using a Spectrum Quality Standard calibration standard at 11.37% isobutanol. For the high-level ethanol content determination method D5501[9], SRM 2900-Ethanol-Water Solution, (nominal 95.6%) was used. The results of the standards were acceptable when within 10% of the target ethanol content. For water content determination by method E203[7], the NIST traceable SRM 2287 was used. The results of the water standard were considered acceptable because the lab results fell within the SRM certification range;

however, it was outside the QAPP acceptance criteria of being within 10% of the target control standard concentration. The analytical methods and their associated PEA material and acceptance criteria are summarized in Table 7. The results from the PEA were sent to the EPA Project Officer (PO) and EPA Quality Assurance Manager (QAM). The PEA report included the raw data, performance evaluation certificate of analysis, calculations of the comparison to the expected concentration, and a discussion of corrective action, if applicable. A summary of the PEA results is presented in Table 8.

Table 7. Analytical Methods and PEA Materials

Method ID	Title	PEA Material	Acceptance Criteria
ASTM D4052	Standard Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter	Fluka Standard N.10 ISO 17025/ ISO Guide 34	Within 10% of the target concentration, repeat analysis if out of range
ASTM D445	Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)	Fluka Standard N.10 ISO 17025/ ISO Guide 34	
ASTM D5501[9]	Standard Test Method for Determination of Ethanol and Methanol Content in Fuels Containing Greater than 20% Ethanol by Gas Chromatography	NSIT SRM 2900	
ASTM D4815[8]	Standard Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C_1 to C_4 Alcohols in Gasoline by Gas Chromatography	NIST SRM 2287	
Modified ASTM D5501	ICFTL In-House Isobutanol Method	Spectrum Calibration standard for Isobutanol	
ASTM E203[7]	Standard Test Method for Water Using Volumetric Karl Fischer Titration (Procedure §10)	NIST SRM 2287	The water content range specified by the SRM of 0.04±0.02 must be met

Table 8. PEA Results for Analytical Methods

Date Completed	Sample ID	Analytical Method	Determination	Lab Result	RPD
4/3/2013	53972-12-15	D4052	Density	0.7814 unit less at 15.6°C	0.33%
4/3/2013	53972-12-10	D5501	High Ethanol Content	94.28 % mass	1.38%
4/3/2013	53972-12-15	D445	Viscosity	1.2 mm^2/sec at 27°C	2.36%
8/6/2013	54013-44-19	D4815	Low Ethanol Content	11.05 % mass	9.73%
8/6/2013	54013-44-19	E203	Water Content	0.052 % mass	30%*
8/13/2013	54013-45-16	Modified D5501	Isobutanol	11.37 % mass	5.01%

*The SRM water content certification range is 0.04 ± 0.02 (0.02 – 0.06). Not considered as a failure, because the lab result falls within the SRM range.

A3.2.2 Technical System Audits

The Battelle QAM performed a one-day TSA of the bench-scale test set on May 1, 2013. The purpose of this audit was to ensure that the tests were being performed in accordance with the AMS Center QMP[3] and the QAPP[1]. During the audit, the Battelle QAM reviewed

- Documentation for the preparation of the test blends and BFW mixtures and the results of the E0 analysis;
- Testing facility equipment (calibration, maintenance, and operation);
- Actual test procedures versus those specified or referenced in the QAPP; and
- Data acquisition and handling procedures, including observation of testing and records (including custody forms).

The TSA was guided by a project-specific checklist based on the QAPP. It was performed during the bench-scale testing because this was where many different steps of the process were performed (sample preparation, shipment to the analytical laboratory, multiple data points collected on one test blend, etc.).

A TSA report was prepared as a memo to the Testing Coordinator (TC) and the completed checklist was attached. The Battelle AMS Center Manager and EPA PO were copied on the memo. The TC responded to the audit. The Battelle QAM verified that all audit findings and observations were addressed and that corrective actions were appropriately implemented. A copy of the complete TSA report with corrective actions was provided to the EPA PO. At EPA's

discretion, EPA QA staff conducted an independent on-site TSA on November 20, 2013 during the execution of the lab-scale testing. The TSA findings were communicated to technical staff at the time of the audit and documented in a similar TSA report following the same documentation and dissemination procedure.

A3.2.3 Data Quality Audit

The Battelle QAM, or designee, audited at least 25% of the sample results acquired in the testing and 100% of the calibration and QC data per the QAPP requirements. A checklist based on the QAPP guided the audit. An initial ADQ was conducted on the first batch of test data and the PEA data on June 26 - July 1, 2013 to identify errors early in the data reduction process. The first batch was defined as the testing and variable data generated over the first two weeks of testing by the TC. The remaining data were audited September 26 - October 2, 2013 at the completion of bench-scale testing after all data for that set of tests was posted on the project SharePoint site. A third ADQ was performed on December 30, 2013 - January 6, 2014 by the Battelle QAM. A final ADQ of this document that traced the data from initial acquisition, through reduction and statistical comparisons, to final presentation was conducted on February 28, 2014. It also confirmed reconciliation of the first two ADQs.

All formulae applied to the data were verified, and 25% of the calculations were checked. Data for all testing were reviewed for calculation and transcription errors and data traceability. An audit report was prepared as a memo to the TC after completion of each data audit; the completed checklist was attached. The Battelle AMS Center Manager, EPA PO and EPA QAM were copied on the memo. The TC responded to the audit. The Battelle QAM verified that all audit findings and observations were addressed and that corrective actions were appropriately implemented. A copy of the complete ADQ report with corrective actions was provided to the EPA PO.

Table 9. Underground Storage Tank Leak Detection Stakeholder Committee

Last Name	First Name	Company
Barbery	Andrea	US EPA OUST
Bareta*	Greg	Engineering Consultant Bureau of Storage Tank Regulation (Wisconsin)
Baustian	James	Butamax
Boucher	Randy	Franklin Fueling Systems
Bradley*	Lamar	Tennessee Department of Environment and Conservation Division of USTs
Brauksieck	Russ	(New York)
Brevard	Danny	AC'CENT Services, Inc.
Chapin	Tom	Underwriters Laboratory (U.L.)
Cochefski	Peter	Ryder Fuel Services
Cornett	Ken	Veeder-Root
Courville	Jamie	Southern Tank Testers, Inc.
D'Alessandro	Tom	OMNTEC Mfg., Inc.
Dockery	Howard	Simmons
Drack	Earle	DirAction, LLC.
Emmington	Dave	Veeder-Root
Fenton	Charles	Hansa Consult of North America, LLC (HCNA)
Fisher	Laura	UST Leak Prevention Unit (California)
Flora	Jerry	JDF Consulting
Folkers	Joie	NOV Fiber Glass Systems
Geyer	Wayne	Steel Tank Institute
Gordji	Sam	SSG Associates, University of Mississippi
Henderson	Kevin	Kevin Henderson Consulting, LLC
Hoffman	Brad	Tanknology
Indest	April	Southern Tank Testers, Inc.
Johnson*	Curt	Alabama Department of Environmental Management (Alabama)
Jones	Bill	Warren Rogers Associates, Inc.
Juranty*	Mike	New Hampshire Department of Environmental Services Waste Management Division
Keegan	Kevin	Tanknology, Inc.
Kubinsky	Ed	Crompco, LLC
Lauen	Dorcee	Williams & Company
Marston	Dan	Franklin Fueling Systems
McKernan	John	US EPA
McMillan	Corey	Ryder Fuel Services
Mills	Tony	OPW Fuel Management Systems
Moore*	Bill	Utah Department of Environmental Quality
Moore	Kristy	Renewable Fuels Association (RFA)

Last Name	First Name	Company
Moureau	Marcel	Marcel Moreau Associates
Muhanna*	Shaheer	Georgia Department of Natural Resources
Neil	Peter	OPW Fuel Management Systems
Nelson	Bill	Franklin Fueling Systems
Parnell	Brian	MAPCO Express, Inc.
Peters*	Heather	Missouri Department of Natural Resources
Poxson*	Marcia	Michigan Department of Environmental Quality
Purpora	Steve	Protanic
Ramshaw	Chris	Purpora Engineering
Reid	Kent	Veeder-Root
Renkes	Bob	PEI
Robbins*	Helen	Connecticut Department of Environmental Protection
Rollo*	Peter	Delaware Natural Resources and Environmental Conservation
Sabo	Lorraine	Franklin Fueling Systems
Scheib	Jeff	Gevo
Smith*	Tim	US EPA OUST
Thuemling	George	Varec, Inc.
Toms	Patrick	Varec, Inc.
Wilcox	Craig	Ken Wilcox Associates, Inc.
Wilcox	Ken	Ken Wilcox Associates, Inc.
Young	Greg	Vaporless Mfg., Inc.

*Designates members of the National Work Group on Leak Detection Evaluation (NWGLDE)

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Appendix B

Fuel Property Testing Methods and Data Results

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Fuel Property Testing Methods and Data Results

B1 BENCH-SCALE TESTING

The bench-scale testing focused on determining several fundamental properties of biofuels and BFW mixtures under typical conditions encountered during operation of UST LD systems. This differentiated whether the range of ethanol blends had properties that behaved significantly different from each other, thereby being the evidence that leak detection technologies may or may not function properly when used in the different blends. Bench-scale testing was divided into four series of tests and followed the QAPP[2]:

a) *Intrinsic Properties of BFW Mixtures:* The properties studied in the first series of bench-scale tests are common to all biofuels and is referred to herein as intrinsic properties because they belong to the biofuel due to its very nature. The intrinsic properties evaluated in the first series of tests include acidity, density, electrical conductivity and viscosity. These are intensive intrinsic properties (i.e., do not change with sample size) and were identified as important factors that may affect the performance of UST LD systems while operating in BFW mixtures.

b) *Coefficient of Thermal Expansion:* The second series determined the coefficient of thermal expansion of different BFW mixtures within a temperature range that is typically experienced in field applications of UST LD systems. The density of biofuels, like all materials, is temperature dependent and the volume of a mass of biofuel changes with temperature in a predictable (anticipated linear) fashion. In the field, temperature fluctuations cause expansion and contraction of BFW mixtures which must be accurately predicted and accounted for by UST LD systems.

c) *Non-additive Volume Changes:* The third series of tests determined the volume effect of water addition on the test blends. When two polar solvents are combined (as in water and ethanol in a biofuel) the resultant volume of the mixture is less than the additive volume of the two components as water is accommodated into the ethanol polar structure. This information is particularly applicable in the situation of water ingress into USTs containing biofuels in that the ethanol in the gasoline will accommodate the water in the gasoline and if the water is in high enough concentration, phase separation will occur.

d) *Interface Determination:* The final series of bench-scale tests focused on the development of a method to optically determine the phase separation of the different BFW mixtures. Once above the saturation level (<1% [v/v]), water separates from an ethanol blend by pulling some

of the ethanol into a denser separated phase at the bottom of an UST. It is important that the location and properties of these layers be able to be independently and objectively identified including not only pure water and hydrocarbon phases, but also the colloidal mixed layers of gasoline/ethanol and water/ethanol.

Each series of the bench-scale testing was executed separately and sequentially in a Battelle laboratory in Columbus, Ohio under ambient laboratory conditions unless otherwise specified. Laboratory temperature was measured with a glass thermometer at the beginning and end of each testing day as well as monitored with a 3M Temperature Data Logger. For tests requiring strict temperature limits, a New Brunswick Series 25 Incubator Shaker and a Lauda Proline Low Temperature Thermostat was employed. Except when specific temperatures are required, all tests were carried out at ambient laboratory temperature (approximately 15 to 20 °C). Class A volumetric glassware and calibrated micro-pipettes (within the last 6 months) were used for all experiments and the accuracy of pipettes was determined gravimetrically at the beginning of each test day when anticipated to be used that day. Glassware was used as received, rinsed with E0 and allowed to air dry overnight before next use. All experiments were carried out in triplicate to facilitate statistical comparisons between BFW mixtures.

B2 TEST PROCEDURES

B2.1 Intrinsic Properties of BFW Mixtures

This first test set aims at determining the pertinent intrinsic properties of BFW mixtures at different ethanol or isobutanol and water contents. After preparation (Appendix A), the BFW mixtures were poured into a 250 mL graduated cylinder. Samples were taken from the middle of the cylinder using a glass pipette and sent to ICFTL for measurement of acidity by ASTM D1613[10], density by ASTM D4052[11], viscosity by ASTM D445[14], and water and ethanol content by either ASTM E203[7] (for water) and ASTM D5501[9] or ASTM D4815[8] (for ethanol) depending on their anticipated water and ethanol contents. Where appropriate, samples were analyzed for isobutanol concentration by a modified ASTM D5501[9]. After sampling, conductivity was measured by ASTM D2624[13] and density was measured by ASTM D287[12] directly in the graduated cylinder. Each intrinsic property was measured in triplicate on the same sample.

Some of the BFW mixtures had separated phases. In this case, the interest in intrinsic properties is in the bulk fuel phase and as such, aliquots sent for analytical analysis were the bulk fuel samples. Where possible, the dense phase (i.e., water-ethanol separated phase) was archived should the analysis of this phase be performed. At this time, it has been determined to only analyze the fuel phase because of the relevance to technology performance for LD, the potential non-availability of enough volume for the

analyses, and to minimize extraneous analytical costs. In some cases, such as with E30 BFWs with 2.5% and 5.0% water, aliquots of sample from both phases were sent for analysis as the sample did not homogenize easily.

B2.2 Coefficient of Thermal Expansion

In order to determine how temperature affects the volume of specific BFW mixtures, a series of experiments was conducted in 10 mL-capacity glass graduated cylinders (±0.1 mL). At ambient temperatures, 5 mL of zero water BFW mixture was added to individual 10 mL graduated cylinders and the appropriate amount of water was added to each cylinder (Table 1) to represent BFW of different water concentrations (0%, 0.25%, 0.5%, 2.5%, and 5.0% water) Each cylinder was capped with a ground-glass stopper. Actual mass of BFW mixture was determined gravimetrically. The BFW mixtures were then allowed to equilibrate for 60 minutes to 5.0°C, 10.0°C, 15.0°C, 20.0°C, 25.0°C and 30.0°C in a Lauda Proline Low Temperature Thermostat. After each 60-minute equilibration time, the volume of the graduated cylinder was recorded before it was returned to the thermostat.

Table 1. Volume of water added to each 10 mL graduated cylinder for Coefficient of Thermal Expansion

BFW Sample Description	Volume of Water Added (µL)
0% water	0
0.25% water	12.5
0.5% water	25
2.5% water	125
5.0% water	250

The coefficient of thermal expansion was calculated using Equation 1:

$$\alpha = \frac{1}{V_{25}}\left(\frac{\partial V}{\partial T}\right)$$

Equation 1

where α is the coefficient of thermal expansion, V_{25} is the volume of the individual BFW mixture at 25°C (normalization temperature) and ($\partial V/\partial T$) is the partial derivative (i.e., slope) of the volume vs. temperature line as calculated by linear regression.

B2.3 Non-additive Volume Changes (Degree of Accommodation)

Because of the varying miscibility of gasoline, water and ethanol, it is expected that as an aliquot of water is added to each of the test blends, the total volume change of the resulting BFW mixture would be less than the volume of that aliquot, and the separated, dense phase would grow disproportionately to the added volume of water. The relative total volume decrease is due to accommodation of polar water molecules into the structure formed by the polar ethanol molecules (degree of accommodation).

This experiment aimed at quantifying this effect. Five (5) mL of each test blend (no water) was added separately by pipette to 10 mL (±0.1 mL) glass-graduated cylinders; the actual mass of the test blend was determined gravimetrically. The graduated cylinders were placed in the thermostat at 25°C for 15 minutes for initial temperature equilibration. After equilibration, the cylinders were removed from the thermostat and a dye solution consisting of water and McCormick Blue Food Dye (1:2,000 dilution) were added in 250 μL increments using a micro-pipette. The actual mass of added dye solution was determined gravimetrically. After the addition of each 250 μL increment of water, the graduated cylinder was sealed with a ground glass stopper. The graduated cylinder was replaced to the thermostat for 5 minutes at 25°C, after which the total volume and the volume of the dense phase was measured. At the time of volume measurement, a photograph of the cylinder was taken to qualitatively record the interface. A total of 5 mL of dye solution was added in this way to each sample (total of twenty 250 μL additions) with measurement of volume change made after each increment.

The effect of fuel:ethanol ratio on relative volume decrease was determined by calculating the following using Equation 2:

$$\gamma = \frac{\Delta V_m}{\Delta V_a}$$

Equation 2

The parameter γ is referred to as the degree of accommodation, ΔV_m is the measured incremental change in total volume with incremental dye solution addition and ΔV_a is the incremental volume addition of dye solution. In this way, γ can be seen as the measure of the amount of ethanol accommodated within the polar water structure which results in relative volume reduction with the addition of water to the test blends. In practice, γ is defined as the slope of the V_m vs. V_a curve as calculated by linear regression.

B2.4 Interface Determination

As water separates from pure gasoline, a well-defined interface is formed which can be visually determined relatively easily and objectively; however, the interface becomes less defined when water separates from an ethanol-gasoline mixture as the water can be absorbed by both the gasoline and ethanol

phases forming a hazy suspension. Gaining an understanding of the separated phase in different ethanol blends is important for identifying and measuring water at the bottom of an UST. This last series of bench-scale tests focused on establishing a method for determination of a water interface in different test blends and mathematically defining the vertical position of the interface.

A sample of 70 mL of each test blend and 70 mL of dye solution consisting of water and McCormick Blue Food Dye (1:2,000 dilution) were measured by glass volumetric pipette into three individual 160 mL glass serum bottles (triplicate samples of each test blend/dye solution mixture). Serum bottles were sealed with Teflon® septa and aluminum caps. The 160 mL serum bottles were agitated with a New Brunswick Series 25 Incubator Shaker at 200 rotations per minute for 60 minutes to ensure mixing. After the mixing period, the septa were pierced with a thin needle protruding to the bottom of each of the serum bottles. The needles were equipped with a Luer-Lok fitting able to be attached to a 10 mL syringe. The serum bottles were left to rest in the incubator at 25 °C for 24 h to reach equilibrium. After equilibration, each serum bottle septum was pierced with a second needle only to the headspace to allow 10 mL of sample to be carefully extracted through the first needle using a 10 mL syringe. 10 mL corresponds to approximately 1 cm liquid height which was subsequently measured to the nearest 0.1 cm. The absorbance of the 10 mL sample was then measured at 630 nm using a Hach DR5000 UV-Vis Spectrophotometer previously zeroed with E0. Following ASTM D7451[15] for mixing and measurement, the cells were briefly and vigorously shaken to ensure homogeneity immediately before absorbance measurements are taken. Triplicate measurements were taken and to be considered acceptable, measurements must display a coefficient of variation of less than 10%.

This extraction and measurement procedure was repeated until the full contents of each serum bottle have been removed (approximately 14 data points per serum bottle). In this way, the transition from water to gasoline can be plotted using visible absorbance of the dye solution as a designation of where the water was located in the sample. Each test blend followed the same procedure.

Table 2 summarizes the series of tests performed on the bench scale. Table 3 presents the data collection QC assessments for the fuel properties being measured in the bench-scale testing.

Table 2. Summary of the Bench-scale Test Set

Test Series	Description	Precision Requirements	Independent Variables	# of Replicates
Intrinsic Properties of BFW Mixtures	Preparation of 35 different test blends and BFW mixtures and analysis of their intrinsic properties including ethanol concentration, water concentration, acidity, density, viscosity, and electrical conductivity	▪ CV < 15% for measurements on triplicate samples	▪ Water concentration ▪ Ethanol concentration ▪ E0 concentration	3 each
Coefficient of Thermal Expansion	Preparation of 35 different test blends and BFW mixtures and measurement of their volume at different temperatures from 5.0 to 30.0 °C	▪ $r^2 > 0.90$ for volume vs. temperature curve ▪ CV < 15% for measurements on triplicate samples	▪ Water concentration ▪ Ethanol concentration ▪ E0 concentration ▪ Temperature	3 each
Non-Additive Volume Changes	Preparation of seven test blends and measurement of volume changes with known addition of aqueous dye solution	▪ $r^2 > 0.90$ for volume measured vs. volume added curve ▪ CV < 15% for single measurements on triplicate samples	▪ Ethanol concentration ▪ E0 concentration ▪ Dye solution added	3 each
Determination of Interface	Mixing 50% of the seven test blends individually with 50% aqueous dye solution and measuring the height-dependent absorbance of the resulting mixture resulting in a height vs. absorbance curve which can be used as a designation of water location	▪ CV < 10% for triplicate measurements of optical absorbance on the same sample ▪ CV < 25% for single, depth-dependent measurements on triplicate samples of optical absorbance	▪ Ethanol concentration ▪ E0 concentration	3 each

Table 3. Data Collection Quality Control Assessments of the Fuel Properties

Measured Fuel Property	Method of Assessment	Frequency	Laboratory	Acceptance Criteria	Corrective Action
Ethanol Concentration	ASTM D5501 and D4815	Once per unique BFW mixture, once per unique test blend and once per collection of E0	ICTFL	RPD < 15% between result and target. Less than 1% for E0	Discard test blend or BFW mixture and re-prepare
Water Concentration	ASTM E203		ICTFL	RPD < 15% between result and target. Less than 0.1% for E0	Discard test blend or BFW mixture and re-prepare
Acidity	ASTM D1613[10]	Once per unique BFW mixture during determination of intrinsic properties	ICFTL	CV < 15% for triplicate measurements	First unacceptable result: Re-test BFW mixture. Second unacceptable result: Discard and re-prepare BFW mixture and retest. Third unacceptable result: trouble shoot the instrumentation[(a)]
Density	ASTM D287[12]		Battelle		
	ASTM D4052		ICFTL		
Viscosity	ASTM D445[14]		ICFTL		
Electrical Conductivity	EMCEE Model 1152; ASTM D2624[13]		Battelle		
Absorbance	Hach DR5000 UV-Vis Spectrophotometer	Zero instrument between test blend replicates	Battelle	CV < 10% for triplicate measurements	First unacceptable result: Re-test samples. Second unacceptable result: trouble shoot the instrumentation
Temperature (incubator)	Glass thermometer	Once each at the beginning and end of each testing day and once during testing	Battelle	±1°C from target, monitored with an audible alarm when out of range	Replace thermometer
Temperature (water bath)	Built-in resistance probe	Immediately after temperature equilibration and every 30 minutes after equilibration	Battelle	±0.1°C from target, monitored and logged with a calibrated electronic thermometer	First unacceptable result: trouble shoot the instrumentation. Second unacceptable result: record temperature using external thermometer

B3 STATISTICS FOR BENCH-SCALE TEST SETS

All BFW mixtures were prepared in triplicate and measurements made on each of the triplicate BFW mixtures were carried out once. Statistics were calculated on each of the measurements as follows:

- Average: The average value ($\overline{X}$) of the single measurements made on the triplicate BFW mixtures was calculated using Equation 3 as follows:

$$\bar{X} = \frac{1}{3}\sum_{i=1}^{3} x_i \quad \text{Equation 3}$$

where $\overline{X}$ is the average value of *n* number of measurements, x_i (i = 1,2,3)

- Standard Deviation: The standard deviation (SD) of a set of triplicate measurements made on BFW mixtures was calculated using Equation 4 as follows:

$$SD = \sqrt{\frac{1}{3}\sum_{i=1}^{3}(x_i - \bar{X})^2}$$

Equation 4

where $\overline{X}$ and x_i are defined above.

- Coefficient of Variation: The CV of a set of measurements is defined as the quotient of the SD of that set of measurements and the average of that same set of measurements and was calculated using Equation 5 as follows:

$$CV = \frac{SD}{\bar{X}}$$

Equation 5

where CV is the coefficient of variation and SD and $\overline{X}$ are defined above.

- Relative Percent Difference: The RPD between a measured (or calculated) value and a target value was calculated using Equation 6 as follows:

$$RPD = \frac{|\bar{X} - T|}{T}$$

Equation 6

where RPD is the relative percent difference between a calculated mean, $\overline{X}$ and a target value, T.

- Coefficient of Determination: The coefficient of determination (r^2) of several calculated dependent variables with respect to their associated independent variables was calculated according to *Principles and Procedures of Statistics*[16] and the formulae are not repeated here. In all cases, r^2 were calculated based on calculated average values of both measured dependent and independent variables by Microsoft® Excel.

B4 PRECISION OF FUEL PROPERTY MEASUREMENTS

The precision requirements of the data collected in the Bench-scale testing are summarized in Table 2 above and explained in more detail below.

B4.1 Intensive Properties: Acidity (pH), Viscosity, Density, Electrical Conductivity, and Optical Absorbance

Measured triplicate values of acidity (i.e., pH), density, viscosity and electrical conductivity measured as part of the intrinsic properties of BFW mixtures experiments were subjected to statistical analysis. The average value, SD and CV were calculated and recorded separately for each set of measured intrinsic properties. With respect to precision, for single measurements taken on triplicate samples to be considered acceptable for reporting, the CV for each set of triplicate measurements of acidity, density, viscosity, electrical conductivity and optical absorbance must be less than 15%.

The single depth-dependent optical absorbance measurements of samples collected during the interface determination experiments were considered acceptable for reporting when triplicate measurements on one test blend in three separate serum bottles display a CV less than 15%. No accuracy criterion was established for depth-dependent measurements taken during the interface determination experiment as this experiment aims at determining properties heretofore undefined.

B4.2 Extensive Properties: Volume Change

Single volume measurements taken on triplicate samples for the non-additive volume and coefficient of thermal expansion experiments were subjected to statistical analysis. The average value, SD and CV were calculated and recorded separately for each triplicate measurement of volume change. With respect to precision, for single measurements taken on triplicate samples to be considered acceptable for reporting, CV for each set of triplicate measurements of volume must be less than 15%.

B4.3 Calculated Properties: Coefficient of Thermal Expansion and Degree of Accommodation

The coefficient of thermal expansion (Equation 1) and degree of accommodation (Equation 2) was calculated from the appropriate equations and results reported with appropriate significant figures. In contrast, within the experimental parameters set forth, the slopes of volume vs. temperature curve (for coefficient of thermal expansion) and measured volume vs. added volume curve (for degree of accommodation) are expected to be linear. Therefore, in order to be considered acceptable, the coefficient of determination calculated from the average values (i.e., volume and temperature) must be greater than 0.90.

B5 BENCH SCALE TESTING RESULTS

B5.1 Intrinsic Properties of BFW Mixtures

The density increases with higher concentrations of water as well as increasing concentrations of ethanol (Figure 1). The density data measurements are summarized in Table 4. The conductivity results follow a similar trend in that as ethanol and water concentration increase (Figure 2). Those data are summarized in Table 5. Likewise, the viscosity of the fuel blends increase with increasing ethanol and water content (Figure 3), and the data are summarized in Table 6. As seen in Figure 4, the acidity is more variable that the other three parameters; however, in general, acidity increases as ethanol content increases. These data are summarized in Table 7.

E30 was a difficult sample to handle as it would not completely homogenize, but would also not completely separate into two phases. As such, the lower water content BFWs allowed for a composite sample to be analyzed whereas a top and bottom phase layer sample were analyzed from the higher water content BFWs (2.5 and % and 5.0% water). Table 8 displays all of the intrinsic properties for E30 BFWs.

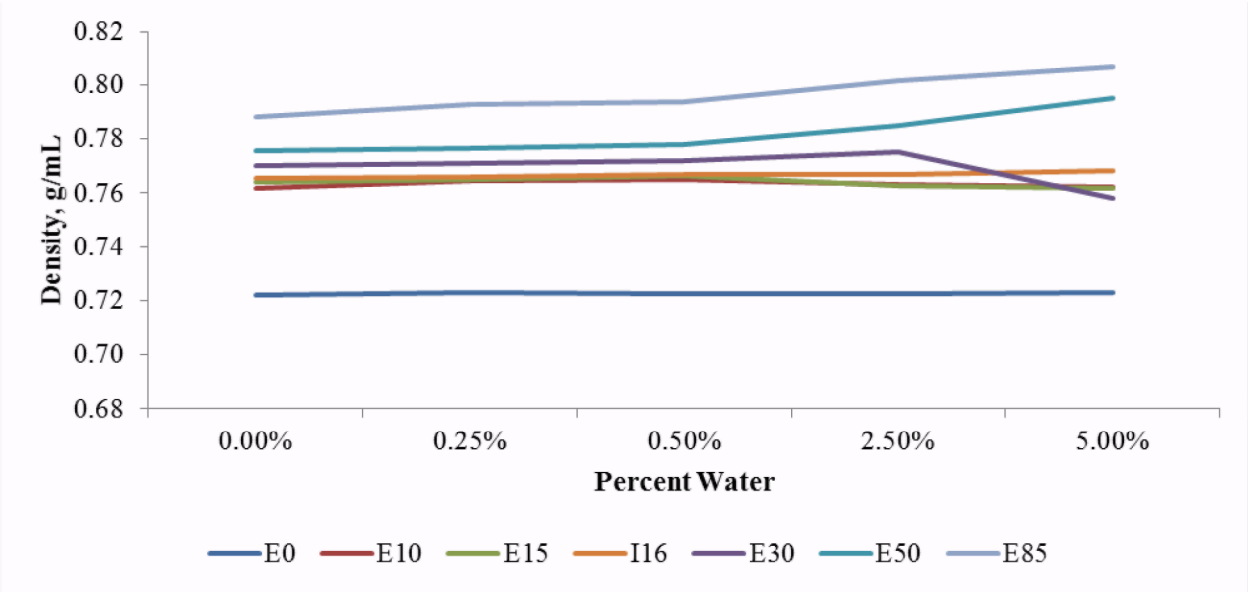

Figure 1. Plot of density (g/mL) for all BFW mixtures.

Table 4. Summary of Density Results for the BFWs (g/mL)

% Water	E0	E10	E15	I16	E30	E50	E85
0.0	0.7222	0.7617	0.7643	0.7656	0.7701	0.7758	0.7883
0.25	0.7228	0.7648	0.7650	0.7658	0.7708	0.7766	0.7927
0.5	0.7227	0.7649	0.7663	0.7669	0.7722	0.7779	0.7937
2.5	0.7224	0.7630	0.7629	0.7669	0.7753	0.7849	0.8014
5.0	0.7230	0.7624	0.7618	0.7684	0.7583	0.7951	0.8067

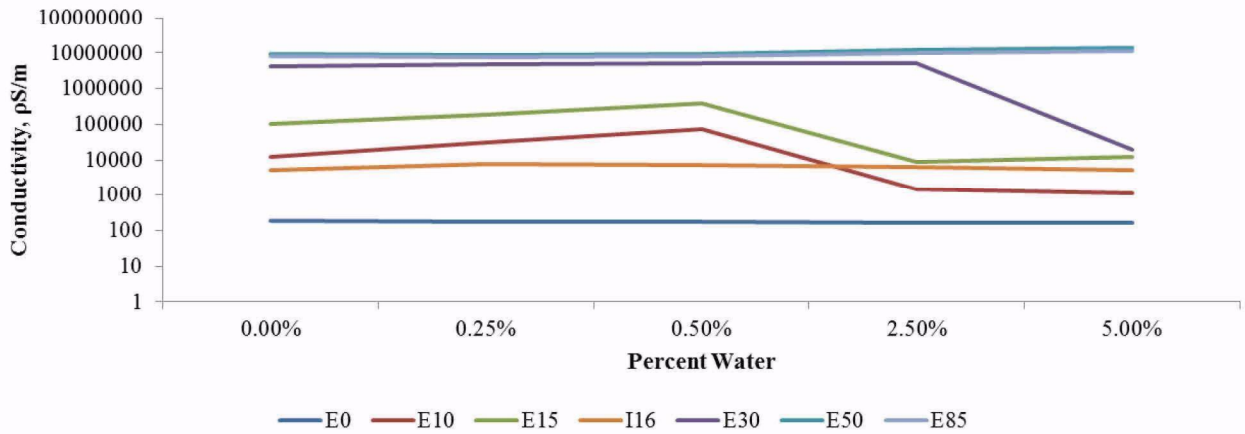

Figure 2. Plot of conductivity (pS/m) for all BFW mixtures.

Table 5. Summary of Conductivity Results for the BFWs (pS/m)

% Water	E0	E10	E15	I16	E30	E50	E85
0.0	192	12233	104722	5163	4321111	9204444	8304444
0.25	176	31900	184644	7531	4683333	8762222	7883333
0.5	177	73578	382222	7200	5238889	9498889	8064444
2.5	161	1444	8833	6378	See Table 8	11910000	9894444
5.0	164	1156	12556	5028		13914444	11172222

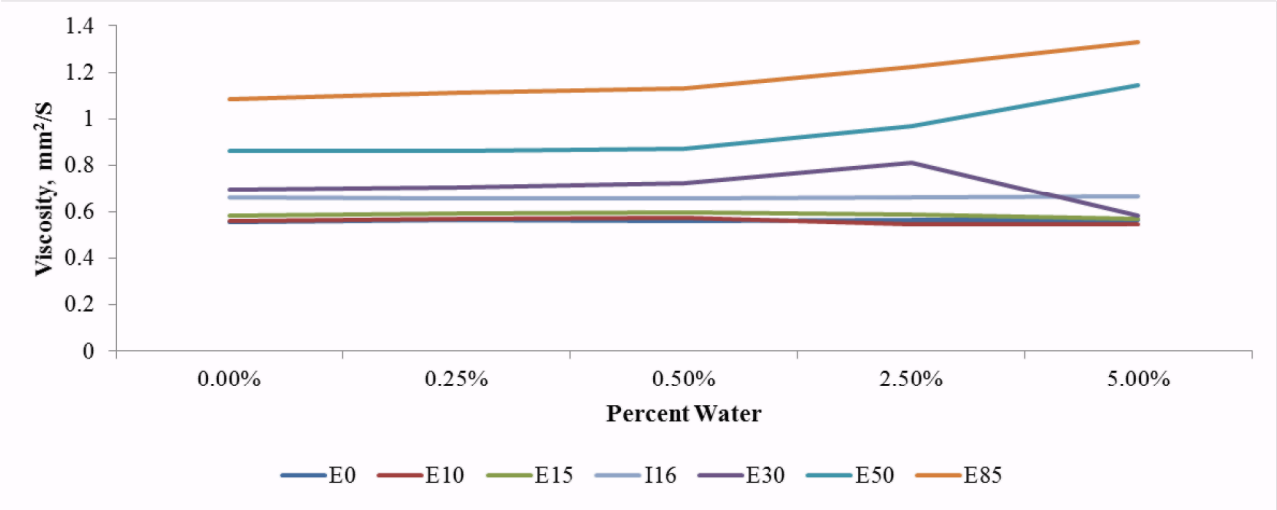

Figure 3. Plot of viscosity (mm^2/s) for all BFW mixtures.

Table 6. Summary of Viscosity Results for the BFWs (mm^2/S)

% Water	E0	E10	E15	I16	E30	E50	E85
0.0	0.555	0.557	0.582	0.659	0.698	0.863	1.085
0.25	0.562	0.568	0.593	0.656	0.704	0.865	1.114
0.5	0.558	0.572	0.596	0.657	0.726	0.873	1.130
2.5	0.561	0.545	0.586	0.660	0.811	0.970	1.223
5.0	0.562	0.544	0.567	0.666	0.582	1.147	1.332

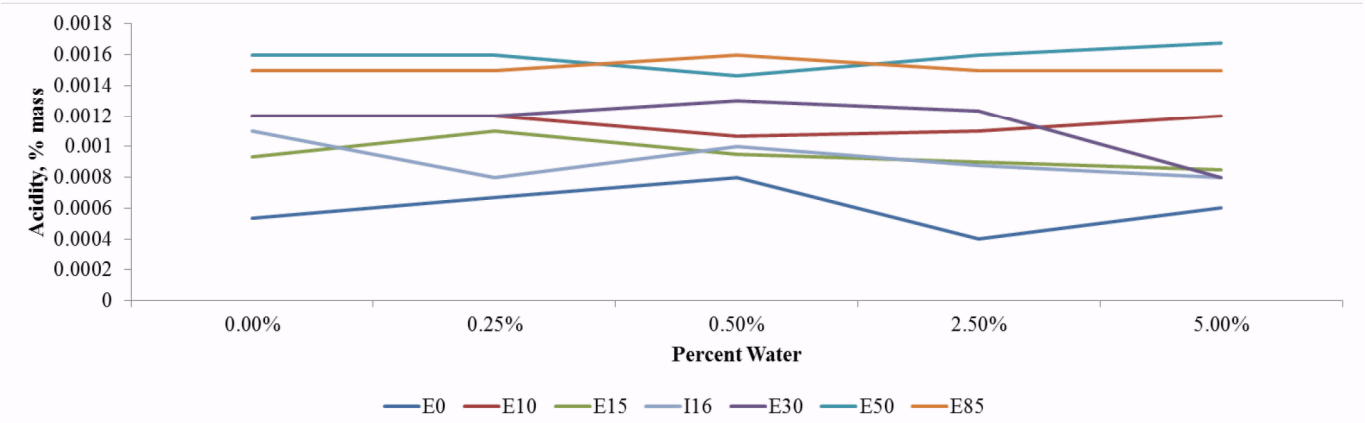

Figure 4. Plot of acidity (% mass) for all BFW mixtures.

Table 7. Summary of Acidity Results for the BFWs (% mass)

% Water	E0	E10	E15	I16	E30	E50	E85
0.0	0.0005	0.0012	0.0009	0.0011	0.0012	0.0016	0.0015
0.25	0.0007	0.0012	0.0011	0.0008	0.0012	0.0016	0.0015
0.5	0.0008	0.0011	0.0010	0.0010	0.0013	0.0015	0.0016
2.5	0.0004	0.0011	0.0009	0.0009	0.0012	0.0016	0.0015
5.0	0.0006	0.0012	0.0009	0.0008	0.0008	0.0017	0.0015

Table 8. Intrinsic Properties of E30

Parameter	Water Content	Average Value and (CV %)		
		Top Layer of BFW	Bottom Layer of BFW	Composite
Density (g/mL)[a]	0.00%	b	b	0.772 (0.00700)
	0.25%	b	b	0.773 (0.0810)
	0.50%	b	b	0.775 (0.0510)
	2.50%	0.792 (0.564)	0.802 (0.155)	c
	5.00%	0.766 (0.0970)	0.841 (0.0720)	c
Conductivity (µS/cm)	0.00%	b	b	4320000 (8.47)
	0.25%	b	b	4680000 (6.09)
	0.50%	b	b	5230000 (6.50)
	2.50%	d	d	6410000 (17.4)
	5.00%	d	d	200000 (0)
Acidity (% mass)	0.00%	b	b	0.00120 (0.00)
	0.25%	b	b	0.00120 (0.00)
	0.50%	b	b	0.00130 (15.4)
	2.50%	0.00120 (18.7)	not enough sample	c
	5.00%	0.000800 (0.00)	0.00230 (15.5)	c
Viscosity (mm^2/S)	0.00%	b	b	0.698 (0.0860)
	0.25%	b	b	0.704 (0.692)
	0.50%	b	b	0.726 (1.02)
	2.50%	0.811 (1.70)	1.06(0.954)	c
	5.00%	0.582 (0.213)	1.66 (2.18)	c
Water (%v/v)	0.00%	b	b	0.0465 (0.355)
	0.25%	b	b	0.334 (2.94)
	0.50%	b	b	0.611 (1.38)
	2.50%	2.46 (1.74)	4.71 (7.69)	c
	5.00%	0.556 (4.61)	15.6 (11.0)	c

Parameter	Water Content	Average Value and (CV %)		
		Top Layer of BFW	Bottom Layer of BFW	Composite
Water	0.00%	b	b	0.0605 (0.355)
	0.25%	b	b	0.432 (2.82)
	0.50%	b	b	0.788 (1.38)
	2.50%	3.10 (1.62)	5.86 (7.80)	c
	5.00%	0.725 (4.55)	18.6 (11.1)	c
Ethanol (%v/v)	0.00%	b	b	28.3 (0.0124)
	0.25%	b	b	29.5 (0.688)
	0.50%	b	b	29.7 (0.753)
	2.50%	28.7 (3.57)	44.0 (2.64)	c
	5.00%	9.70 (0.514)	67.2 (2.60)	c
Ethanol (% mass)	0.00%	b	b	29.5 (0.0112)
	0.25%	b	b	30.3 (0.608)
	0.50%	b	b	30.4 (0.771)
	2.50%	28.8 (3.59)	43.5 (2.49)	c
	5.00%	10.0 (0.470)	63.5 (2.55)	c

(a) Density values reported are from Iowa Fuel Testing Laboratory

(b) No separation between hydrocarbon and water layer was evident, so a composite sample was analyzed.

(c) A homogenous composite sample was not easily obtained, instead an aliquot from the top and bottom layer of the BFW were analyzed.

(d) Conductivity was analyzed on the composite sample, despite not being able to obtain a homogenous sample

B5.2 Coefficient of Thermal Expansion

In order to determine how temperature affects the volume of specific BFW mixtures, the test blends were plotted as volume (mL) against the temperature (°C), for each water content. The slopes of the lines generated are reported as the coefficient of thermal expansion in Table 9. The associated r-squared values are listed as well as the predicted volumes at 0°C (y-intercept). All blends appear to be impacted by temperature similarly as all have a coefficient of thermal expansion near 0.0010 mL/°C.

Table 9. Coefficient of Thermal Expansion Data

Test Blend	Water Content	Normalized at 25 °C		
		R^2	Coefficient of Thermal Expansion (mL/ °C) (slope)	Predicted Volume at 0°C (y-intercept)
E0	0.00%	0.9659	0.0010	0.9748
	0.25%	0.9711	0.0011	0.9716
	0.50%	0.9357	0.0009	0.9746
	2.50%	0.9282	0.0090	0.9726
	5.00%	0.9882	0.0010	0.9750
E10	0.00%	0.9641	0.0013	0.9964
	0.25%	0.8906	0.0011	0.9715
	0.50%	0.9546	0.0012	0.9735
	2.50%	0.9262	0.0010	0.9725
	5.00%	0.9379	0.0009	0.9759
E15	0.00%	0.9726	0.0011	0.9749
	0.25%	0.9429	0.0012	0.9691
	0.50%	0.9247	0.0012	0.9706
	2.50%	0.9282	0.0012	0.9713
	5.00%	0.9623	0.0012	0.9739
I16	0.00%	0.9849	0.0011	0.9728
	0.25%	0.9809	0.0011	0.9743
	0.50%	0.9946	0.0011	0.9716
	2.50%	0.9642	0.0010	0.9744
	5.00%	0.9730	0.0011	0.9737
E30	0.00%	0.9650	0.0012	0.9673
	0.25%	0.9948	0.0011	0.9730
	0.50%	0.9676	0.0010	0.9736
	2.50%	0.9658	0.0010	0.9754
	5.00%	0.9655	0.0009	0.9797
E50	0.00%	0.9909	0.0009	0.9756
	0.25%	0.8864	0.0010	0.9792
	0.50%	0.8992	0.0011	0.9774
	2.50%	0.9500	0.0011	0.9709
	5.00%	0.9964	0.0010	0.9752
E85	0.00%	0.9041	0.0009	0.9730
	0.25%	0.9854	0.0010	0.9720
	0.50%	0.9782	0.0010	0.9782
	2.50%	0.9625	0.0011	0.9745
	5.00%	0.9628	0.0011	0.9719

B5.3 Non-additive Volume Changes

Table 10 shows as the test blends increase in ethanol content, the amount of ethanol accommodated within the polar water structure increases which results in a relative volume reduction upon addition of water. Similarly, as the ethanol content of the test blends increase, the growth of the dense phase occurs at a greater rate. I16 test blend behaved similarly to E15. The degree of accommodation was calculated by determining the slope of the lines plotted as the incremental water volume added (μL) by total volume measured (mL) for each test blend. The growth of the total volume was calculated by determining the slope of the lines created by plotting the measured total volume (mL) by the expected total volume (mL) for each test blend.

Table 10. Degree of Accommodation Summary for the Test Blends

Test Blend	Growth of Total Volume (Slope of Δ measured total volume/Δ expected total volume)
E0	0.9557
E10	0.9953
E15	0.9915
I16	1.0039
E30	0.9665
E50	0.9838
E85	0.9510

Furthermore, the photo in Figure 5 provides a visual representation of the un-proportional growth of the measured dense phase to what would be expected if there was no ethanol accommodation within the polar water structure. The photo was taken after the last water addition during the Non-Additive Volume Experiment for E85. If there was no accommodation, the dense, water phase would measure a volume of 5 mL, however, due to the accommodation, the volume of the dense phase is around 9 mL.

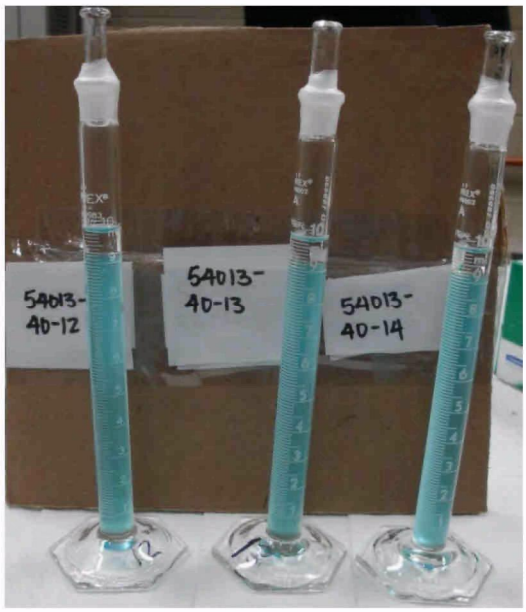

Figure 5. Photo taken during Non-Additive Volume Experiment for E85. The test was completed in triplicate. This particular photo occurred after the last water addition. The water was dyed with blue food coloring.

B5.4 Interface Determination

For each replicate of each test blend, one serum bottle was prepared with 70 mL of test blend and 70 mL of water dyed with blue food coloring (Figure 7). A needle was inserted to draw out ten mL of sample from the bottom into individual sample cells for optical absorbance analysis (Figures 8 and 9).

In order to make comparisons across test blends, all data was normalized to the original height of the fluid in the serum bottle. Five different parameters were calculated for each test blend: (1) onset of interface, (2) location of interface, (3) supervention of interface, (4) thickness of interface, and (5) intensity of interface. Figure 6 is provided as an example to how these parameters were measured. The onset of the interface is intended to be the point at which the optical absorbance begins to increase and is measured in centimeters. The location of the interface is the height (cm) at which the peak occurred. The supervention of the interface is the height (cm) at which the optical absorbance plateaus. The thickness of the interface is how wide (cm) the peak is between the onset and supervention of the interface. Lastly, the intensity of the interface is the change in optical absorbance (abs) between the peak and supervention of the interface.

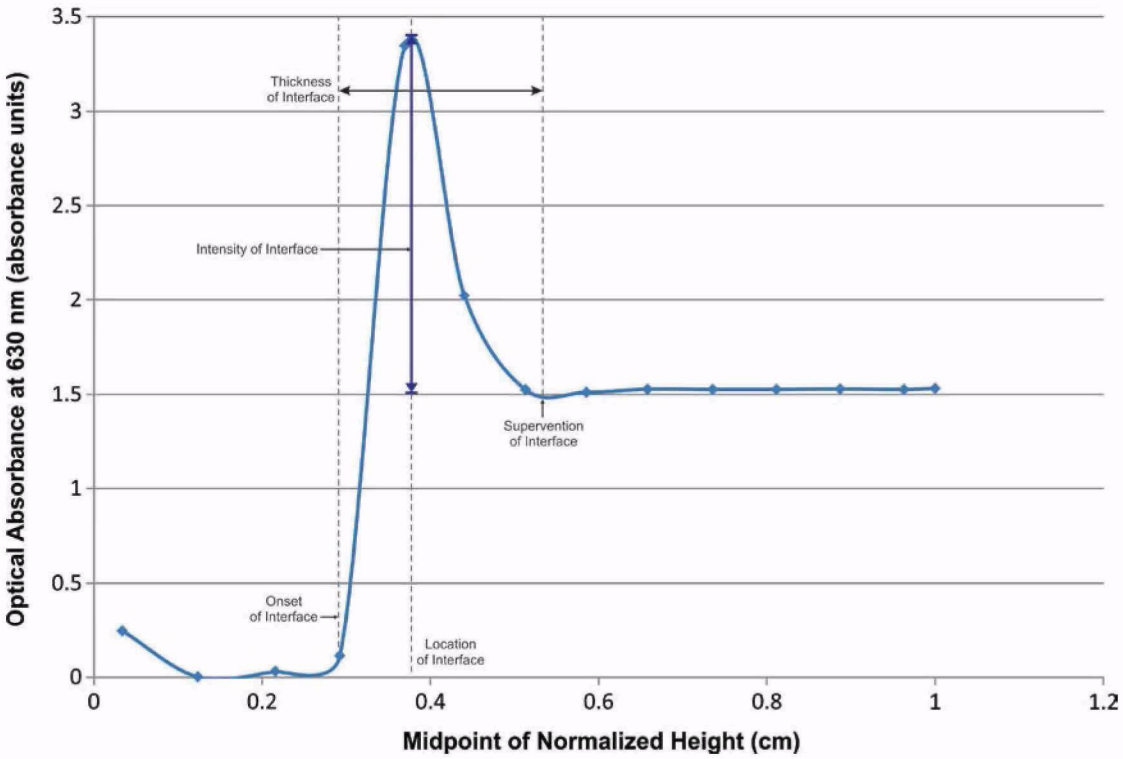

Figure 6. An example of E50 test blend showing how the interface determination data was calculated

Table 11 shows as the concentration of ethanol increases that the onset, location, and supervention of the interface decrease in height. This observation is further supported in Figures 8 and 9. Figure 8 represents one replicate of E10 and Figure 9 represents one replicate of E85. Figure 8 (E10) shows that the dense, water phase is evident in the vials only until draw #8 which corresponds to a height of about 0.630 cm whereas in Figure 9 (E85), the water phase is evident until much later, in draw #13 which corresponds to a height of about 0.220 cm. The height values were measured by affixing a ruler to the side of the serum bottle and measuring to the nearest tenth of a centimeter the height of the fluid after every draw. The thickness of the interface is similar for all test blends and ranges from 0.08 cm to 0.190 cm. The intensity of the interface increases from 1.00 to 19.00 abs in E0 to E50, then the intensity drops to 7 abs in E85. I16 behaves similarly to E15.

Table 11. Interface Determination Summary Table [(a)]

Test Blend	Onset of Interface (cm)	Location of Interface (cm)	Supervention of Interface (cm)	Thickness of Interface (cm)	Intensity of Interface (abs)
E0	0.504	0.670	0.730	0.090	1.00
E10	0.470	0.630	0.760	0.185	2.50
E15	0.444	0.520	0.580	0.080	3.00
I16	0.522	0.522	0.670	0.100	4.50
E30	0.369	0.450	0.580	0.170	11.00
E50	0.292	0.380	0.515	0.190	19.00
E85	0.047	0.220	0.310	0.140	7.00

(a) All heights were normalized to the original height

Figure 7. Photo shows one serum bottle from the Interface Determination Experiment with I16.

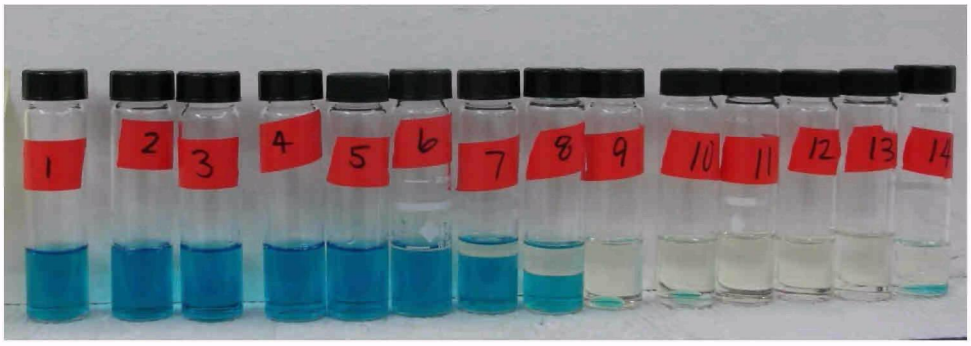

Figure 8. One replicate from E10 Interface Experiment.

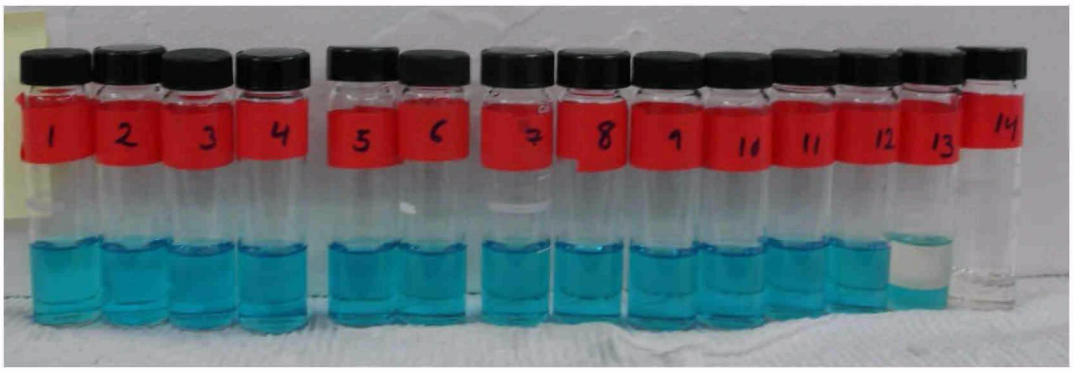

Figure 9. One replicate from E85 Interface Experiment

B6 REFERENCES

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Appendix C

UST LD Operating Principle Testing Methods and Data Results

Appendix C

UST LD Operating Principle Testing Methods and Data Results

C1 LABORATORY SCALE TESTING

This section describes the materials, methods and data collection procedures for the evaluation of operating principles central to underground storage tank leak detection (UST LD) systems in alcohol-blended fuels. The methods were adaptations of previously established standard test procedures.[17, 18] These procedures have been adapted to incorporate testing with alcohol-blended fuels. The purpose of the laboratory-scale testing was to evaluate a select number of operating principles of UST LD technologies in a small laboratory scale. The specific focus was to determine various performance parameters of those operating principles in detecting the presence of fuel and detecting water ingress in four different alcohol-blended fuels (i.e., ethanol and isobutanol). Described herein are the operating principles tested, the laboratory scale setup in which operating principles were evaluated, the specific test procedures, and the data to be collected. Also included is a description of how these data were reduced followed by the results.

In reading and applying this document, it is important to distinguish the difference between the terms *technology*, *technology category* and *sensor*:

- A *technology* is a specific product marketed by a vendor.
- A *technology category* is a group of technologies whose operation depends on a common operating principle (e.g., automatic tank gauges).
- A *sensor* is the physical means for implementation of a specific operating principle within a technology.

It was not the intent of the tests described herein to evaluate the ability of a specific technology or technology category to perform in alcohol-blended fuel systems. Rather, these tests evaluated specific operating principles for LD and water ingress detection in alcohol-blended fuels by testing sensors based on those principles in a laboratory.

C2 SENSOR SELECTION

This evaluation focused on the appropriateness and effectiveness of the sensor operating principles. For this reason, three technologies were selected for evaluation of five operating principles. For this evaluation, sensors were selected:

- To represent a range of operating principles (conductance and capacitance, optical principles, and float switches with a hydrocarbon polymer sensor) and technology vendors;
- To represent a range of intended operating conditions (i.e., liquid in-tank, interstitial); and
- To use testing resources wisely with the cost appropriateness of the various sensors.

A review of candidate sensors for evaluation was conducted through an internet search and follow-up conversations with sensor suppliers. The results of this review were incorporated into a decision matrix provided to U.S. Environmental Protection Agency's (EPA's) Office of Underground Storage Tanks (OUST). Further conversations were held with EPA OUST and other stakeholders regarding the sensors selected and the sensor selection matrix approach. These conversations resulted in the selection of the three technologies for evaluation. Table 1 lists the operating principle(s), the dimensions and types of sensors incorporated into each technology tested. For the purposes of this testing, these sensors served as surrogate testing technologies; i.e., operability determinations for each sensor were extrapolated to serve as an evaluation for the operating principles on which they are based. For this reason, this document will refer to technologies by their operating principles as shown in Table 1. The technologies and their operating principles are described in more detail in the following sections.

Table 1. Technologies and Associated Sensors Used for Evaluation of Operating Principles

Sensor Operating Principle(s) (Sensor Identifier)	Dimensions	Sensor Type
Interstitial Optical Sensor (Optical Sensor)	4.3 in. L x 1.5 in. W x 0.5 in. H	Qualitative Detects liquid (non-discriminating)
Magnetic Float Switch and Fuel-Sensitive Polymer Sensor (FS/FSP)	2.5 in. D x 8.86 in. H	Qualitative Detects hydrocarbons and liquid (somewhat discriminating)
Capacitance and Conductance Sensor (Complex impedance) (C/C Sensor)	2 in. D x 12 in. H	Quantitative Detects and quantifies hydrocarbons and water (discriminating)

C2.1 Interstitial Optical Sensor (Optical Sensor)

The Optical Sensor uses solid-state liquid level sensing technology to detect liquid in the interstitial space of the tank. A schematic of the Optical Sensor is presented in Figure 1 along with its intended installation configuration and dimensions. The operating principle of this sensor is optical, in which changes in refraction of light are detected based on the medium through which the light passes. When liquid ingresses into an interstitial space, the refractive index of that interstitial space changes based

on the differences in refractive index between air (dry condition) and liquid (wet condition indicative of a leak). The refraction of light passing through the interstitial space is detected by the sensor and an alarm condition is triggered. Potential issues for use in ethanol-blended fuel systems include sensitivity of the operating principle to detect changes in the refractive index of blended fuels. This sensor has been specifically developed for use in unleaded gasoline containing up to 85% ethanol. Unlike earlier versions of this sensor tested in low-ethanol blended gasoline, the Optical Sensor does not discriminate between hydrocarbon and water and therefore contact of the sensor with liquids will trigger an alarm.

C2.2 Magnetic Float Switch and Fuel Sensitive Polymer (FS/FSP)

The FS/FSP sensor is used to monitor for the presence of liquid hydrocarbons (fuel product) in dispenser sumps. A schematic of the FS/FSP is presented as Figure 2. This sensor combines two operating principles: magnetic float switch and hydrocarbon-sensitive polymer. The sensor has an upper and lower liquid float for liquid detection as well as a conductive polymer strip that reacts specifically with liquid hydrocarbons. The environmental data are transmitted to an automatic tank gauge console where data can be collected in electronic format. Specifically, the FS/FSP transmits when liquid is detected by means of the lower liquid float, when hydrocarbons are present by means of the polymer strip, and when a high liquid level condition is present by means of the top liquid float. In this way FS/FSP is able to detect hydrocarbons along the polymer strip as well as floating on top of an aqueous layer. A potential issue for use in alcohol-blended fuel systems is the specificity of the hydrocarbon polymer in detecting diluted hydrocarbons mixed with alcohols.

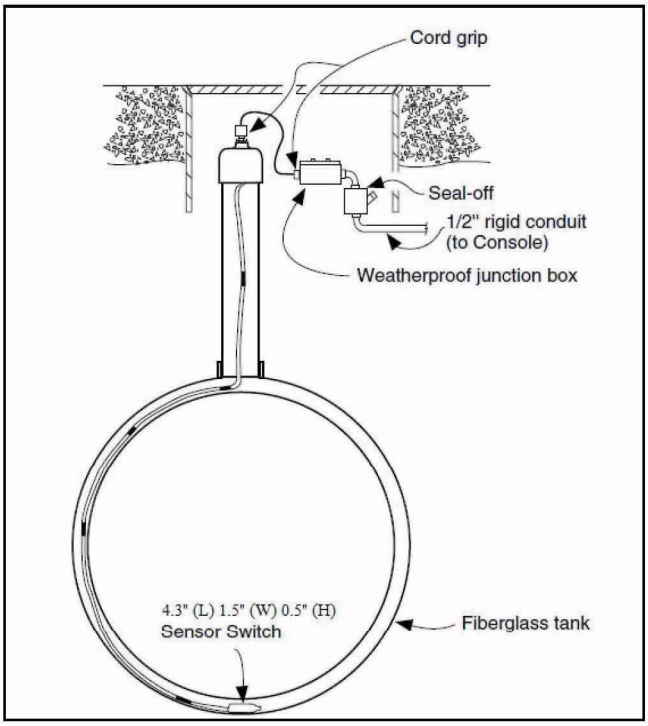

Figure 1. Optical Sensor

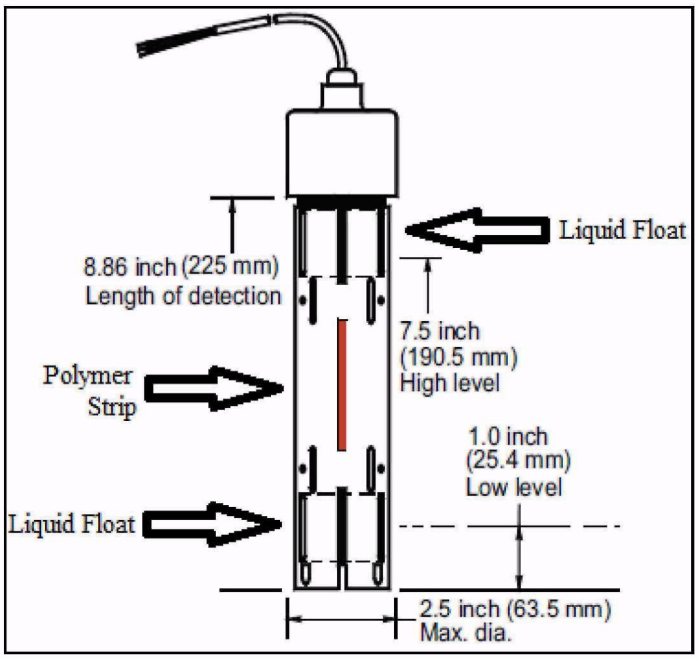

Figure 2. Magnetic Float Switch and Fuel-Sensitive Polymer (FS/FSP)

C2.3 Capacitance and Conductance (Complex Impedance) (C/C)

The C/C Sensor is used primarily to determine the approximate liquid level, to determine the vertical fuel/water profile, and to detect ingress of water. A photograph of the C/C Sensor is shown in Figure 3. The C/C Sensor operates under the complex impedance principle which combines two operating principles: electrical conductivity and capacitance. As the composition of the liquid between two series of parallel plates changes, the liquid's complex impedance, measured by the C/C sensor, also changes. After laboratory calibration, the water content, fuel content and alcohol content of the liquid can be determined at various heights along the sensor. Challenges for use in alcohol-blended fuels include specificity, accuracy, and precision of the operating principle to detect changes in liquid and interface height. Advantages include precise response to complex impedance changes in alcohol-fuel blends and alcohol-fuel-water mixture.

Figure 3. Capacitance and Conductance (Complex Impedance) (C/C)

C3 TEST SETUP

All sensors were evaluated within clear glass containers with a sufficiently large inner diameter to accommodate the sensors without being excessively wide. The FS/FSP and C/C Sensor were tested in a graduated cylinder and the Optical Sensor was tested in a 4-L beaker. A ruler, graduated in millimeters, was affixed to the outside of the test containers to monitor the liquid rise height with more resolution during the testing. An explosion-proof pump was used for the alcohol blend ingress and a peristaltic

pump delivered water into the test chamber. The fuel pump used tubing that is compatible with fuel. The tubing was secured in place so the liquids flowed along the side of the container to the bottom without touching the technology. The fuel and water ingress rates were between 13 and 100 milliliter per minute (mL/min) to achieve a height increase rate of approximately 5 mm/min. The rate of height increase was calculated by taking into account the volume displacement of the technology in the test chamber. Once the technology and ingress lines were situated in the test chamber, Parafilm® was used to cover the top of the chamber to minimize volatilization.

Before initiation of testing, the sensor was inserted through the top of the test chamber. The sensor configuration with respect to the test chamber (e.g., suspended, vertically resting on the bottom of the test chamber, horizontally resting on the bottom of the test chamber) was in concert with requirements of the vendor-supplied literature and as close to intended field-operating configuration as possible. All sensors were operated in accordance with vendor-supplied operations manuals and guidance including wiring, data collection and maintenance. The Optical Sensor testing was performed in a dark environment by taking measures to minimize light as much as possible without compromising safety. The test chamber was wrapped and the lighting in the lab was minimized.

C4 TEST PROCEDURES

The tests were designed to simulate ingress of water or alcohol-blended fuel into a dry environment and where applicable, water ingress into an alcohol-blended fuel. For each sensor, groundwater and four different alcohol-blended fuels (referred to as test blends from this point forward) will be used during testing: 0% ethanol v/v (E0), 15% ethanol v/v (E15), 85% ethanol v/v (E85) and 16% isobutanol v/v (I16). The FS/FSP sensor was also tested in 30% ethanol v/v (E30) and 50% ethanol v/v (E50). Test blends were prepared as stated in the original QAPP in 4-L or 2-L batches (Section B1.1).[1]

Groundwater used for this testing was collected from the tap in Battelle's Environmental Treatability Laboratory. The tap was opened and flushed for at least 5 minutes before the groundwater was collected. The groundwater was collected in a 5-gallon container and a sub-sample was measured for pH, conductivity, and oxidation/reduction potential. After collection, groundwater was poured from the container into a 2-L graduated cylinder (±20 mL) as needed for the water ingress detection test. A peristaltic pump and associated tubing was dedicated for the water ingress test. The water was pumped into the test chamber at a rate of 24.5 mL/min for FS/FSP, 37.0 mL/min for Optical Sensor and 21.4 mL/min for C/C for the initial test blend detection tests. For the water ingress testing of the C/C sensor, water was pumped at a rate of 13.9 mL/min.

The three technologies have different test procedures due to their specific abilities for detection and discrimination. Tests conducted were dependent on the abilities of the sensor. Table 2 presents the test

matrix including the test blend, number of replicates, and tests performed. The number of replicates was determined using a power analysis which provides a 95% probability of detection in gasoline with 83% power. The Optical Sensor was tested to detect liquid without discriminating between test blend and water (Initial Water/Test Blend Detection Test). The FS/FSP Sensor is somewhat discriminating as it has the float switch ability to detect liquid and the polymer strip ability to detect hydrocarbons (Initial Water/Test Blend Detection Test). There is a second float switch sensor at the top of the technology that has the same ability as the bottom sensor, so the top float switch was actuated with fuel height for only one of the replicates (High Detection with Water 1 Replicate Test). The C/C Sensor discriminates between the test blend and water. Therefore, the initial liquid was introduced for detection (Initial Water/Test Blend Detection Test), and then the technology was submerged to half of its height in test blend and thereafter, water was allowed to ingress for a water detection test (Water Ingress Detection).

Table 2. Test Matrix for Lab-Scale Testing

Technology	Test Blend	Replicates	Tests
Optical	Water	10	Initial Water Detection
	E0	10	Initial Test Blend Detection
	E15	10	Initial Test Blend Detection
	E85	10	Initial Test Blend Detection
	I16	10	Initial Test Blend Detection
FS/FSP	Water	10	Initial Water Detection
			High Detection with Water 1 rep
	E0	10	Initial Test Blend Detection
			High Detection with Water 1 rep
	E15	10	Initial Test Blend Detection
			High Detection with Water 1 rep
	E30	10	Initial Test Blend Detection
			High Detection with Water 1 rep
	E50	10	Initial Test Blend Detection
			High Detection with Water 1 rep
	E85	10	Initial Test Blend Detection
			High Detection with Water 1 rep
	116	10	Initial Test Blend Detection
			High Detection with Water 1 rep
C/C Sensor	Water	10	Initial Water Detection
	E0	10	Initial Test Blend Detection
			Water Ingress Detection
	E15	10	Initial Test Blend Detection
			Water Ingress Detection
	E85	10	Initial Test Blend Detection
			Water Ingress Detection
	I16	10	Initial Test Blend Detection
			Water Ingress Detection

During testing, liquids (test blends and water) was pumped to the test chamber using an appropriate peristaltic pump from a 2 L (±20 mL) graduated cylinder reservoir. The reservoir was sealed with Parafilm® with a hole in the center for the pump tubing. The graduated cylinder was used to periodically monitor the cumulative liquid volume pumped in the chamber during testing. Monitoring the cumulative liquid volume pumped ensured accurate and constant flow rates to the test chamber and also allowed for calculation of liquid height rate within the chamber.

At the completion of the tests, the technology and the liquid were removed from the test chamber. The liquid volume without the technology was measured and then transferred into an approved waste container. The technology was cleaned following the vendor-stated recovery procedure and monitored for recovery time. The FS/FSP Sensor is the only sensor that required a recovery time. The test chamber was rinsed with deionized water and then acetone before being left to dry in the ventilated room. Specific details of the tests are described in the sections below.

C4.1 Initial Water/Test Blend Detection Test

The efficacy of each operating principle to detect groundwater and the test blends into the empty test chamber was determined by the initial water/test blend detection test. After the sensor has been placed inside the empty test chamber and activated for data collection as per the manufacturer instructions, the output was monitored for a minimum of 30 minutes as a blank test to establish the baseline signal. The specified liquid was pumped from the graduated cylinder into the test chamber between 19.2 and 98.5 mL/min for the 2-L graduated cylinder and 4-L beaker, respectively, which corresponds to an empty-chamber fuel height increase of approximately 5 mm/min.

It should be noted that each sensor has different dimensions and occupies a different volume within the test chamber. In all tests, the actual liquid height was higher than that of an empty test chamber due to the volume displaced by the sensor. Therefore, the actual liquid height was determined through observation of the graduations on the side of the test chamber and by calculation after the testing was complete.

Because of the difference in dimensions of each sensor and locations of sensing elements, different amounts of fuel was pumped into the test chamber depending on the sensor tested. In all cases the amount of fuel pumped into the system was sufficient to activate the appropriate part of the specific technology being tested. Once the sensor activated, the initial detection test was complete. If the sensor did not activate, the liquid height was brought to at least 20% higher than the vendor-stated actuation height and the pump was turned off. A 60-minute wait time elapsed before the test was aborted.

C4.2 High Detection

For the FS/FSP sensor, a second float switch is located at the top of the technology. It was tested with one replicate by allowing the liquid to ingress to activation height using the same flow rate and procedure explained above for the initial detection tests.

C4.3 Water Ingress Detection

The water ingress detection test was performed using the C/C Sensor only. It was half submerged in the test blend at the beginning of the test and then groundwater was allowed to ingress into the test chamber until the sensor at the lowest segment changed enough to exceed a gross cutoff for signaling fluid change. Once the sensor activated, the water ingress detection test was complete. If the sensor would not have activated for every water ingress detection test, the water height would have been brought to 20% higher than the vendor-stated actuation height and the pump turned off. A 60-minute wait time would have elapsed before the test was aborted.

C4.4 Recovery Time

After the end of the test the pump was shut off and the technology removed from the chamber. The vendor-stated recovery procedure was followed for each technology and monitored for recovery time. The FS/FSP Sensor is the only sensor that required a recovery time. The other two sensors had immediate recovery once removed from the liquid.

C5 SENSOR DATA AND EVALUATION METRICS

As each test proceeded, different environmental conditions prevailed within the test chamber. It was the goal of the test to determine the operability of each sensor to produce the correct sensor output depending on liquid present. Each sensor has different capabilities and therefore had different data outputs. The performance parameters and evaluation metrics are the means of determining the operability of each sensor; these are described in Table 3.

Table 3. Performance Parameters

Performance Parameter	Evaluation Metric	Data recorded
Average Detection Time	Difference between actuation time and test start times	Test start time and actuation time calculated for each liquid
Average Recovery Time	Average of difference between recovery and test end times	Test end time and recovery time calculated for each liquid
Liquid Activation Height	Average activation height and standard deviation	Liquid height level at activation, calculated for each liquid
Specificity	% Specificity	Liquid height level at activation, calculated for each liquid
Accuracy (qualitative only)	Relative % Accuracy	Liquid height level at activation, calculated for each liquid
Accuracy (quantitative only)	% Accuracy	Liquid height level at activation, calculated for each liquid
Precision (quantitative only)	% Coefficient of Variation	Liquid height level at activation, calculated for each liquid

C5.1 Liquid Detection Time and Recovery Time

Detection time was evaluated for all three sensors. During the initial fuel/water detection tests, test blends of different alcohol concentrations and groundwater were pumped into an empty test chamber. All of the sensors were expected to be able to detect the presence of the liquid and differentiate from the empty condition and the liquid present condition. Because of the different configurations of the sensors, the presence of fuel and water will be detected at different times (heights) after fuel pumping begins. The elapsed time between the test start time and when the detector responded was the detection time for the initial water/test blend detection test.

During the water ingress test, groundwater was pumped into the test chamber that had the test blend filled at 50% height at the beginning of the test. Due to operating principles, only the C/C sensor was expected to be able to differentiate the water absent and water present conditions in the test blend. The elapsed time between the start time and when the detector responded was the detection time for the water ingress detection test.

The recovery time was recorded from the FS/FSP Sensor console output when it ceased to be in alarm mode. The elapsed time between the test end time and when the detector was no longer alarming was the recovery time.

C5.2 Average Detection Time and Average Recovery Time

The liquid detection time and the recovery times were reported as the average ($\bar{x}$) and the standard deviation (S) of the observed values for each liquid. They were calculated following Equations 3 and 4 from the original QAPP, respectively.

C5.3 Specificity

The percent (%) specificity was calculated using the following equation for each of the liquid individually as follows:

$$\text{Specificity, \%} = 100 \times \left(\frac{\bar{x}}{x_t}\right)$$

$\bar{x}$ = mean of observed values, cm

x_t = the theoretical value, cm

C5.4 Accuracy (Qualitative Sensors Only)

Accuracy for the qualitative detectors was determined by calculating percent accuracy of replicates as follows

$$\text{Accuracy, \%} = 100 \times \left(\frac{r}{n}\right)$$

r = the number of positive responses

n = the number of tests for a particular liquid

C5.5 Relative Percent Accuracy (Quantitative Sensors Only)

Accuracy in measuring the liquid level was computed for each measurement made for the water ingress detection test replicates by the following equation:

$$\text{Accuracy, \%} = \frac{|M - D|}{M} * 100$$

M = Measured liquid level, mm

D = Detected liquid level, mm

C5.6 Precision (Quantitative Sensors Only)

Precision was calculated as the percent coefficient of variation (%CV) for quantitative sensors only as follows:

$$\%CV = 100 \times \left(\frac{S}{\bar{x}}\right)$$

S = standard deviation of n values, cm

$\bar{x}$= mean of observed values, cm

C6 TECHNOLOGY RESULTS

Using the above performance parameters the data collected are summarized below according to each operating principle.

C6.1 Optical Sensor Performance

The optical sensor tested is an interstitial monitoring device which is used on secondarily contained tanks and piping. This interstitial monitor performs by utilizing a refractive index and can be performed continuously or intermittently, and no other parameters must be monitored to adjust the observations. Only qualitative leak determinations are possible as the sensor is not able to discriminate between water and hydrocarbons. The sensor is expected to alarm in the presence of liquid which was confirmed during testing. The sensor was effective at distinguishing when liquid was present regardless of the ethanol concentration and showed an accuracy rate of 100% for all blends (Table 4). The recovery time for the optical sensor was instantaneous upon removal from the fluid present condition for all blends (Table 4).

Table 4. Optical Sensor Performance Summary (n=10)

Performance Parameter	*Test Blends*				
	E0	**E15**	**I16**	**E85**	**Water[a]**
Average Detection Time (hh:mm:ss)	0:01:09	0:01:25	0:00:58	0:01:21	0:04:49
Average Recovery Time (hh:mm:ss)	0:00:03	0:00:02	0:00:02	0:00:02	0:00:03
Average Activation Height (mm)	4.9	7.1	4.5	7.1	9.9
Activation Height Standard Deviation (mm)	3.1	1.8	2.1	1.7	0.6
Specificity (%)[b]	95.1%	139%	87.3%	139%	193%
Relative Accuracy (%)	100%	100%	100%	100%	100%

(a) Water was ingressed at half the flow rate of product due to limitations of the water pump
(b) Source of theoretical value (<0.2 inch) is from NWGLDE website

C6.2 Float Switch Performance

The FS/FSP sensor was composed of two float switches, one is on the bottom on the sensor and is described as the bottom float switch (Table 5), the second float switch is higher on the sensor and is referred to as the top float switch (Table 6). Both float switches operate on the same principle where the buoyancy of float allows the signal generated to coincide with the top of the liquid layer. The float switch cannot discriminate between hydrocarbons and water, instead it only distinguishes between liquid present and liquid absent conditions. Both float switches were effective at distinguishing when liquid was present regardless of the ethanol concentration of the test blend and showed an accuracy rate of 100% for all blends (Table 5 and Table 6). The recovery time for the float switches was instantaneous upon removal from the fluid present condition for all blends (Table 5 and Table 6).

Table 5. Bottom Float Switch Sensor Performance Summary (n=10)

Performance Parameter	*Test Blends*						
	E0	**E15**	**I16**	**E30**	**E50**	**E85**	**Water**
Average Detection Time (hh:mm)	0:07	0:07	0:06	0:07	0:06	0:05	0:05
Average Recovery Time (hh:mm)	0:00	0:00	0:00	0:00	0:00	0:00	0:00
Average Activation Height (mm)	36.1	36.1	36.2	35.9	36	36.1	31.6
Activation Height Standard Deviation (mm)	2.1	0.3	0.4	0.2	0.0	0.4	0.3
Specificity (%)[a]	98.4%	94.8%	94.9%	94.2%	94.5%	94.8%	82.9%
Relative Accuracy (%)	100%	100%	100%	100%	100%	100%	100%

(a) Source of theoretical (1.5 inches) is from the manufacturer's specification sheet.

Table 6. Top Float Switch Sensor Performance Summary (n=1)

Performance Parameter	*Test Blends*						
	E0	**E15**	**I16**	**E30**	**E50**	**E85**	**Water**
Detection Time (hh:mm)	0:47	0:39	0:36	0:37	0:34	0:33	0:35
Recovery Time (hh:mm)	0:00	0:01	0:01	0:00	0:00	0:00	0:00
Activation Height (mm)	205.0	205.0	201.0	200.0	201.0	201.0	197.0
Relative Accuracy (%)	100%	100%	100%	100%	100%	100%	100%

C6.3 Fuel Sensitive Polymer Performance

The FS/FSP sensor was also composed of a fuel sensitive polymer strip in addition to the two float switches. The FSP operates on the principle where a fiber optic cable is coated with a polymer that interacts with fuel. When fuel is present, the light passing through the cable will be affected. The FSP can discriminate between hydrocarbons and water and the sensor alarms in the presence of fuel. The FSP was effective at distinguishing that fuel was present with 100% accuracy in test blends of E0, E15, I16, E30, and E50. However, E85 contained too high of an ethanol content for the FSP to distinguish that fuel was present and therefore had a 0% accuracy (Table 7). The recovery time for the FSP is not instantaneous and requires, on average, one hour to return to its non-activated state (Table 7).

Table 7. FSP Performance Summary (n=10)

Performance Parameter	*Test Blends*					
	E0	**E15**	**I16**	**E30**	**E50**	**E85**
Average Detection Time (hh:mm)	0:05	0:05	0:05	0:06	0:10	NA
Average Recovery Time (hh:mm)	1:11	1:01	1:02	0:42	0:24	NA
Average Activation Height (mm)	27.5	26.9	28.1	32	57.8	NA
Activation Height Standard Deviation (mm)	13.1	15.5	20.8	23.4	41.2	NA
Specificity (%)[a]	549%	537%	562%	640%	1156%	NA
Relative Accuracy (%)	100%	100%	100%	100%	100%	0%

(a) Source of theoretical value (0.50 cm) used in calculation is from NWGLDE website

C6.4 Capacitance and Conductance Performance

The C/C Sensor operates under the complex impedance principle which combines two operating principles: electrical conductivity and capacitance. As the composition of the liquid between two series of parallel plates changes, the liquid's complex impedance, measured by the C/C sensor, also changes. As the C/C sensor was the only sensor that can discriminate between hydrocarbons and water, it was the only technology that underwent the initial detection and water ingress performance testing. During the initial detection testing, for all blends the C/C sensor properly activated and was able to detect the appropriate fuel/water types present (Table 8). In addition, the C/C was able to detect water ingress when submerged in any of the test blends (Table 9).

Table 8. Capacitance and Conductance Initial Detection Performance Summary (n=10) [1]

Performance Parameter	*Test Blends*				
	Groundwater	**E0**	**E15**	**E85**	**I16**
Average detection time (mm:ss.0)	01:25.0	02:02.3	02:37.8	01:31.4	02:27.2
Average Activation Height (mm)	5.7	7.85	9.95	5.55	9.75
Average Activation Standard Deviation (mm)	2.275	0.337	0.158	0.599	0.425
Specificity (%) [2]	114.00%	157.00%	199.00%	111.00%	195.00%
Relative Percent Accuracy (%) [3]	11.40%	19.10%	36.20%	14.40%	34.90%
Precision (%CV)	39.90%	4.30%	1.60%	10.80%	4.40%

(1) Values calculated according to Table 3 in Section B1.4.4 of QAPP Addendum 110113
(2) The theoretical detection height was based on the sensor window estimated at 5mm from the bottom Assumed that detected liquid level is the height of the segments detecting water (0.25in * number of segments)

Table 9. Capacitance and Conductance Water Ingress Performance Summary (n=10) [1]

Performance Parameter	*Test Blends*			
	E0[5]	**E15[5]**	**E85[4]**	**I16[5]**
Average detection time (mm:ss.0)	02:04.6	01:42.1	00:19.5	01:56.9
Average Activation Height (mm)	10.6	9.4	2.0	10.0
Average Activation Standard Deviation (mm)	1.165	1.696	1.462	0.577
Specificity (%) [2]	211.0%	188.0%	39.0%	200.0%
Relative Percent Accuracy (%) [3]	39.8%	32.4%	98.4%	36.5%
Precision (%CV)	11.0%	18.0%	75.0%	5.8%

(1) Values calculated according to Table 3 in Section B1.4.4 of QAPP Addendum 110113
(2) The theoretical detection height was based on the sensor window estimated at 5mm from the bottom
(3) Assumed that detected liquid level is the height of the segments detecting water (0.25in * number of segments)
(4) Detection time is time to sensor reading 'Aqueous Ethanol'
(5) Detection time is time to sensor reading 'Water'

C7 GROUNDWATER QUALITY

At the recommendation of the UST LD Stakeholders, groundwater was used to simulate water ingress during testing. There is a lot of variation in groundwater characteristics; therefore, the groundwater used was generally characterized to document the water being used for testing. A sub-sample of the groundwater was analyzed for conductivity, pH and oxidation/reduction potential (ORP)

using the appropriate meters and probes (Hach LDO meter and VWR meter with ThermoScientific probes). Because the characteristics were reported for an understanding of the type of water only and not to achieve certain characteristics, no DQOs were associated with these data. Table 10 presents the average of three measurements taken on the groundwater used for testing.

Table 10. Summary of Groundwater Characteristics

Groundwater	Conductivity (µs/cm)	pH	ORP (mV)	Temperature (°C)
Average (n=3)	1133	7.62	408.1	20.3

C8 REFERENCES

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Appendix D

Pressure Decay Testing Methods and Results

Appendix D

Pressure Decay Testing Methods and Results

D1 TEST SETUP AND PROCEDURE

Limited information is available as to the impact of different ethanol/isobutanol blended fuels on the functionality of pressure decay as a pipeline LD method. Pressure decay relies on the concept that a pipeline containing fuel is pressurized and sections isolated to show a loss of pressure overtime if a leak is present. This pressure decay test was focused on whether the fuel would affect the leak rate. The pressure decay rate was associated with leak rate according to the following equation (when temperature is kept constant):

$$Q = \frac{V}{\bar{P}}\left(\frac{P1 - P2}{T}\right)$$

where Q = the leak rate (cm^2/min)

V = test volume (cm^2)

$\bar{P}$ = average absolute gas pressure (psi)

P1 - P2 = change in pressure (psi)

T = test duration (min)

This test utilized a leak tight 1-gallon pressure vessel set up as depicted in Figure 1. The test was conducted individually on the same test blends utilized in the sensor testing (Deionized [DI] water, E0, E15, E85, and I16). A pressure environment was established in the vessel (initial pressure was 20 psig), a specific leak rate was induced (average flow rates ranged between 4-6 mL/min), and the pressure decay was monitored and timed.

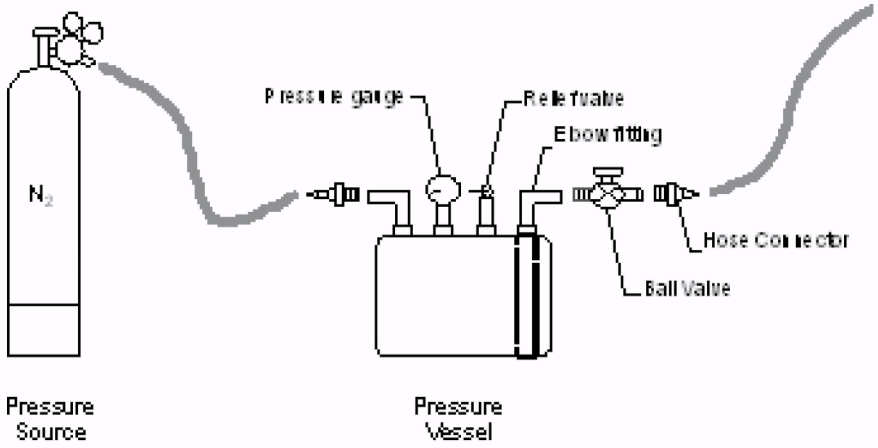

Figure 1. Pressure Decay Test Setup

This stepwise approach was followed to produce a plot of the decay over time for each test blend.

1. Fill pressure chamber to the manufacturer recommended level with test blend (DI water, E0, E15, E85, and I16).
2. Pressurize system with dry air. Initial pressure (P1) should be 20 ± 1 pounds per square inch (psi) for each test blend.
3. Isolate system from the gas pressure.
4. Allow system to stabilize for 15 minutes. Ensure pressure remains at 20 ± 1 psi using a mechanical pressure gauge to monitor the pressure.
5. Generate a leak using 0.1 gallon per hour rate for each test blend. Start a timer and monitor using a metering valve.
6. Liquid product is allowed to flow out of the pipe through a valve with a flow meter and is collected in a graduated cylinder. The amount collected is divided by the time of collection to provide an average leak rate.
7. Monitor the change in pressure over the leak duration.
8. Stop the timer at the end of the test duration (T).
9. The test should be designed so that the total pressure change is less than 10 % of the starting pressure.

D2 PRESSURE DECAY RESULTS

The pressure decay results were similar across the test blends and water. Table 1 summarizes the results and reports the average and standard deviation of the replicates. Figures 1 – 5 present plots of the change in pressure (psi) (y-axis) that was observed over the test duration in minutes (x-axis).

Table 1. Summary of Pressure Decay Testing

Pressure Decay Rate (psig/min) [a]	*Test Blends*				
	E0	**E15**	**I16**	**E85**	**Water[b]**
Replicate 1	-0.0466	-0.042	-0.0549	-0.0242[c]	-0.0465
Replicate 2	-0.0484	-0.0339	-0.0535	-0.0445	-0.0426
Replicate 3	-0.045	-0.0447	-0.0504	-0.054	-0.0543
Replicate 4	-0.0543	-	-	-0.0547	-
Average	-0.0486	-0.0402	-0.0529	-0.0511	-0.0478
Standard Deviation	0.00406	0.00562	0.00230	0.00570	0.00596

(a) Pressure decay rate is the slope of decay over time
(b) DI water
(c) Replicate 1 for E85 was not included in the average or standard deviation calculations

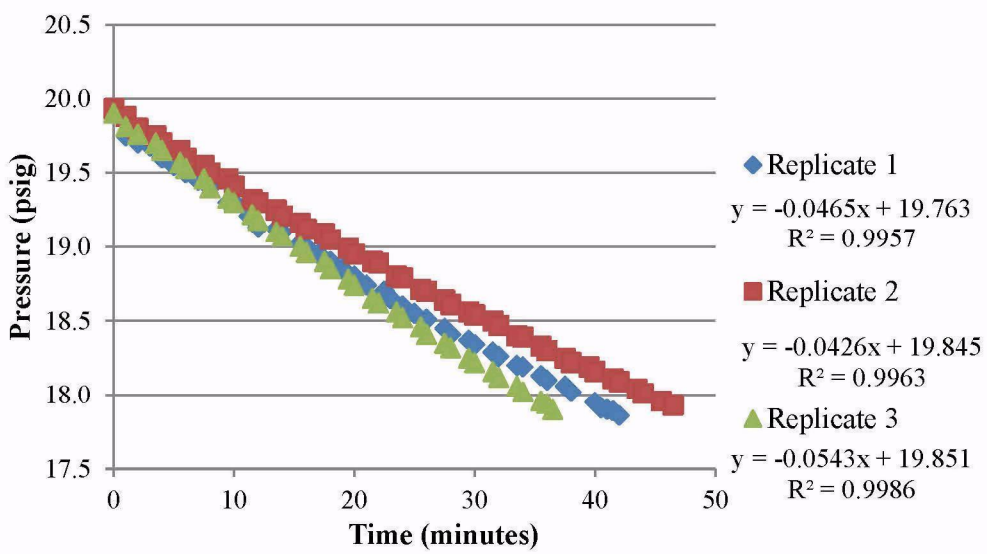

Figure 2. Pressure Decay Test with three replicates DI Water

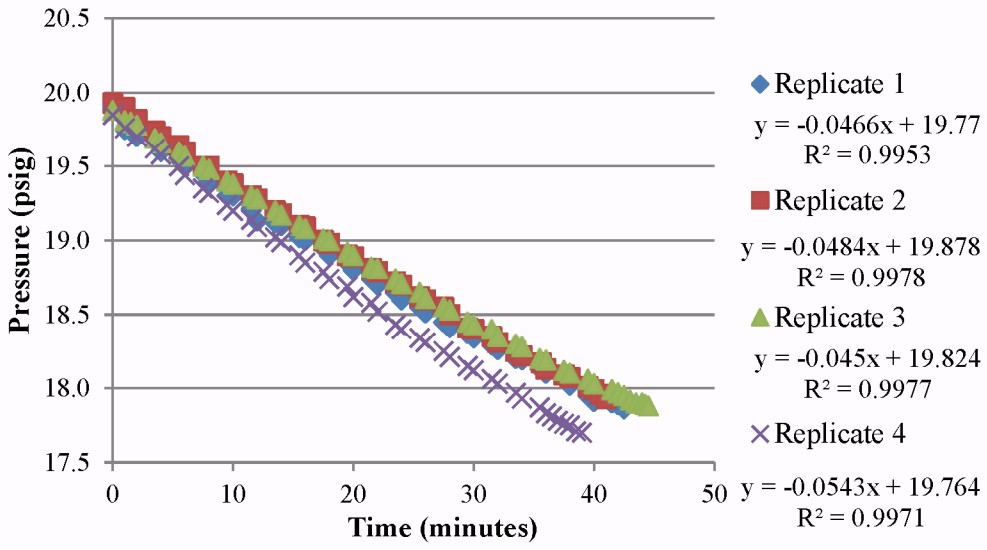

Figure 3. Pressure Decay Test with four replicates of E0

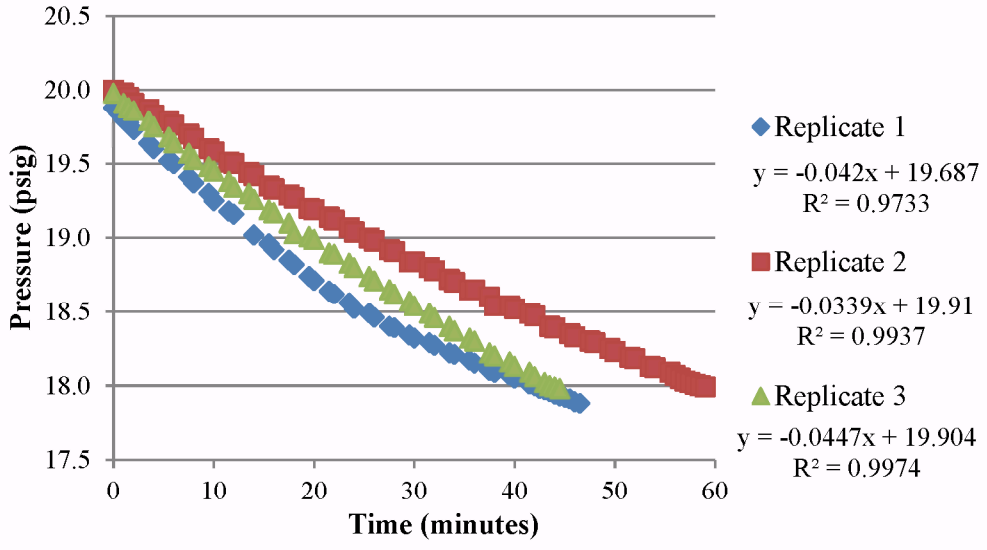

Figure 4. Pressure Decay Test with three replicates of E15

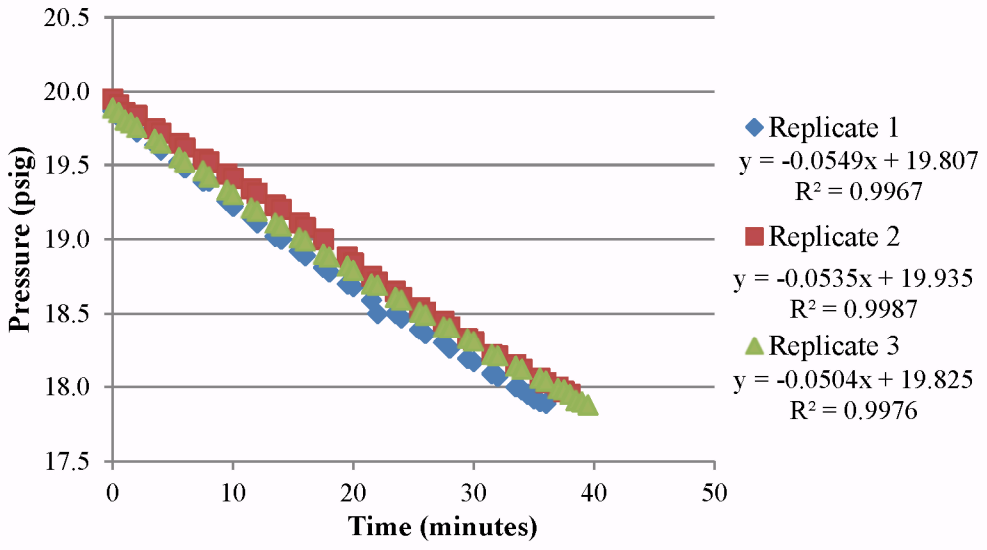

Figure 5. Pressure Decay Test with three replicates of I16.

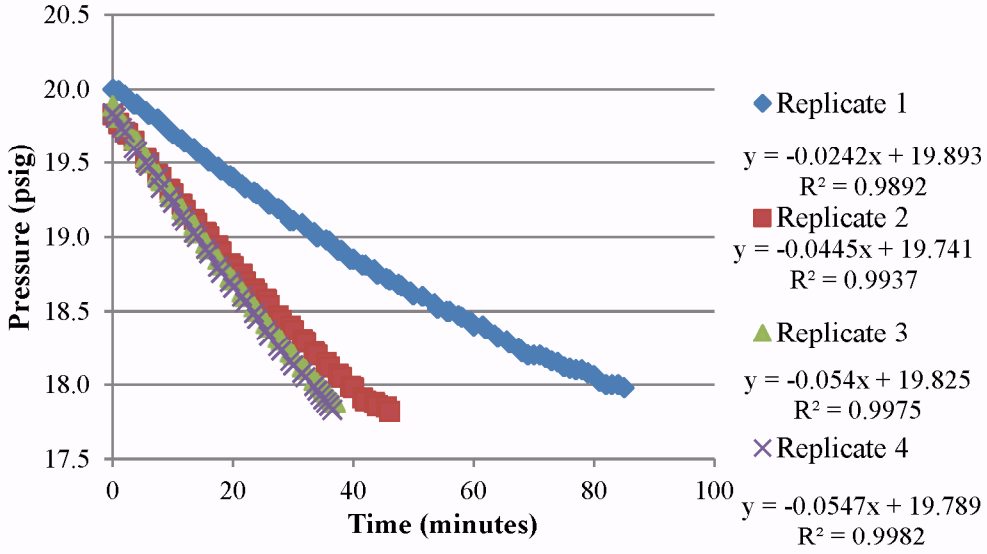

Figure 6. Pressure Decay Test with three replicates of E85

Appendix E

ETV Automatic Tank Gauging Verification Test Summary

Appendix E

ETV Automatic Tank Gauging Verification Test Summary

E1 INTRODUCTION

In 2011, automatic tank gauging (ATG) systems were tested to evaluate their functionality in ethanol-blended fuels[19, 20]. A total of four (4) technologies from two (2) different vendors were tested in three (3) fuel blends (i.e., E0, E15, and E85). The following sections provide a general description of the ATGs tested, an overview of the testing procedure, and summarized the results and findings from the testing.

E2 TECHNOLOGY DESCRIPTIONS

ATG systems are volumetric leak detection technologies that rely on various physical properties of the storage system to generate an electronic signal that can be converted into a value representing a volume in a tank. An ATG system consists of a probe or sensor located inside the UST and a controller (or console) mounted in an indoor location. Descriptions of each technology are summarized below:

- Vendor A-Technology 1 (A1): A1 is designed to detect and measure the level of water present at the bottom of a fuel storage tank in conjunction with a magnetostrictive level probe and ATG system. The probe is installed in the storage tank by suspending it from a chain such that the bottom of the probe is near the bottom of the tank. Specific versions of the water float are available for use in diesel fuel and (non-ethanol-blended) gasoline. This float is ballasted to have a net density intermediate to that of water and the respective fuel present in the tank such that it is intended to float at the water-fuel interface.
- Vendor A-Technology 2 (A2): A2 is designed to detect and measure the level of a dense phase present at the bottom of a fuel storage tank in conjunction with a magnetostrictive level probe and ATG system. The probe is installed in the storage tank by suspending it from a chain such that the bottom of the probe is near the bottom of the tank. Specific versions of the water float are available for use in ethanol blended gasoline with up to 15% ethanol. This float is ballasted to have a net density intermediate to that of the dense phase and the respective fuel such that it is intended to float at the dense phase-fuel interface.
- Vendor B-Technology 1 (B1): B1 is designed to detect and measure the level of water present at the bottom of a fuel storage tank in conjunction with a magnetostrictive level probe and ATG system. The water float, which represents a non-volumetric test technology, is located on the bottom of the tank where water collects as a dense phase in gasoline. As the water depth increases, the float rises and transmits an electronic signal proportional to the level of water in

the bottom of the tank. Specific versions of the float are available for use in diesel fuel and (non-ethanol blended) gasoline. These floats are ballasted to have a net density intermediate to that of water and their respective fuels such that they will float at the water-fuel interface. The evaluation was performed using a standard float for use in gasoline.

- Vendor B-Technology 2 (B2): B2 is a concentric, dual-float system designed specifically for low-ethanol blend gasoline up to E15. The float is installed at the bottom of a fuel storage tank and is used in conjunction with a magnetostrictive level probe and ATG system. An inner float is designed to move freely within the limits of a protective housing attached to the outer float to respond to all phase separation compositions in these fuels. The outer float is ballasted to remain responsive to water and water-rich compositions of phase separation. This allows the inner float to measure the full depth of water in the case of a massive ingress (lifting both floats), while preventing the inner phase separation float from interfering with the fuel float in the rare situation that an unusually dense, cold gasoline is delivered into the tank. As the detected phase separation depth increases, the float rises and transmits an electronic signal proportional to the level of phase separation in the bottom of the tank.

E3 TEST OVERVIEW

For the technology evaluation a test vessel was fabricated from a 6-ft diameter piece of a fiberglass storage tank shell that was fitted with glass ends to allow visual observations of the conditions within the vessel during testing. All four ATGs were installed in the vessel according to the manufacturer's specifications.

The following three test designs were incorporated to evaluate performance parameters, which were used to characterize the functionality of the ATG system:

1. A continuous water ingress test consisting of two parts:
   - Determination of minimum detection height
   - Determination of smallest detectable incremental change in height
2. A quick water dump followed by a fuel dump

The first part of test one determined the minimum detection height by introducing water into the test vessel using two methods of ingress – with splash and without splash. The water ingress method/rate was selected to establish conditions that impact the degree of mixing that occurs in a tank using the three ethanol blends – E0 (no ethanol), E15 (15% ethanol), and E85 (85% ethanol). Two fuel height levels (i.e., 25% [170 gallons] and 65% [610 gallons]) were specified to establish different splash mixing regimes and diffusion columns. Once the technology reacted to the minimum water height, the smallest increment in water height was determined by continuing to ingress water at a height increase rate of 1/16-

inch every 10 minutes. Readings from the technology along with visual measurement were recorded and used to determine the smallest detectable increment.

The second test was designed to simulate a quick water ingress rate followed by a high degree of mixing such as might occur if a large volume of water was dumped into the tank at a 25% fill height and then fuel was delivered to fill the tank to a 65% fill height. This test was performed using all three blends of fuel.

E4 RESULTS

A summary of the results and findings for each of the four technologies tested is presented below:

- Vendor A-Technology 1: A1 responded to the water ingress when the test fuel was E0 and E15, but showed no response when E85 was used as the test fuel. The reason for the lack of response was that no clear separated dense phase was formed in the flex fuel when water was added to the test vessel. As a result, the performance parameters defined in the QAPP could not be determined for this technology when E85 was employed.
- Vendor A-Technology 2: A2 responded to the water ingress when the test fuel was E0 and E15, but moved up the probe shaft to the upper fuel float when tested in E85. No clear separated dense phase was formed in the E85 when water was added to the test vessel. As a result, the performance parameters defined in the QAPP could not be determined for this technology when E85 was employed.
- Vendor B-Technology 1: B1 responded to the water ingress when the test fuel was E0 and E15, but showed no response when E85 was used as the test fuel. The reason for the no response was that no clear separated dense phase was formed in the E85 when water was added to the test vessel. As a result, the performance parameters defined in the QAPP could not be determined for this technology when E85 was employed.
- Vendor B-Technology 2: B2 responded to the water ingress when the test fuel was E0 and E15, but showed no response when E85 was used as the test fuel. The float appeared to be neutrally buoyant in the E85/water mixture. The reason for the no response was that no clear separated dense phase was formed in the E85 when water was added to the test vessel. As a result, the performance parameters defined in the QAPP could not be determined for this technology when E85 was employed.

Currently 40 CFR, Section 280.43(a) states water detection technologies should detect “water at the bottom of the tank,” which does not address water entrained in the fuel due to increased miscibility with the presence of ethanol. The ATG reports[19, 20] written after this testing state that they "did not detect water in the test vessel containing either intermediate (E15) or high (E85) ethanol blends if the water was

suspended in the product or the water did not reach the bottom of the tank. Because of this, there is not sufficient data to evaluate whether these technologies, when used with UST systems containing intermediate or high ethanol blends, would indicate a potential release under every circumstance."

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Appendix F

ATG Simulated Leak Results

Appendix F

ATG Simulated Leak Results

This appendix is presenting data collected from an underground storage tanks (UST) testing company and the quality of the data was not verified by the EPA or Battelle. Battelle has no reason to suspect the result as being poor quality; it just could not be verified.

In 2013, simulated leak tests were conducted on single-walled USTs with the automatic tank gauging (ATG) systems as the primary method of leak detection. Tests were conducted as part of annual monitoring system certification test by a contracted testing company at sites servicing E10 (Premium, Mid-grade, and Regular Unleaded) and diesel fuels. Using a peristaltic pump calibrated for the regulatory leak level, technicians remove 0.2 gallons per hour (gal/hr) of fuel while conducting a static leak test with the ATGs. If the ATG reported a failed static test, meaning the technology determined the tank was not tight, then the simulated leak test was reported in the below table as a "Pass". Of the 71 tests conducted, 14 were “Inconclusive.” The majority of "Inconclusive" test results were due to the product level being below the minimum required by local requirements for the ATG setup. Other “Inconclusive” tests were due to the temperature change during the test being too large. These results indicate that ATGs are able to detect leaks at the regulatory level in diesel and E10 fuels.

ATG Performance Test Results in Southern California in 2013

County in Southern California	# of Tests Conducted - 0.2gal/hr Test Results	Comment
Kern	1-Pass	All Ok.
Kern	2-Pass, 1-Inconclusive	Tank #1 and #3 Passed. Tank # 2 Mid-grade unleaded (MUL) was inconclusive due to Temp Change Too Large.
Kern	2-Pass, 2-Inconclusive	Tank #1 and #2 Passed. Tank #3 Premium unleaded (PUL) tested twice, inconclusive both times due to Temp Change Too Large.
Kern	1-Pass	All Ok. Tank #3 PUL retested and Passed.
Los Angeles	3-Pass	All Ok.
Los Angeles	3-Pass	All Ok.
Los Angeles	1-Pass	All Ok.
Los Angeles	3-Pass, 1-Not Tested	All Ok. Diesel Tank #4 was not tested due to low product level.
Los Angeles	1- Inconclusive, 1-Pass	Diesel Tank #4 showed a gross increase during first test, Re-test Passed.
Los Angeles	3-Pass	All Ok.

County in Southern California	# of Tests Conducted - 0.2gal/hr Test Results	Comment
Orange	4-Pass	All Ok.
Orange	1-Pass	All Ok.
Orange	3-Pass, 1-Inconclusive	Diesel Tank #4 percent volume was too low and caused Inconclusive.
San Bernardino	4-Pass	All Ok.
San Diego	1-Pass, 2-Inconclusive	Tank # 1 - Pass. Percent Volume too low on other two Tanks and caused Inconclusive.
San Diego	2-Inconclusive	Percent Volume too low on both Tanks and caused Inconclusive.
San Diego	3-Pass	All Ok.
San Diego	1-Pass	All Ok.
San Diego	1-Pass	All Ok.
San Diego	2-Pass, 1-Not Tested	All Ok. Tank #1 PUL Not Tested-Product too low.
San Diego	1-Pass, 2-Inconclusive	Tank #2 Regular unleaded (RUL) - Pass. Tank #1 PUL and #3 MUL percent volume too low caused Inconclusive
San Diego	2-Pass, 1-Inconclusive	All Ok. Tank #1 PUL percent volume too low caused inconclusive.
San Diego	2-Pass, 1-Inconclusive	Tank #2 RUL and Tank #3 RUL - Pass. Tank #1 PUL percent volume too low caused inconclusive.
San Diego	2-Pass, 1-Inconclusive	All Ok. Tank #1 PUL percent volume too low caused inconclusive.
San Diego	1-Pass	All Ok.
San Diego	3-Pass	All Ok.
San Diego	3-Pass	All Ok.
San Luis Obispo	3-Pass	Tapes showed that the probes detected the simulated leaks, but, the ATG did not sound an alarm. Maintenance was dispatched.