Corrosion in Systems Storing & Dispensing Ultra Low Sulfur Diesel (ULSD), Hypotheses Investigation

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Overview

- Identify Issue
- Where have we been
- Where are we now
- Where are we going

energy API

From as early as 2007, PEI started receiving reports of unusually severe and accelerated corrosion in ULSD USTs

Initial observations

Corrosion appears in both liquid and vapor areas

Metallic wetted and unwetted areas are susceptible

No reported evidence of corrosion

- at refineries
- within pipelines
- in terminals

No apparent connection between

- geographical region
- supplier
- age of equipment

Equipment Issues Reported

- Filters clogging/requiring more frequent replacement
- Seal/gasket/o-ring deterioration
- STP replacement/column pipe wear/motor problems
- Tanks rusting/leaking
- Meter failure
- Line leak detectors damaged or broken
- Automatic nozzle shutoff failure/shorter lifespan
- Tank probes malfunctioning
- Check valves not seating
- Shear valves not sealing/failing tests
- Swivels failing/shorter lifespan
- Dispenser leaks/failures/ premature replacement
- Solenoid valves clogged/failing
- Corrosion on the riser pipe

The CDFA Decides on Two Courses of Action

Guidance for Underground Storage Tank Management at ULSD sites (Published Aug 2010)

Research and testing to determine links, if any, between ULSD and corrosion

Guidance for UST Management at ULSD Dispensing Facilities

Sources:

- American Petroleum Institute RP 1621, Bulk Liquid Stock Control at Retail Outlets
- American Trucking Associations, Technology and Maintenance Council (TMC) RP 345A, Diesel Fuel
- TMC RP 518, Fuel Station Planning
- Publically-Available Tank Maintenance Documents
- Steel Tank Institute's "Keeping Water Out of Your Storage System"
- EPA's "Operating and Maintaining Underground Storage Tank Systems: Practical Help and Checklists"

Guidance Introduction

If a fuel storage facility is not properly maintained, bacteria and fungi can grow the fuel-water interface, causing filter problems and deactivating the water monitoring system. With the exception of fuel with inadequate low-temperatur fluidity (i.e., wax formation in diesel tanks at cold temperatures), **most problem can normally be avoided by keeping the fuel storage system clean and as water-free as possible.**

Water in the storage system can accelerate fuel degradation which should be avoided in order to assure vehicle performance and because it can increase sludge accumulation in the bottom of tanks. Contaminants such as salts in the water may cause the fuel chemical structure to degrade into components that may be detrimental to storage system components. These contaminants may also cause fuel additives necessary for maintaining the quality of the fuel distribution system to leave the fuel and enter the water.

Not only is water a problem in itself, but it is also the environment for biological growth within the fuel. Less than 0.25 inches of water is more than sufficient to promote microbial growth. Microorganisms live at the fuel-water interface and feed on the fuel. The presence of microorganisms can lead to f plugging, pump and injector problems, deactivation of the water monitor and buildup within the tank that is costly to remove.

Available at: http://www.clean-diesel.org/compliance.html

Regulatory Drivers

2005: Energy Policy Act of 2005:

- Established Renewable Fuel Standard (3.5 billion gallons renewable)

2006: US EPA Clean Air Highway Diesel final rule

- Required 97% reduction in sulfur content of highway diesel fuel
- Low Sulfur Diesel Fuel (LSD) : 500 parts-per-million (ppm) → 15 ppm in ULSD

2007: Energy Independence and Security Act of 2007

- Sets Renewable Fuel Standard (36 B gallons by 2022, 13.2 B gallons in 2012)

Current status

- ULSD: 80% of the change over occurred in 2006 and the remaining 20% occurred by 2010
- Ethanol: Over 90% of all gasoline is being sold with 10% ethanol content

Members of CDFA

AAA
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Association of American Railroads
Association of International Automobile Manufacturers
Association of Oil Pipe Lines
Diesel Technology Forum
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Manufacturers of Emission Controls Association
National Automobile Dealers Association
National Association of Convenience Stores
National Association of Fleet Admins.
NATSO, Inc., representing Truck Stops & Travel Plazas
National Petrochemical & Refiners Association
National Tank Truck Carriers, Inc.
Petroleum Equipment Institute
Petroleum Marketers Association of America
Society of Independent Gasoline Marketers of America
Steel Tank Institute
Truck Renting and Leasing Association
U.S. Environmental Protection Agency
U.S. Department of Energy
U.S. Energy Information Administration
Western States Petroleum Association

Who's Who

Clean Diesel Fuel Alliance Corrosion Taskforce

- www.clean-diesel.org

Contracted with Battelle teamed with Tanknology through competitive RFP to provide objective evaluation

- Association of American Railroads
- American Petroleum Institute
- Ford Motor Company
- National Association of Convenience Stores
- National Association of Truck Stop Operators
- Petroleum Equipment Institute
- Petroleum Marketers Association of America
- Steel Tank Institute

Project Design
Hypotheses Investigation

Phase 1

- Industry observations, anecdotal information, and Tanknology inspection database
  - ~12 potential hypotheses
  - Concluded 3 working hypotheses

Phase 2

- Detailed investigation of 6 sites
  - Field sampling
  - Chemical and microbiological components
- Interpretation of results
- Concluded final hypothesis

Project Design

Phase 2: Working Hypotheses

1. **Aerobic and anaerobic microbes** produce byproducts that establish a corrosive environment in ULSD systems
2. **Aggressive chemical specie(s)** present in ULSD systems promote aggressive corrosion
3. **Additives** in the fuel contribute to the corrosive environment in ULSD systems

Selecting the Inspection Sites

12 sites were considered, 2 did not have symptoms

Minimize Variety in:

Tank Material

Fuel Throughput

Tank Size

Maximize Variety in:

Installation Year

Prior Fuel Service History

Geographic Location thereby adding variety in:

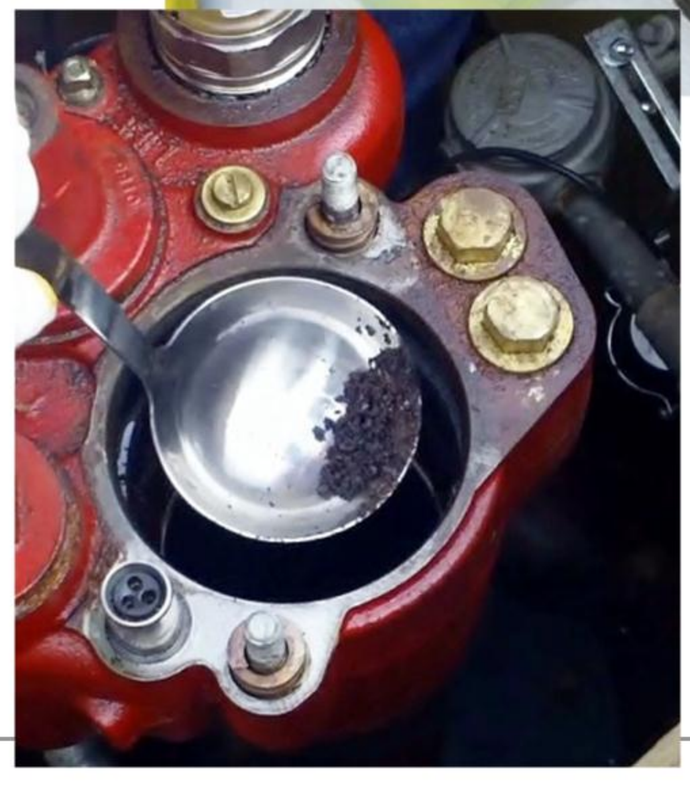
- Climate
- Fuel Supplies (refinery)
- Fuel Routes (pipelines, barge)
- Carriers (company owned, third party)

6 Sites Selected

- 1 site that was believed to not have symptoms of corrosion
- 5 sites with a history of severe, rapidly induced corrosion

Inspection and Sampling Plan

- Data collected on inspection checklist, in laboratory record book, with photos and video
- Each site inspected in February 2012
- Samples collected
  - Fuel
  - Water bottom
  - Vapor
  - Bottom sediment
  - Scrape samples
- Analyses conducted by 5 independent laboratories



Genomics Biological Analysis

Extracted DNA from 16 samples

Analyzed 4 samples from 3 sites using genomics techniques

- Compared data to library of DNA to identify organisms
- Bacteria, fungi, viruses, and metabolic pathways

- Confirmatory test for the presence of bacteria on samples with DNA yield too low for genomics analysis
  - PCR amplification of 16s rRNA gene

Dominant Organisms by Site

Bacteria of the acetic acid producing family (*Acetobacteraceae*) were prevalent at three inspection sites.

The hydrocarbons contained within the diesel fuel may not be the primary carbon source for the consortium of bacteria present.

Diversity Assessment

- All sites inspected displayed presence of bacterial DNA, although in different abundances.
- The conditions of the ULSD tanks are conducive to growth of limited, specialized organisms.

Chemical Analyses Summary

Fuel

- Acetate and trace amounts of ethanol
- 3 failing NACE ratings
- Sulfur 5.9 - 7.7 ppmv

Water

- Acetate, ethanol and glycolate
- High conductivity, chlorides, and low pH at all sites

Vapor

- High humidity, acetic acid, formic acid, and propionic acid at all sites

Corrosion Inducing Factors

Conditions exist to lead to observed attack

1. Corrosion of metallic components– observed during inspections
2. Ingredients for a corrosive aqueous electrolyte exist
   - Water, oxygen, acid content, aggressive species (Chlorides) at all 6 sites
3. Microbiological activity determined at all 6 sites
4. Mechanism for electrolyte and aggressive species dispersion exists during fuel deliveries
   - With higher vapor pressure than ULSD, acetic acid is dispersed into vapor space

Possible Ethanol Sources

Switch Loading

- Diesel fuel is often delivered in the same trucks as ethanol-blended gasoline.

Ventilation Systems

- ULSD USTs that have been converted from a gasoline tank could have manifolded ventilation systems with gasoline tanks.

Symbiotic Biological Activity

- Microbes or fungi using or producing ethanol

Is it possible for *Acetobacter* to create enough acetic acid in the UST environment to cause the corrosion?

Upper bound on the amount of acetic acid required

One of the most common reaction pathways for acetic acid production = (1 mol of ethanol per 1 mol of acetic acid)

Yes

Can this amount of acetic acid be created in a timeframe consistent with the observations?

- Acetic acid production has been reported steady at 4.55g/Lh for 27 g (dry weight) of *Acetobacter* in a 1-L reactor
- If there is sufficient O_2 and ethanol, ~650 g of acetic acid can be produced in the course of 1 week (144 hours)

Yes

Final Hypothesis and Study Conclusions

- Acetic acid was determined to be a likely cause of the corrosion
  - Ubiquitous in the USTs inspected and was not intentionally introduced
- A plausible source of the acetic acid is from *Acetobacter* producing it as a metabolic by-product
- The components for identified *Acetobacter* to thrive were present in the tested USTs (oxygen, water, low pH, ethanol)
- Acetic acid repeatedly “doses” the equipment when the UST contents are disturbed
- It is feasible for enough acetic acid to be produced in the timeframe being reported
- It is possible that there are other mechanisms in play

Unanswered Questions

- Is accelerated corrosion only associated with FRP USTs or is it also present in steel USTs?
- Is accelerated corrosion limited to the retail site level or is it present in upstream systems?
- Is a different contaminant (not ethanol) entering the fuel supply before the retail site?
- Is acetic acid the major contributor or are there other organic and inorganic contaminants present in the UST bottom water reacting synergistically resulting in accelerated corrosion?
- Is the formation of acetic acid exclusively due to the oxidation of fugitive ethanol or are there other source(s) of acetic acid present in the UST?

Possible Goals

- Determine if the accelerated corrosion phenomena is exclusive to fiberglass UST systems or does it equally affect steel systems as well.
- Determine if the cause of the accelerated corrosion is introduced at the retail site or some upstream modality or facility.
- Determine if the accelerated corrosion phenomena is restricted to UST systems at retail sites or does it equally affect other upstream supply chain equipment
- Identify the leading factors, (i.e., contaminants and/or chemicals), that contribute to and promote the corrosive environment seen inside the ULSD systems.

Next Steps: New Project?

Goal: To understand which factors do and do not contribute to the corrosion in systems storing and dispensing ULSD.

- Analyze four retail diesel UST systems to determine the difference between the environments in two corroded sites (one steel and one FRP) and two sites without corrosion (one steel and one FRP).
- Conduct a root cause analysis through another mechanism
- Conduct a survey of all systems to determine the extent of the corrosion in the US
- Conduct a laboratory bench test

Thank you to the CDFA Taskforce, Battelle, Marathon Petroleum, Chevron, Ford, Inspection Site Owners/Operators, and Tanknology

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The report is posted at:

http://www.clean-diesel.org/pdf/ULSDStoringSystemCorrosion.pdf

Guidance for UST Management at ULSD Dispensing Facilities

http://www.clean-diesel.org/pdf/GuidanceforUndergroundStorageTankManagement_FINAL.pdf

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Questions?