



Fuels 101

9th Annual California Unified Program Conference

**Garden Grove, California
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OVERVIEW

- Introduction
- System Configuration
- Fuel Chemistry
- Risk Factors for material compatibility
- ULSD
- Biodiesel
- E10
- Fuel Ethanol E85
- Conclusion

Introduction

- For almost a century the U.S. has relied on petroleum based fuels,
- Environmental concerns has forced improvement in fuel chemistry,
- Disruptions in foreign crude oil supply has required the need to diversify the sources and pursue alternative fuels,
- How will changes in fuel chemistry and alternative fuels impact our retail fuel infrastructure?

Introduction

- Current changes to our fuel supply include:
 - Ultra Low Sulfur Diesel
 - Biodiesel
 - Elimination of MtBE resulting in the increased use of Ethanol Blended Fuel (E10)
 - Increased production and use of Ethanol Fuel (E85)

Introduction

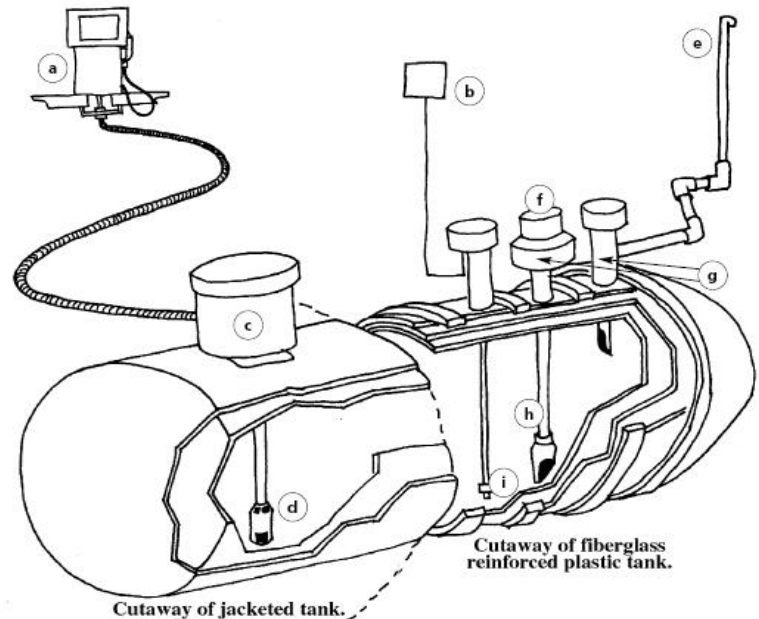
- Materials Compatibility
 - Are there material compatibility issues with system metals and non-metals,
- Technical issues involve
 - Specific needs for system preparation & system conversion, and concerns with material compatibility,
 - Source of feedstock,
 - Dissolved and free water,
 - Biodegradation,

Storage & Dispensing



System Configuration / Materials

- Will discuss materials that are found in a UST and dispensing system configuration:
 - Tank & Piping
 - Pump System
 - Dispenser & Nozzle
 - Vapor Recovery System



System Configuration / Materials

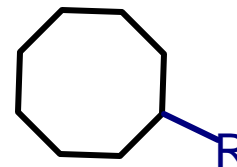
- Typical materials include,
 - Metals generally found in fueling systems:
 - aluminum, brass, copper, steel, zinc
 - Non-metals generally used in fueling systems:
 - Elastomers - Flexible hoses, seals, gaskets and packing,
 - Thermoplastics - Underground flex piping, sumps and vapor recovery tubing,
 - Thermosets - Rigid piping and USTs,
 - Ceramics, pipe dope, and organic coatings

Fuel Chemistry - Petroleum

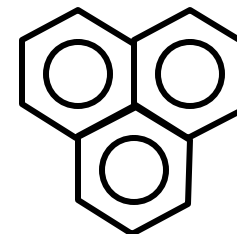
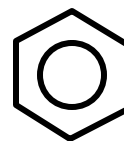
1. Linear & branched



2. Cyclic



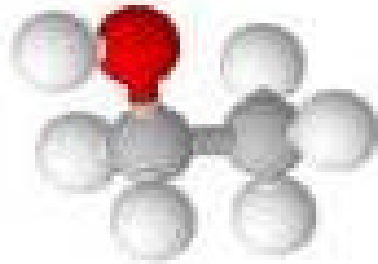
3. Aromatic & Polyaromatic



- Desulfurization of diesel feedstock to make ULSD will open cyclic rings resulting in a greater percentage of linear molecules.

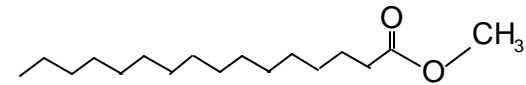
Fuel Chemistry - Biomass

- Ethanol Fuel Blends

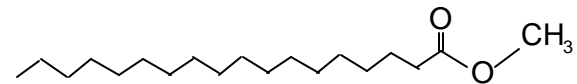


- Biodiesel Fuel Blends

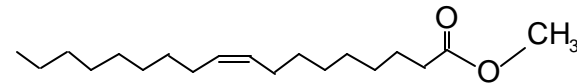
Methyl
Palmitate 16:0



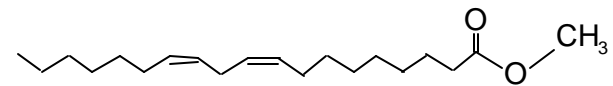
Methyl Stearate
18:0



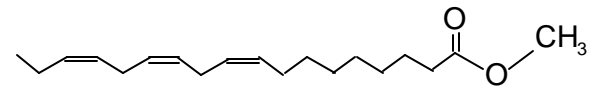
Methyl Oleate
18:1



Methyl
Linoleate 18:2



Methyl
Linolenate 18:3



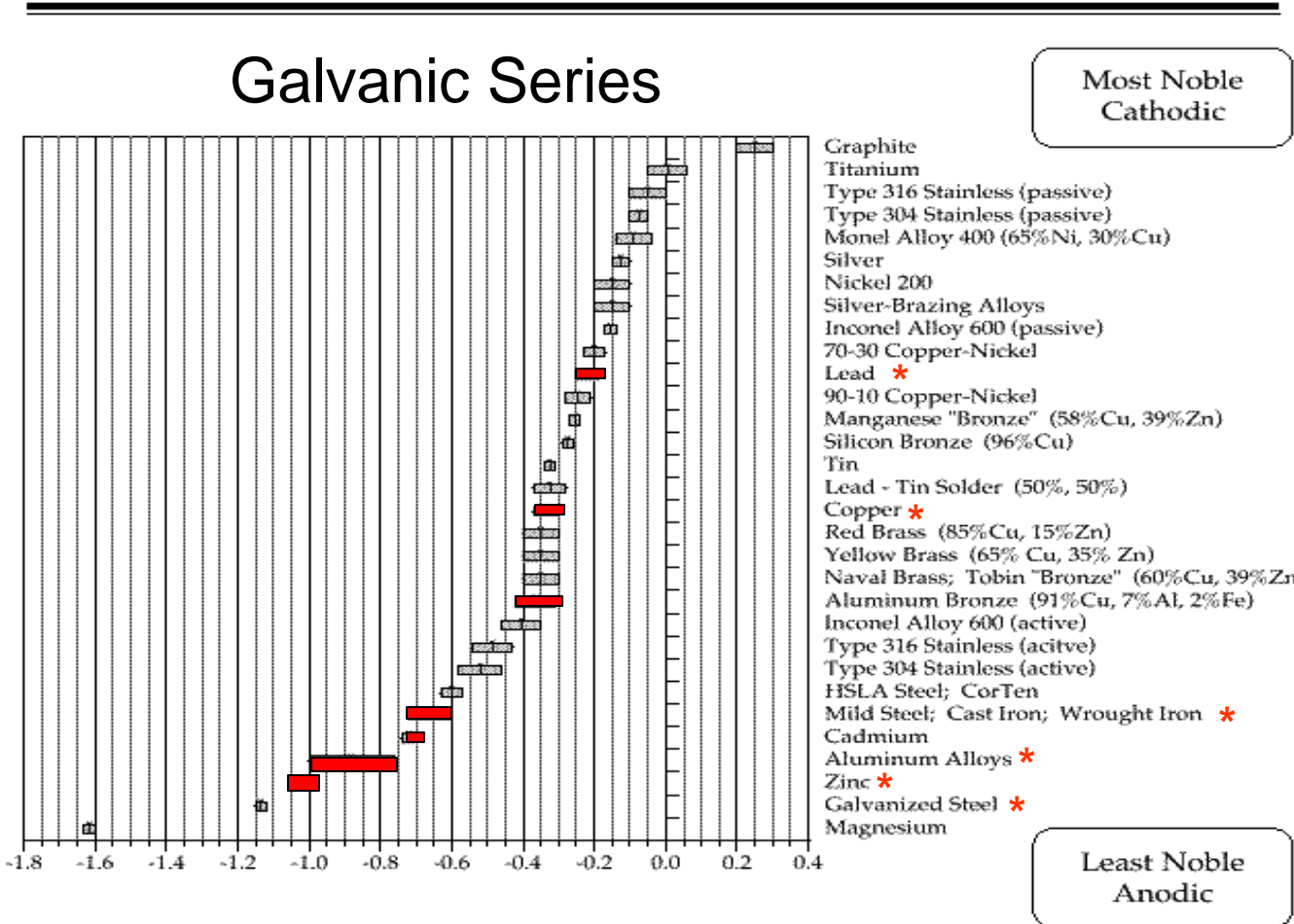
Fuel Chemistry - Comparison

Petroleum Base Fuels:	Biomass fuels:
Have low conductivities <ul style="list-style-type: none"> ▪ Gasoline 1×10^{-14} mho/cm ▪ Diesel 1×10^{-12} mho/cm 	Are more conductive <ul style="list-style-type: none"> ▪ Neat Ethanol 10^{-9} S/cm, ▪ Neat Methanol 10^{-7} S/cm
Hold very little water dissolved water <ul style="list-style-type: none"> ▪ 60-100 ppm 	Hold much more water dissolved water <ul style="list-style-type: none"> ▪ E10 3000-5000 ppm (~0.3 - 0.5%) ▪ E85 ~100,000 ppm (~10%) ▪ B100 1200-2500 ppm
<ul style="list-style-type: none"> ▪ do not absorb or permeate through <u>metals</u>, ▪ To date no information in the public domain indicating, compatibility issues with thermoset USTs, ▪ Compatibility issues have been noted thermoplastic and elastomeric materials ▪ E10 & E85 contains a functional groups that increase chemical activity, reactivity, and bioavailability 	

Risk Factors - Metals

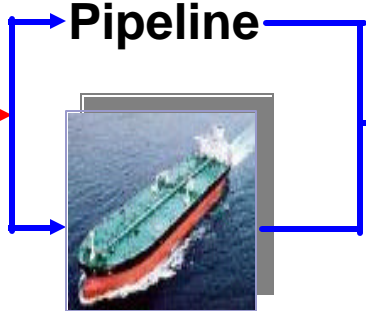
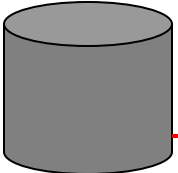
- Recognized risk factors for metal corrosion:
 - Anodic metals tend to corrode more readily in a given environment or in the presence of cathodic metals (metals that are widely separated relative to the galvanic series),
 - Water, chemical contaminants, and salts in the fuel system can increase system conductivity,
 - Microbial involvement can accelerate galvanic and pitting corrosion of metal that would normally take much longer under “sterile” conditions,

Risk Factors - Metals



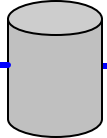
Risk Factors – Water

Refinery Storage

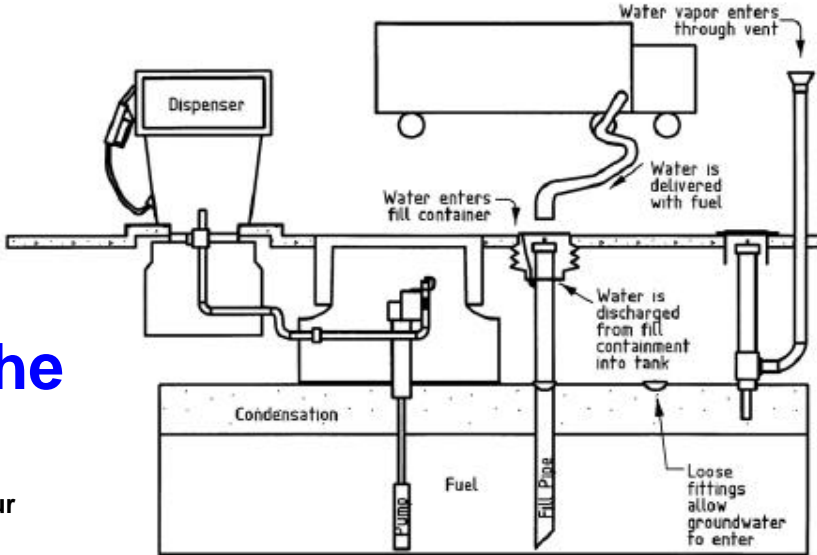


Water Intrusion Storage and Distribution Level

Retail Distribution

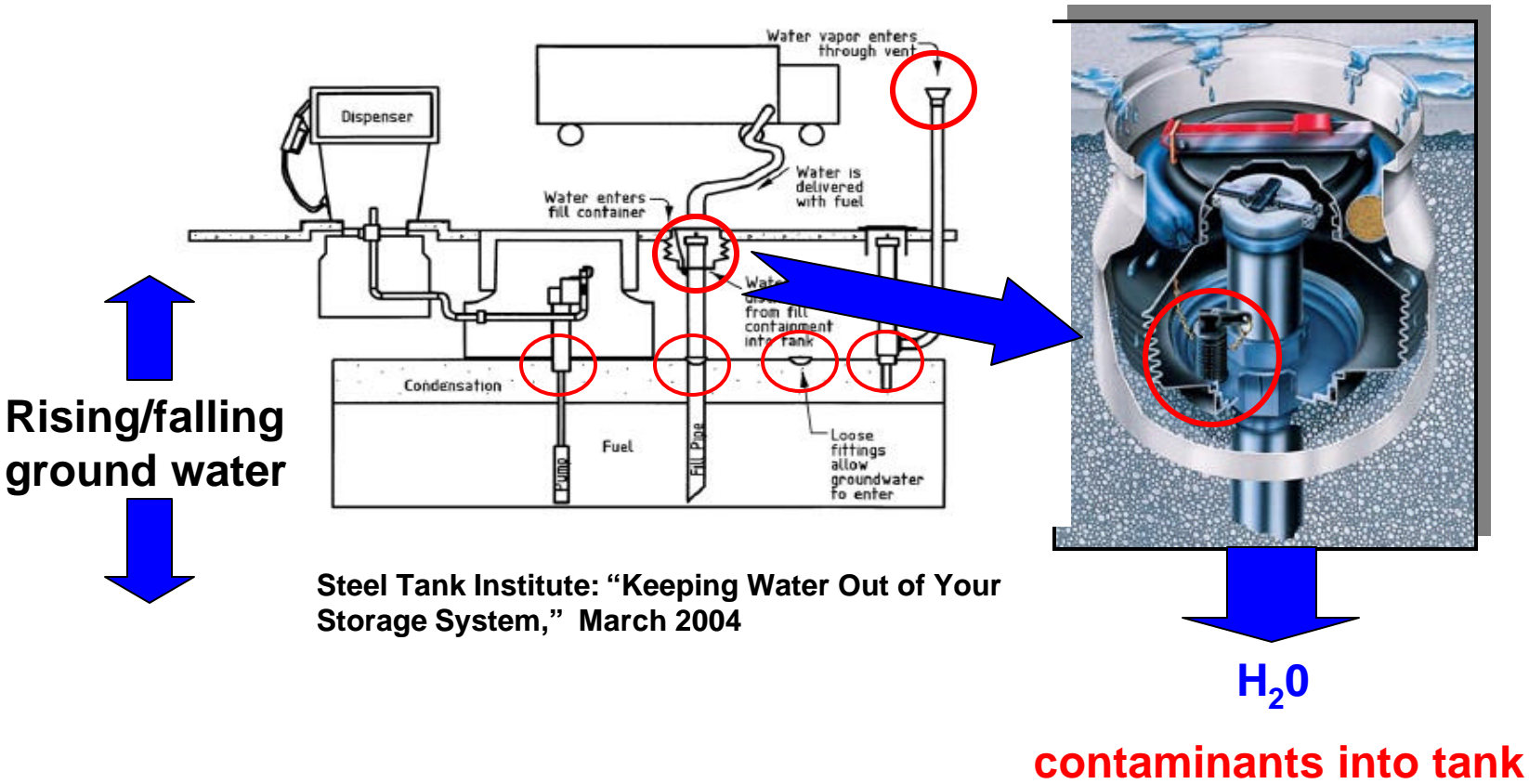


Water Intrusion at the Retail Level



Courtesy of Steel Tank Institute: "Keeping Water Out of Your Storage System," March 2004

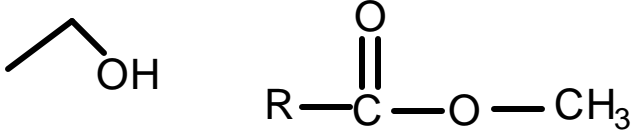
Risk Factors - Water



Steel Tank Institute: "Keeping Water Out of Your Storage System," March 2004

Risk Factors for Non-metals

Recognized risk factors for degradation of non-metals include

Permeation...solvent ingress related to chemical potential driven by activity gradient,	$\mu = \mu_o + RT \ln a/a_o$
Swelling...interaction between the solvent molecule and the polymer matrix,	 <p>The image shows two chemical structures. On the left is ethanol, represented as a skeletal structure of a two-carbon chain with a hydroxyl group (-OH) attached to the second carbon. On the right is a plasticizer molecule, represented as a carbonyl group (C=O) bonded to an 'R' group, an oxygen atom, and a methyl group (-CH₃).</p>
Leaching...loss antioxidants, fillers, heat stabilizers, plasticizers due to solvent permeation,	Loss of plasticizers from polymer matrix
Plasticization...loss in mechanical properties	Potentially affecting strength and integrity of the non-metal matrix,

Risk Factors for Non-metals

- Symptoms of polymer incompatibility,
 - Discoloration
 - Swelling
 - Degradation
 - Elongation/Creep
 - Softening / Jellying
 - Embrittlement
 - Delamination



Courtesy: Ernest M. Roggelin, FDEP/UST, Lustline #47

Ultra Low Sulfur Diesel

- Composition / Feedstocks
 - Desulfurization of diesel feedstock
 - Hydrotreatment,
 - Hydrocracking,
- Benefits / Comments:
 - Lower sulfur content (= 15 ppm)
 - Better for the environment,
 - ULSD will allow newer emission control systems on diesel engines to perform more efficiently,



Ultra Low Sulfur Diesel

- Potential Issues and Concerns:
 - Severity in the desulfurization of feed stock:
 - Potential reduction in aromatics by ring opening
 - Problems with elastomers not likely,
 - Higher percentage of n-alkanes (linear molecules) will increase problems with microbial contamination.
 - Lubricity issues resulting from desulfurization:
 - Corrected with synthetic esters or biodiesel (B1),

Ultra Low Sulfur Diesel

A Sampling of Generally Compatible Materials

- Metals
 - No known issues with existing system metals.
- Elastomers
 - Possible shrinkage of elastomers with the reduction of aromatics,
 - No other performance issues anticipated,
- Polymers
 - No known issues with existing system polymers.

Ultra Low Sulfur Diesel

A Sampling of Vulnerable Materials

- Metals
 - Copper and zinc should not be in contact with ULSD,
 - Both are oxidative catalysts and will accelerate the formation of sediment, gels and soaps (ASTM D975, Appendix X2.7.2)
- Elastomers
 - No known elastomer material issues.
- Polymers
 - No known issues with existing elastomers,

Biodiesel

- Composition/Feedstock
 - Feedstock vegetable oils, used grease, or animal fats.
 - Different fractions of FAME influence some of the properties of the fuel (e.g., saturated vs. unsaturated FAME),
- Benefits/Comments
 - No sulfur
 - Reduces need for foreign crude oil



Biodiesel

- Potential Issues and Concerns (B100):
 - B100 is a strong solvent and will release varnish and gums from diesel fuel tank walls and piping into the bulk fuel plugging in-line filters,
 - B100 can degrade, soften, seep through certain hoses, gaskets, seals, elastomers glues and plastics with prolonged exposure
 - Biodiesel retains more dissolved water 1200-2500 ppm,
 - Biodiesel not meeting ASTM D6751 can potentially damage equipment, plug filters, and shutdown vehicles,

Biodiesel – B100

A Sampling of Generally Compatible Materials

- Metals
 - Aluminum
 - Steels
- Elastomers
 - Fluorocarbon
 - PTFE
- Polymers
 - Fluorinated polyethylene
 - Fluorinated polypropylene
 - Polyamide
 - Fiberglass Reinforces Polymers.

Biodiesel – B100

A Sampling of Vulnerable Materials

- Metals
 - brass, bronze, copper, lead, tin, and zinc
 - Lead solders, zinc linings, copper pipes, brass regulators and copper fittings should be avoided,
- Elastomers
 - Buna-N
 - Nitrile Rubber
 - Natural rubber
 - Polyvinyl chloride
- Polymers
 - Polyethylene
 - Polypropylene
 - Polyvinyl chloride

Biodiesel – B20

A Sampling of Generally Compatible Materials*

- Metals
 - stainless steel,
 - carbon steel, or
 - Aluminum
 - Elastomers
 - Fluorocarbon
 - PTFE
 - Polymers
 - Fluorinated Plastics
 - Polyamide
 - Thermoplastics
 - Thermoset
- Most metals found in a retail dispensing facility

* *Strongly recommend consulting with UL or OEM*

Biodiesel – B20

A Sampling of Vulnerable Materials*

- Metals
 - brass, bronze, copper, lead, tin, and zinc
 - Lead solders, zinc linings, copper pipes, brass regulators and copper fittings should be avoided,
- Elastomers
 - Problems tend to diminish as biodiesel concentration decreases
- Polymers
 - Problems tend to diminish as biodiesel concentration decreases

* *Strongly recommend consulting with UL or OEM*

Biodiesel

Elastomers	Blend	Compared to Diesel
PTFE	B100	Little Change
Polyamide	B100	Little Change
Fluorocarbon	B100	Little Change
Nitrile	B100	Hardness ? - 20% : Swell ? - 18%
Fluorosilicone	B100	Hardness Neg. : Swell ? - 7%
Polyurethane	B100	Hardness Neg. : Swell ? - 6%
Polypropylene	B100	Hardness ? - 10% : Swell ? - 8-15%
Polyvinyl	B100-B30	Worse
Polyvinyl	B20 – B10	Comparable
Polyvinylchloride	B100	Worse

Biodiesel / Biodeterioration

- Other Important Issues and Concerns:
 - Biodiesel has a very favorable biodegradation profile
 - Aerobically, biodiesel will biodegrade in seven (7) days
 - Anaerobically, biodiesel will biodegrade in 14 days,
 - B100 can biodegrade 4 times faster than petroleum diesel
 - B20 can biodegrade twice as fast as petroleum diesel,

Biodiesel

Biodiesel Metabolism EPA Standard 560/6-82-003

CO₂ Evolution (%)

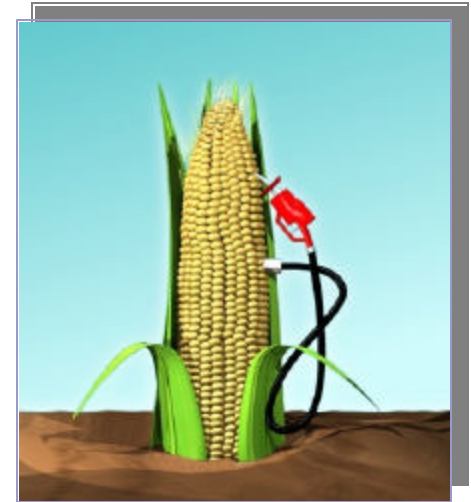
Days	Rape Ethyl Ester	Rape Methyl Ester	Soy Ethyl Ester	Soy Methyl Ester	Neat Rape	Neat Soy	#2 Diesel	Dextrose
0	0	0	0	0	0	0	0.00	0.00
7	69.01	66.32	67.68	68.4	58.39	60.57	13.20	59.84
14	79.15	80.72	78.40	77.83	70.47	70.12	21.04	80.19
28	86.92	88.49	86.40	85.54	78.45	75.95	26.24	87.79

Biodiesel

Cometabolism EPA Standard 560/6-82-003					
CO ₂ Evolution (%) From REE/Diesel Mixture					
Days	REE100	R80/D20	R50/d50	R20/D80	D100
0	0	0	0	0	0
7	64.09	52.33	37.85	25.24	2.08
14	77.51	61.26	45.74	31.59	2.08
28	84.37	67.82	51.90	35.67	14.96

Ethanol Blend E10

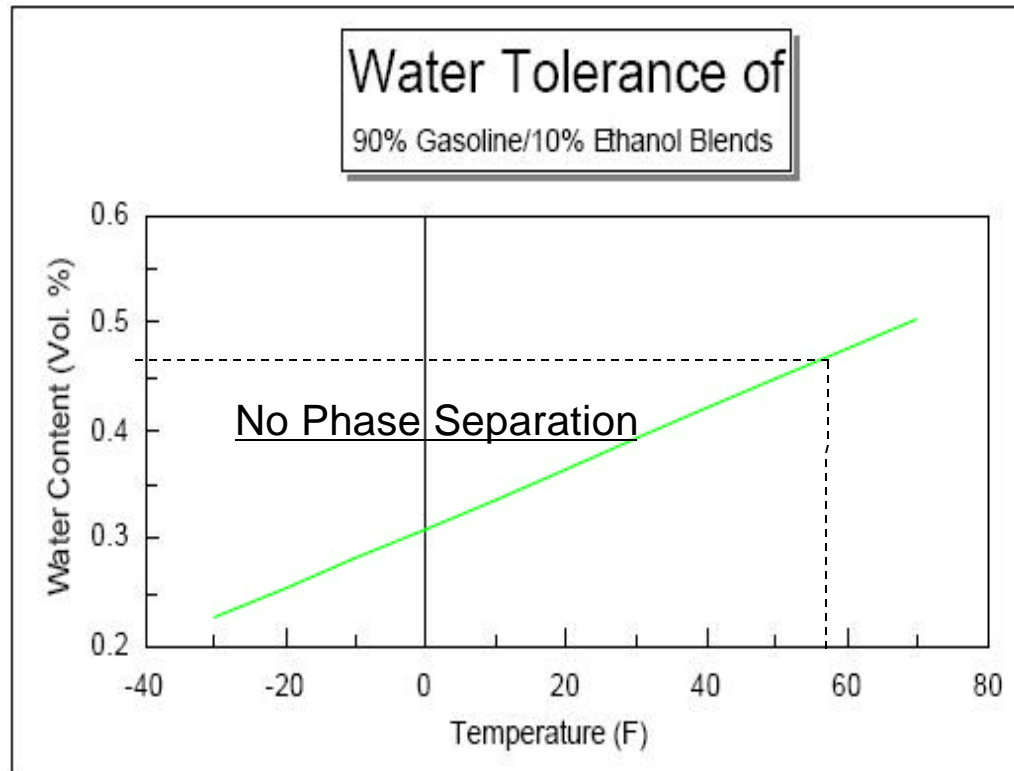
- Composition & Feedstock
 - 10% Ethanol/90% Unleaded gasoline
 - Sources of ethanol are:
 - Corn, Ethylene, Cellulose agricultural waste, starch, or sugar,
- Benefits / Comments:
 - Octane improver that replaced tetraethyl lead (TEL)
 - provides oxygen for more efficient burn of fuel
 - reduces tailpipe emissions/greenhouse gases,
 - Reduces our reliance on foreign oil



Ethanol Blends E10

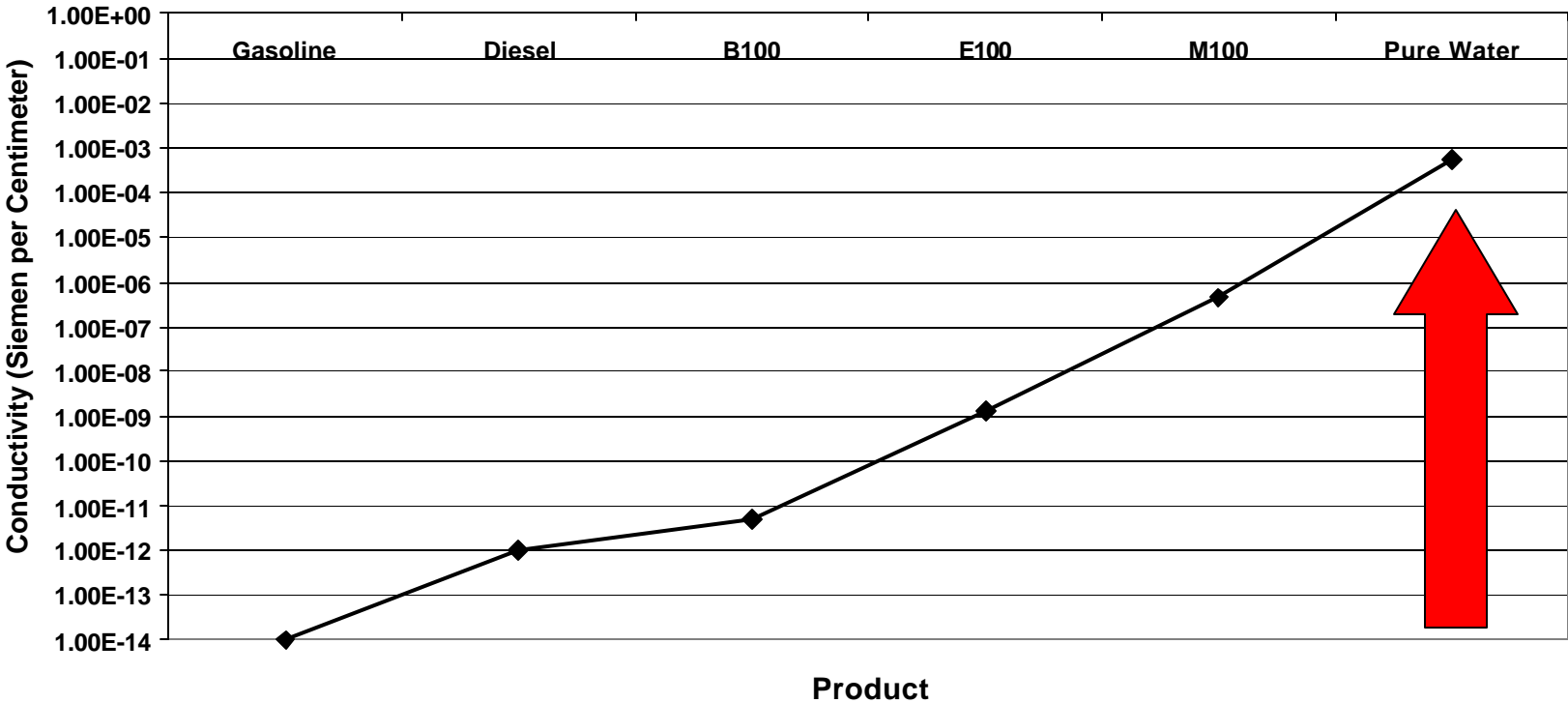
- Potential Issues and Concerns
 1. Phase Separation:
 2. Increased conductivity/corrosion
 3. Permeation
 4. Solvent Action

Phase Separation



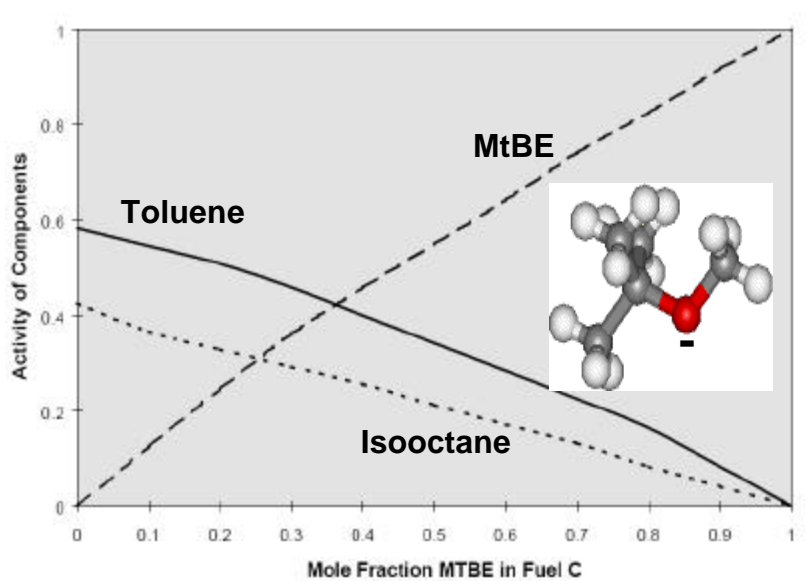
Conductivities of Various Fuels

Electrical Conductivity

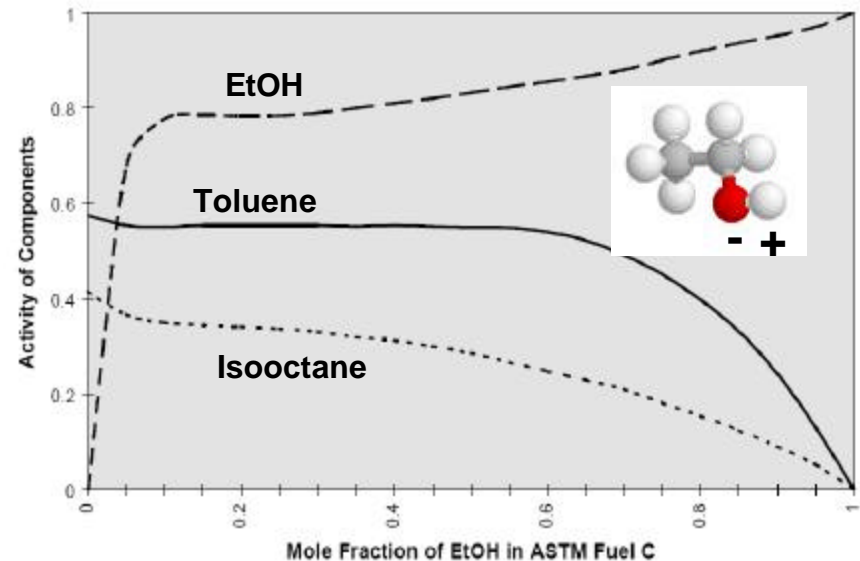


Ethanol Blends E10

Permeability Activity:



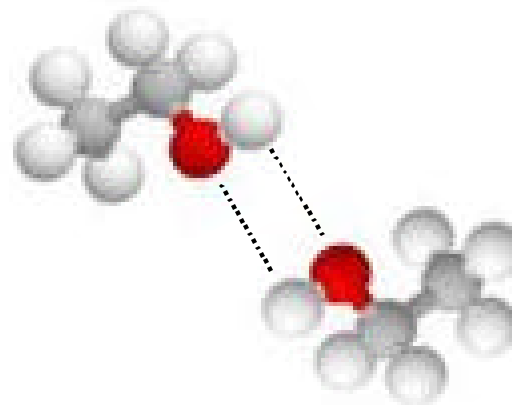
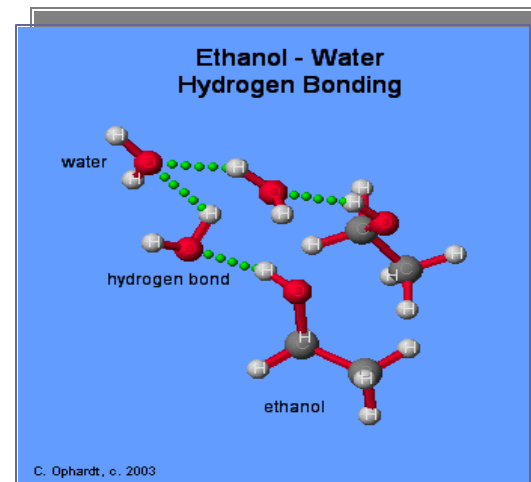
Activity of MtBE, Toluene, and Isooctane as a function of ether in ASTM Fuel C



Activity of EtOH, Toluene, and Isooctane as a function of ether in ASTM Fuel C

Solvation

- Polar Molecule
 - Soluble in water,
 - Hydrogen bonds with similar functional groups,
 - Can dissolve polar compounds,
- Non-polar polymer
 - Not soluble in water,
 - Can act like a non-polar compound or solvent,



Ethanol Blends E10

A Sampling of Generally Compatible Materials

- Metals
 - Aluminum,
 - Brass,
 - Bronze,
 - Carbon steel,
 - Stainless steel,
- Elastomers
 - Fluorocarbons
 - Fluorosilicone,
 - Buna-N (hoses & gaskets),
 - Natural rubber
 - Polychloroprene (hoses & gaskets),
 - Polysulfide rubber
- Polymers
 - Acetal
 - Polyamides
 - Polypropylene
 - PTFE
 - Thermoplastics
 - Thermoset

Ethanol Blends E10

A Sampling of Generally Vulnerable Materials

- Metals
 - Zinc-galvanized
- Elastomers
 - Buna-N (seals only),
 - Polychloroprene (seals only),
 - Urethane rubber
- Polymers
 - Polyurethane
 - Alcohol-based pipe dope

Ethanol Blends E10

- E10 blends have been in use for nearly three decades and most issues have been identified and corrected,
- In some instances, aged gasoline dispensing systems that are recently converted to E10 may see issues with:
 - Mechanical seals, Meters, Filters
 - Accelerated Corrosion
- Metals, elastomers, and polymers that are compatible with 100% MeOH or E85 should be certainly compatible with E10 fuel,

Ethanol Fuels E_d85

- Compositions & Feedstocks:
 - 75% - 85% Ethanol (EtOH) & 15% - 25% Unleaded gasoline
 - Formulation seasonally adjusted
- Benefits / Comments:
 - Reduces reliance on foreign oil
 - Environmental
 - provides oxygen for more efficient burn of fuel
 - significantly reduces tailpipe emissions and greenhouse gases (~60%),

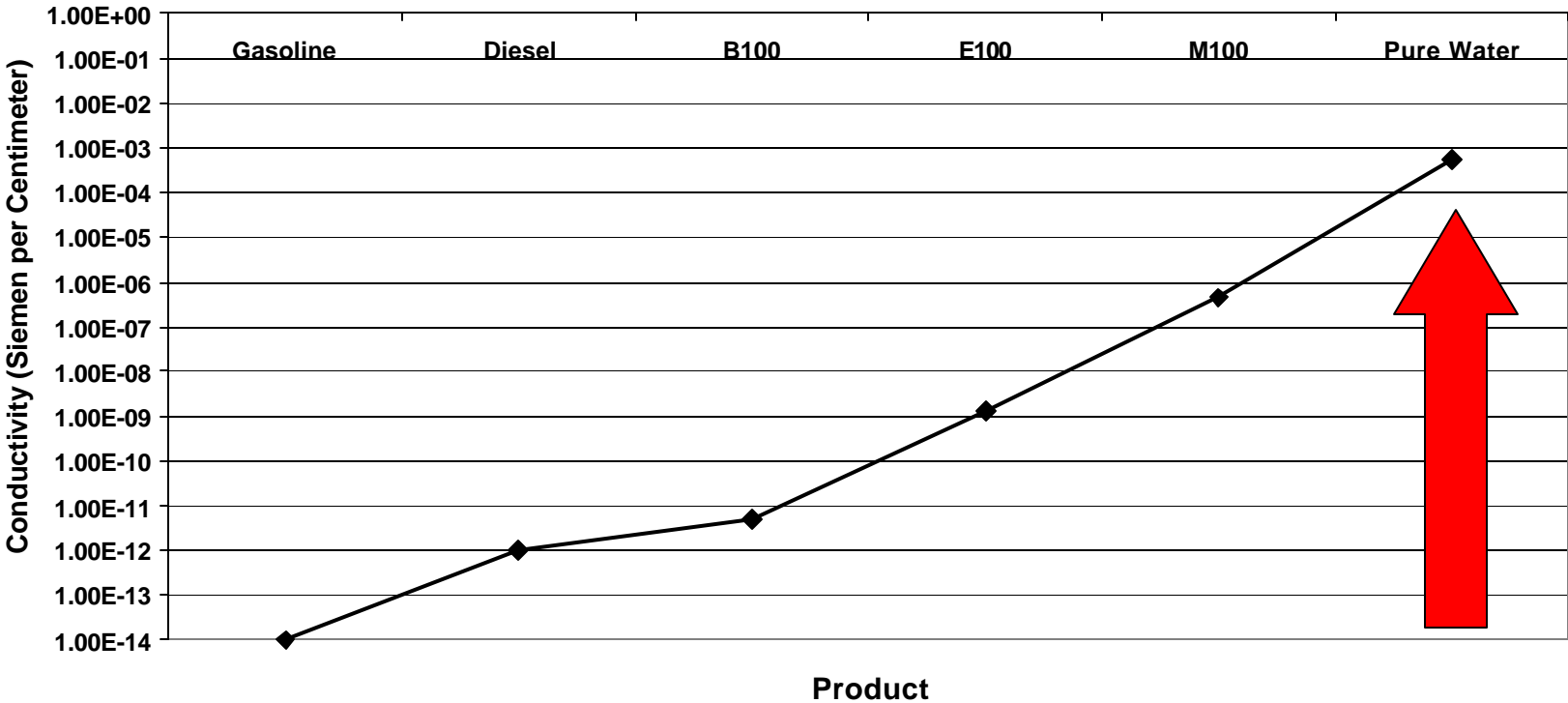


Ethanol Blends – E85

- Potential Issues and Concerns
 - Increased Conductivity
 - Solvent Action
 - Compatibility / Permeability
 - Phase Separation

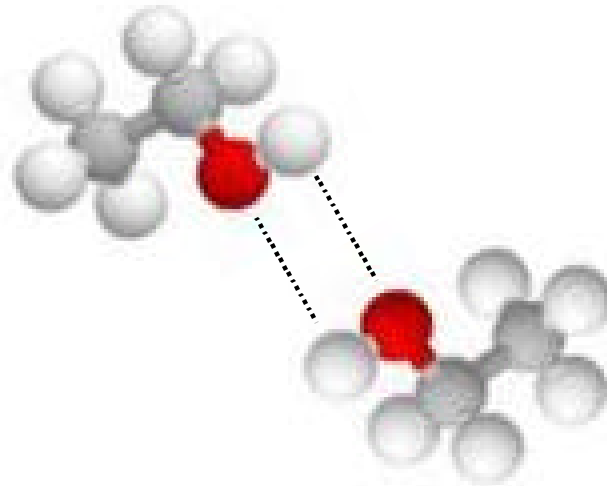
Conductivities of Various Fuels

Electrical Conductivity



Solvent Action

- Non-polar polymer
 - Not soluble in water,
 - Can act like a non-polar compound or solvent,



Ethanol Blends – E85

A Sampling of Generally Compatible Materials

- Metals*
 - Black Iron
 - Bronze
 - Mild steel
 - Stainless steel
 - Unplated steel
 - Nickel Plating for soft metals (i.e., aluminum)
- Elastomers
 - Buna-N (hose & gaskets)
 - Fluorocarbons
 - Nitrile Rubbers
 - Polychloroprene (hose & gaskets)
 - PTFE
- Polymers
 - Polypropylene
 - Thermoplastic piping*,
 - Thermoset reinforced fiberglass tanks*

*In the fuel path

*As listed by UL

Ethanol Blends – E85

A Sampling of Vulnerable Materials

- Metals
 - Aluminum
 - Brass
 - Copper Alloys
 - Lead
 - Lead Solder
 - Tern-plated steel (Fuel Tanks)
 - Zinc
- Elastomers
 - Buna-N (seals only)
 - Polychloroprene (seals only)
 - Natural rubber
 - Cork gasket material, *
 - Leather, *
- Polymers
 - Certain polyamides
 - Polyurethane,
 - Polyvinyl chloride,
 - Methyl-methacrylate,
 - Certain polymer liners*

***Epoxy and polyester resins manufactured between 1970's and 1980's**

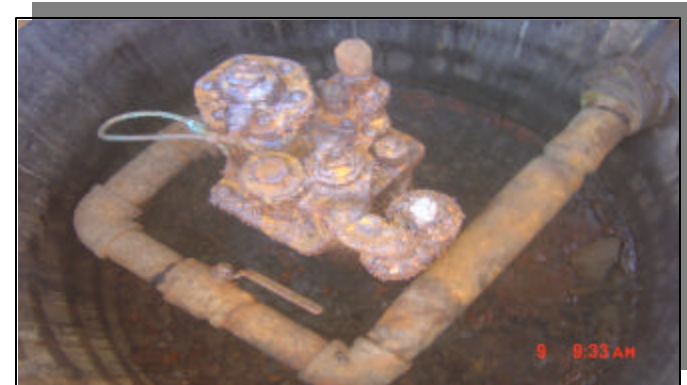
* Natural material not elastomer

Ethanol Blends – E85

- Potential Issues and Concerns:
 - Materials that are in continuous contact with E85 fuel,
 - Improper system inspection prior to conversion,
 - Certain metals and non-metals are vulnerable to corrosion or degradation due to E85,
 - Fuel filters with improper pore size or efficiency rating may allow dissolved contaminants from the UST and dispensing system to enter the vehicle fuel tank significantly compromising vehicle driveability,

E_d85- Example of Corrosion

- Same facility
- Same install date
- Top is E85 STP
- Bottom is standard non-E85 fuel STP



Photograph Courtesy of Rounds and Associates (Public Domain Information)

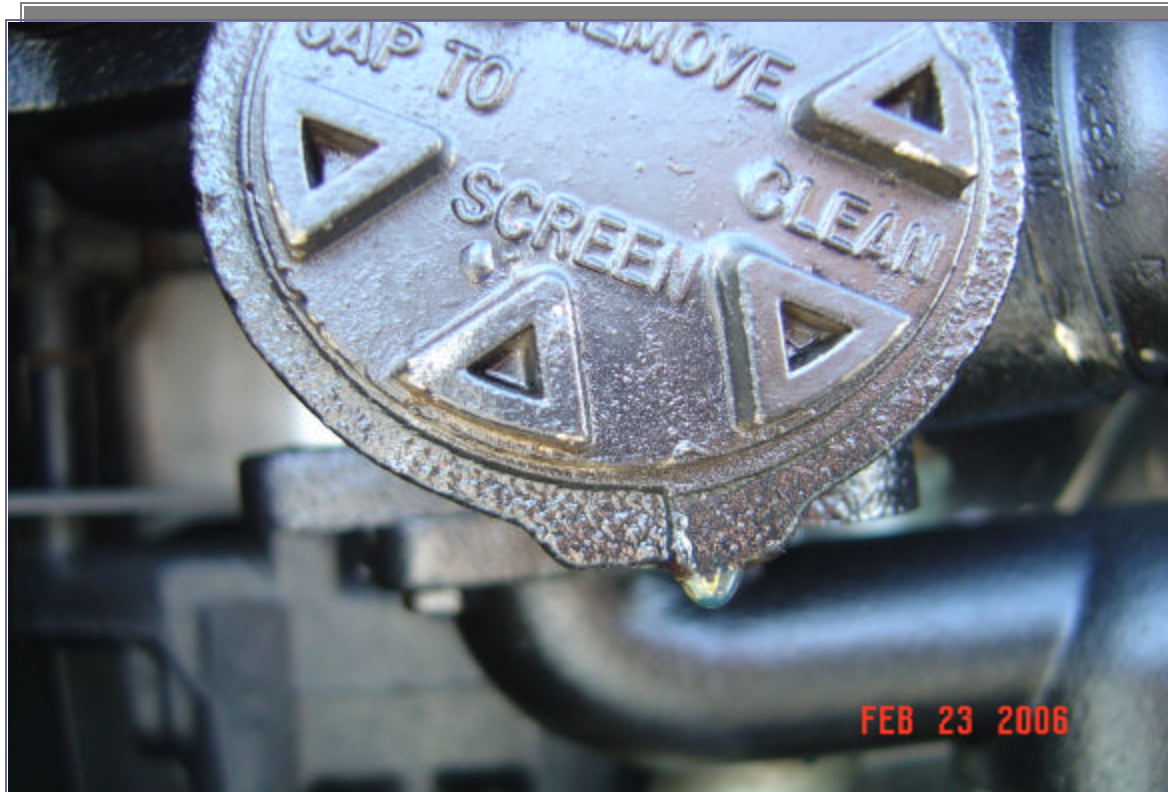
E_d85 – Vent Pipe Deterioration



Photograph Courtesy of Rounds and Associates (Public Domain Information)

9th Annual CalcUPA, Garden Grove, California, February 12-15, 2007

E_d85 - Seals and Gasket Leak



Photograph Courtesy of Rounds and Associates (Public Domain Information)

E_d85 - Catastrophic Failure



Photograph Courtesy of Rounds and Associates (Public Domain Information)

9th Annual CalcUPA, Garden Grove, California, February 12-15, 2007

Conclusion

Be Informed

Biomass BIODIESEL
Handling and Use Guidelines

DOE/GO-102006-2368
 Third Edition
 September 2006

U.S. Department of Energy
Energy Efficiency and Renewable Energy
Bringing you a prosperous future where energy is clean, abundant, reliable, and affordable

10. INFORMATION RESOURCES

The National Biodiesel Board has compiled an impressive library of online documents located at <http://www.biodiesel.org/resources/reportsdatabase/>. It can add detail to these guidelines. The search engine is set up by market segment. You have to be creative and use a variety of key words to search on specific non-market topics or call 1-800-841-5849 for information.

The U.S. Department of Energy has some technical documents located at http://www.eere.energy.gov/biomass/document_database.html.


The EPA has reviewed many emission reports and has summarized them at <http://www.epa.gov/OMS/models/biodiel.htm>.

Iowa State University has an online tutorial on biodiesel at <http://www.me.iastate.edu/biodiesel/Pages/biodiesell.html>. They also offer classes in biodiesel production, analytical test methods, and business management for producers and marketing firms.



Department of Defense A-A-59693A Biodiesel Commercial Item Description (CID) is located at <http://assist.daps.dla.mil/docimages/0004/29/73/AA59693.PDF> in PDF format.

Also contact your Clean Cities representative, biodiesel suppliers, and others for information.

Be Informed



Handbook for Handling, Storing, and Dispensing E85

For More Information

For More Information

General

U.S. Department of Energy
Alternative Fuels Data Center
E85 Fleet Toolkit
www.eere.energy.gov/afdc/e85toolkit/

National Ethanol Vehicle Coalition
33216 Emerald Lane, Suite C
Jefferson City, MO 65109
(573) 635-8445/Toll-free (877) 485-8595
www.e85fuel.com

National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401-3393
www.nrel.gov

Governors' Ethanol Coalition
P.O. Box 95085
Lincoln, NE 68509
www.ethanol-gec.org

National Corn Growers Association
632 Cepi Drive
Chesterfield, MO 63005
636-733-9004
www.ncga.com

Renewable Fuels Association
One Massachusetts Avenue, NW - Suite 820 W
Washington, DC 20001
202-289-3835
www.ethanolrfa.org/

U.S. Environmental Protection Agency
Office of Transportation and Air Quality
www.epa.gov/otaq/consumer/fuels/altfuels/altfuels.htm

Ethanol Fuel Codes and Safety

Alternative Fuels Data Center
E85 Fleet Toolkit
www.eere.energy.gov/afdc/e85toolkit/

National Fire Protection Association
1 Batterymarch Park
Quincy, Massachusetts 02169-7471
617-770-3000
www.nfpa.org

Standards

ASTM International
100 Bar Harbor Drive
West Conshohocken, PA 19428-2959
Publications and Customer Service
610-832-9500
www.astm.org

Society of Automotive Engineers
400 Commonwealth Drive
Warrendale, PA 15096-0001
724-776-4841
www.sae.org

Equipment

Petroleum Equipment Institute
Ethanol Compatible Equipment Guide
www.pei.org/e85/

Fiberglass Tank and Pipe Institute
11150 South Wilcrest Dr., Suite 101
Houston, TX 77099-4343
www.fiberglassstankandpipe.com/

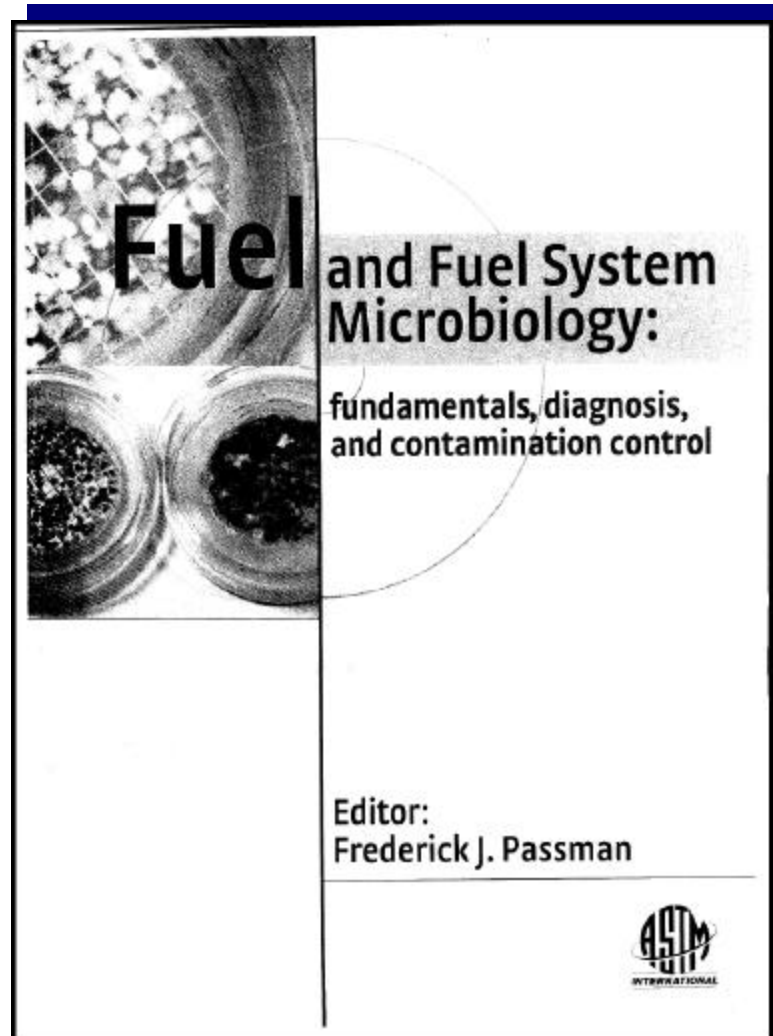
Flexible-Fuel Vehicles

Alternative Fuels Data Center
www.eere.energy.gov/afdc/afv/eth_vehicles.html
and
www.eere.energy.gov/afdc/e85toolkit/eth_vehicles.html

National Ethanol Vehicle Coalition
Flexible-Fuel Vehicle Listing
www.e85fuel.com/e85101/flexiblevehicles.php?topic=For%20Fleets

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Be Informed



Conclusion

Thank You