# ORNL
# Ethanol Pipeline Corrosion Literature Study

## Final Report

May 19, 2008

Oak Ridge National Laboratory

# ORNL Ethanol Pipeline Corrosion Literature Study Final Report

May 19, 2008

Prepared by

BCS

A woman-owned small business

# Acknowledgements

## Disclaimer

# Contents

# 1. Purpose of Search

Pipelines are essential to the nation’s fuel infrastructure and are the only economically feasible solution for widely distributed, large-scale transport of ethanol in the United States. Pipelines are systems for transportation of liquids (as in this case) or gases and consist not only of the actual pipes, but of gaskets, pumps, pump seals, valves, storage tanks, compression stations, mixing stations, and connected infrastructure. Thus corrosion in pipelines concerns not only the metals, metallurgy of pipes, and compatibility with other pipe materials, but also the general materials compatibility of all components in the system.

The ORNL Ethanol Pipeline Corrosion Study aims to provide a baseline on corrosion related to ethanol in pipelines. This Literature Study report was conducted to review and collect the current data on ethanol corrosion and compatibility for storage, transport, and use. The search topics covered pipelines, metals and non-metals exposed to ethanol and ethanol-related fuels, processing conditions, storage conditions, and use in vehicles. Documents were collected from universities, independent research labs, company labs, national organizations, and governments. The range of document types included reports, studies, presentation materials, books, press releases, brochures, and abstracts or references to the same.

## 1.1 Duration and Extent of Search

The search was carried out over three months and represents approximately 180 hours of labor for literature searching, identifying, and extracting information from 269 relevant documents and reports on materials that could be reasonably collected and reviewed in that timeframe.

# 2. Search Results

## 2.1 Materials Compatibility

Ethanol fuels can react adversely in a number of ways with polymers. Elastomers and thermoplastics are susceptible to permeation and swelling which can result in leaks and failure (due to brittleness or stiffening). Swelling of up to 20% can occur, affecting strength by 60%. Materials with alcohol-based components can experience leaching. Fluoroelastomers are often cited as being more resistant to these problems, but have also experienced low temperature failures due to stiffness.

Ethanol and metals react in a completely different way. Permeability and swelling are not problems, but erosion and corrosion are. A variety of corrosion effects can occur in metals in contact with ethanol solutions; these include dry, wet, galvanic, and electrolytic corrosion, stress corrosion cracking, erosion-corrosion, and other effects from time, temperature, and contaminants/additives.

Dry corrosion (corrosion with no water present) of metal in ethanol is proposed to occur naturally in the presence of oxygen and generates water as a by-product; thus dry corrosion and the eventual presence of water may be unavoidable in ethanol environments.

Water in small amounts (0.1 to 0.2 percent) can have a passivating effect on ethanol systems, but in larger concentrations it enables other corrosion mechanisms and problems including most of the non-dry corrosion mechanisms. Also, the effects in the various gasoline/ethanol blends are not well understood. Electrolytic corrosion is not a problem associated with gasoline because it is not conductive even when water is present, but it is a problem with ethanol. Increasing absolute amounts of water increases conductivity and increases the potential for electrolytic corrosion.

Galvanic corrosion (starting when conductivity is as low as 40-70 microsiemens per meter) is a major concern because a variety of metals are used in typical station designs. These designs were generally made for gasoline dispensing, and since gasoline is not conductive, galvanic corrosion was not considered. The presence of water in ethanol makes this type of corrosion a problem.

Above the concentration where water passivates the metal, two adverse reactions occur. Increased conductivity is the first. The second averse reaction comes in ethanol-gasoline blends, at high enough concentrations (approximately 0.5% in E10) the water and ethanol bond and can phase separate from the rest of the gasoline over time. The gasoline phase will be alcohol-poor and the ethanol phase will be water-rich. This separated aqueous phase causes wet corrosion. This is typically seen at the bottom of storage vessels. But even before the phase separation point is reached, corrosion in the solution can be enhanced because of micro-domains of precipitated aqueous ethanol.

Stress corrosion cracking (SCC) depends strongly on tensile stresses in the metal as a result of residual stresses (from forming or working methods) or active stresses from operation. This is probably the most studied of corrosion mechanisms related to ethanol. SCC can be a major problem in pipelines due to the cyclical pressure from pumping, often seen around compression stations. SCC is also seen in other pipeline sections where tensile stress is present. The presence of oxygen has been found to be the key factor in ethanol-related SCC. Ethanol purged of oxygen doesn't exhibit SCC even in the presence of aggressive species in excess of ethanol standard concentrations.

Erosion-corrosion is a concern because in addition to the corrosive mechanisms above, ethanol is recognized as a strong scouring agent. It will remove built-up materials in the storage vessels or pipelines.

If these vessels were used previously for other fuels, or are not properly maintained, there will be a large amount of such built-up contaminants. The scouring action, plus corrosion, plus flowing ethanol produces strong erosion-corrosion potential.

Time is a consideration for ethanol-related materials compatibility, because even though general corrosion rates in ethanol have been measured to be slow, localized corrosion has been seen to cause failure in only a short time. Increased temperature accelerates corrosion processes, and the high temperatures of ethanol combustion produce byproducts (acids, etc.) that are especially reactive. Combustion-related corrosion is not a problem in transport and storage, but rather when ethanol is in use as a fuel or fuel mixture.

Finally, the last major factor in ethanol corrosion mechanisms is contaminants. The most important contaminants for ethanol-related corrosion are water (covered above), oxygen, and ions. Ions include chloride, sulfide, $H^+$ (affecting pH), and metal ions. These contaminants can leach into the system (for example, at a failure point in an underground pipe), can contaminant the system at ports or seals where the ethanol enters or exits, can be scoured from the pipes and storage facilities, or can be the result of chemical reactions. Additionally, because ethanol is produced from a variety of complex, organic sources, and because of the complexity of processing, there are a large number of micro-contaminants that can be found in the ethanol batch straight from the production facility. The number and concentration of components vary from batch to batch even within the same facility. These components are not specified or limited by current ethanol standards, but like the other contaminants have the potential to greatly affect solution chemistry and corrosion potential. While some facilities and researchers have experience with these micro-contaminants, they have not been recognized or studied as extensively as other ethanol-related corrosion factors.

## 2.2 Compatibility Suggestions

| | **Avoid** | **Preferred** |
|---|---|---|
| **Non-metals:** | natural rubber, elastomers, resin-bonded or resin-sealed materials, epoxy, cork, leather, PVC, polyamides, methyl-methacrylate plastics, and some thermoplastic and thermoset polymers | fluoroelastomers (in some cases), urethane coatings (may be suitable for splash protection but not long-term immersion), ethylene acrylic acid polymer coatings, nylon (for low temp applications), thermoplastics as hose liners, ceramics, thermoset reinforced fiberglass, thermoplastic piping, Buna-N, Neoprene rubber, polypropylene, nitrile, Viton, and Teflon |
| **Metals:** | tin/lead coatings or plates (terne), zinc or zinc alloys, cast-iron, magnesium, lead, bare aluminum, copper, pure brass, galvanic contact between stainless steel and Al6061 or Al319, galvanic contact between cast iron and Al6061 or Al319, and lead-based solder | pure tin, cadmium-brass, iron-cobalt alloy, carbon steel, stainless steel, bronze, nickel plate, pre-painted zinc-nickel, and cadmium plate |
| | **Notes** | |
| **Ethanol:** | The most important components that should be monitored or controlled are oxygen, chloride and other ions (including sulfides, metal ions, and H+), and water. | |

| | |
|---|---|
| **Other:** | Fuel tank electrical connections may require sealed connections and the use of water resistant grease.<br>Cathodic polarization is a potential protective measure, but sacrificial anodes are unacceptable due to increased contaminants in the fuel.<br>Keep fluid cavities full eliminating air, design meters to keep them “flushed”. |

# 3. Conclusion

Materials compatibility of ethanol is not a simple issue. The non-metals compatibility issues are fairly well understood, being mostly permeation, swelling, and leaching. Prediction of the swelling and permeation potential is progressing, looking at dependence on the volatility and molecular size of the components; though much work remains to be done in finding reliably resistant materials. Ethanol related corrosion of metals is a much more complicated issue. At least five corrosion mechanisms, plus erosion-corrosion, have been documented. Corrosion in ethanol, like corrosion elsewhere, involves a number of factors including the numerous chemical and electrochemical properties of the ethanol solution, the presence of contaminants (most importantly oxygen, water, and ions), the metals, coatings, use and maintenance history of the systems, the design of the systems, how long the ethanol stays in the system, whether the ethanol is flowing or stationary, and the chemical reactions the ethanol undergoes when exposed to all of these.

Despite the apparent wealth of related documents, much of which is scientific in nature, there isn't a strong body of knowledge about the specific needs of this topic; hence the existence of this ethanol pipeline corrosion project. The most important documents can be broken down into the following categories: case studies of corrosion failures in pipelines, vessels, or end use; surveys using self-reported corrosion failures; corrosion studies of iron or steel in methanol solutions; corrosion studies of the effects of sulphates, oxygen, water, or chlorides; ethanol and SCC of pipelines and vessels; and, ethanol or methanol and automotive applications.

The case studies provide valuable information on a single failure and a single system but don't provide systematic tools. The surveys don't cover all failures, provide mostly statistical information, and rarely go into the material and electrochemical issues of the failures. The specific studies of corrosion of iron and steel have mostly involved methanol and rarely consider the larger variety of potential metals. Studies focusing on contaminants, while extremely productive, generally focus on those chemicals known to cause or affect corrosion and don't consider the variety of other ethanol micro-contaminants. Studies of ethanol and SCC form a large part of current research but don't address other equally problematic corrosion issues. Studies involving automotive systems provide good information on specific failures and deal with a variety of materials, but most can't speak to specific pipeline or storage issues.

Basically, the science is not developed enough nor experience widespread enough for these corrosion issues to be considered well understood. Because of this lack of knowledge (and some lack of need until now) there are no standards for ethanol transportation, storage, and dispensing as have been developed for other fuels. Much research will have to occur to fill in the gaps of knowledge, and based on the industry's mandates, a lot of that information will have to come rapidly through practical experience.

# 4. Summary of Search

## 4.1 Methods and Procedures

The search was composed of two main activities: a general internet search and a technical publication search (both electronic documents and hardcopies). The internet search used Google and site-specific search engines to find articles, reports, proceedings, presentations, and other documents related to the topic. The technical publication search included electronic databases of periodicals, books, proceedings, and announcements. The libraries of the University of Maryland at College Park (McKeldin and Engineering and Physical Sciences) were also used to obtain copies of documents not electronically available. Additionally, after a cursory review of the documents, relevant references were specifically added to the search. The electronic resources that were of the most help were Science Direct (full text journal articles), Engineering Village 2 (with Compendex and Inspec databases providing full text or abstracts), and CSA Illumina (100 databases from CSA and partners), and the ASTM Standards Database.

### 4.1.1 Keywords

A number of keywords were used either as search terms or to find relevant infomation within the identified documents. These keywords included:

azeotrope
batch composition
cathodic protection
closed loop venting
corrosion potential
deaeration
denaturant
di-ethyl amine (DEA)
discrete batching (in pipelines)
distillation column
electrical conductivity
ethanol
ethyl alcohol
gasoline blending
heat affected zone
hydrazine
hydrogen embrittlement
inhibitors
methanol
methyl alcohol
molecular sieve (zeolites)
organic components (micro-organic)
oxygen content
oxygen solubility in ethanol
pH (and acidity)
phase separation
pipeline
pitting corrosion
pipe weld heat treatment (PWHT)
scavengers
simulated fuel-grade ethanol (FGE)
standard inhibitor (e.g. Octel DCL-11)
steel (stainless)
stress corrosion cracking (SCC)
terne metal
water content (dewatering)
welding

### 4.1.2 Web Resources

The following is a list of web resources that were either reviewed in the search or are likely to contain additional relevant information:

- Allegheny Technologies Inc. (www.alleghenytechnologies.com/)

- Alternative Fuels Data Center (www.eere.energy.gov/afdc)
- American Coalition for Ethanol (www.ethanol.org)
- American Petroleum Institute (www.api.org)
- ASTM (www.astm.org)
- CSA Illumina/Proquest (www.csa.com/)
- DOE/EERE (www.eere.energy.gov/afdc/)
- E10 Unleaded (www.e10unleaded.com)
- Engineering Village 2 (www.engineeringvillage2.org)
- Ethanol Across America (www.ethanolacrossamerica.net)
- Ethanol Producers and Consumers (www.ethanolmt.org)
- Governor's Ethanol Coalition (www.ethanol-gec.org)
- IL-DECO (www.illinoisbiz.biz/com/energy/alternate.html)
- Illinois Corn Growers (www.ilcorn.org)
- Indiana IDEM document database (www.in.gov/apps/idem/media/publications)
- InterCorr (www.intercorr.com/, bought by Honeywell)
- Iowa, Ethanol Resources (www.iowarfa.org/resources_ethanol.php)
- Magellan Midstream Partners (www.magellanlp.com/)
- Minnesota Corn Growers (www.mncorn.org)
- NACE International (http://web.nace.org/)
- NASEO (www.naseo.org/)
- National Corn Growers Association (www.ncga.com)
- National corn to ethanol research center (www.siue.edu/ethanol)
- National Ethanol Vehicle Coalition (www.e85fuel.com)
- National Renewable Energy Laboratory (www.nrel.gov/)
- OSTI (www.osti.gov/bridge)
- Pipeline Research Council International (www.prci.org/)
- Renewable Fuels Association (www.ethanolrfa.org)
- Science Direct (www.sciencedirect.com)
- Sulzer Pumps (www.sulzerpumps.com/desktopdefault.aspx)
- Underwriters Laboratories Inc. (www.ul.com/)

## 4.2 Documents Reviewed

269 documents were identified and/or reviewed in the search:

- 108 were full text articles,
- 40 were abstracts to articles,
- 26 were full text reports,
- 39 were abstracts to reports,
- 12 were presentations,
- 30 were references to documents,
- 3 were standards, and
- 11 were a variety of miscellaneous types.

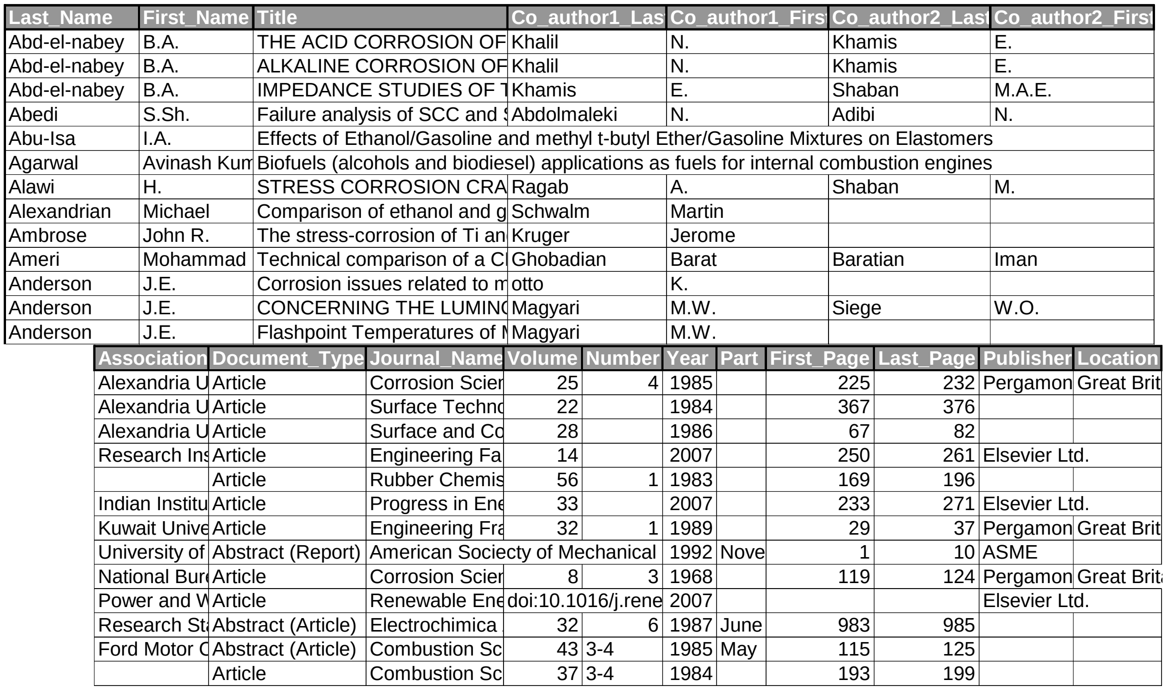
All documents collected in the search were reviewed and evaluated on their general relevance to the search. Each document was given a rating of 0-3 with: 0 being of no relevance, 1 of low relevance, 2 of moderate relevance, and 3 of highest relevance. Documents that received no rating were generally those that were only available as references (pulled from other documents) where not even their titles were available. Using this rating scheme:

- 34 documents were rated a 3,
- 45 rated a 2,
- 84 rated a 1,
- 75 rated a 0, and
- 31 have no rating.

A database was created to hold and organize the document data. The database includes two categories of information. The bibliographical information includes the authors' and co-authors' names, titles, authors' affiliations, publication name, volumes, numbers, dates, page numbers, publication location, publication organization, and ISSN or ISBN. The non-bibliographic information includes the document types (article, report, abstract, presentation, reference, etc.), funding sources, abstracts, relevance ratings, file names, web links, key words, and a place for validity ratings (expert ratings of the validity of the science/methods in the document in question or the reliability of the source). A second table contains more non-bibliographical information including a summary of each document (with key ethanol and corrosion data and conclusions), as well as references cited from the summarized portions of the document. Summaries note when documents aren't relevant to the search. All documents collected in the search are included in the database, even those which receive a 0 relevance rating, in order to assist later researchers in eliminating those documents from future search and review. The information was entered into Excel for easy conversion to Access or similar programs with standard database functions.

## 4.3 Database Sample

Below is a sample of the first 13 entries from the database:



| Last_Name | First_Name | Title | Co_author1_Las | Co_author1_Firs | Co_author2_Last | Co_author2_First |
|---|---|---|---|---|---|---|
| Abd-el-nabey | B.A. | THE ACID CORROSION OF | Khalil | N. | Khamis | E. |
| Abd-el-nabey | B.A. | ALKALINE CORROSION OF | Khalil | N. | Khamis | E. |
| Abd-el-nabey | B.A. | IMPEDANCE STUDIES OF T | Khamis | E. | Shaban | M.A.E. |
| Abedi | S.Sh. | Failure analysis of SCC and S | Abdolmaleki | N. | Adibi | N. |
| Abu-Isa | I.A. | Effects of Ethanol/Gasoline and methyl t-butyl Ether/Gasoline Mixtures on Elastomers | | | | |
| Agarwal | Avinash Kum | Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines | | | | |
| Alawi | H. | STRESS CORROSION CRA | Ragab | A. | Shaban | M. |
| Alexandrian | Michael | Comparison of ethanol and g | Schwalm | Martin | | |
| Ambrose | John R. | The stress-corrosion of Ti an | Kruger | Jerome | | |
| Ameri | Mohammad | Technical comparison of a Cl | Ghobadian | Barat | Baratian | Iman |
| Anderson | J.E. | Corrosion issues related to m | otto | K. | | |
| Anderson | J.E. | CONCERNING THE LUMINO | Magyari | M.W. | Siege | W.O. |
| Anderson | J.E. | Flashpoint Temperatures of M | Magyari | M.W. | | |

| Association | Document_Type | Journal_Name | Volume | Number | Year | Part | First_Page | Last_Page | Publisher | Location |
|---|---|---|---|---|---|---|---|---|---|---|
| Alexandria U | Article | Corrosion Scier | 25 | 4 | 1985 | | 225 | 232 | Pergamon | Great Brit |
| Alexandria U | Article | Surface Technc | 22 | | 1984 | | 367 | 376 | | |
| Alexandria U | Article | Surface and Co | 28 | | 1986 | | 67 | 82 | | |
| Research Ins | Article | Engineering Fa | 14 | | 2007 | | 250 | 261 | Elsevier Ltd. | |
| | Article | Rubber Chemis | 56 | 1 | 1983 | | 169 | 196 | | |
| Indian Institu | Article | Progress in Ene | 33 | | 2007 | | 233 | 271 | Elsevier Ltd. | |
| Kuwait Unive | Article | Engineering Fra | 32 | 1 | 1989 | | 29 | 37 | Pergamon | Great Brit |
| University of | Abstract (Report) | American Sociecty of Mechanical | | | 1992 | Nove | 1 | 10 | ASME | |
| National Bur | Article | Corrosion Scier | 8 | 3 | 1968 | | 119 | 124 | Pergamon | Great Brit |
| Power and W | Article | Renewable Ene | doi:10.1016/j.rene | | 2007 | | | | Elsevier Ltd. | |
| Research St | Abstract (Article) | Electrochimica | 32 | 6 | 1987 | June | 983 | 985 | | |
| Ford Motor C | Abstract (Article) | Combustion Sc | 43 | 3-4 | 1985 | May | 115 | 125 | | |
| | Article | Combustion Sc | 37 | 3-4 | 1984 | | 193 | 199 | | |

| Funding | Description | Abstract | File_Name | Web_Link | Key_words | Relevance | Validity | ISSN |
|---|---|---|---|---|---|---|---|---|
| University of Alexandri |  | The corro | abd-el-nabe | www.elsevier.com/locat |  | 2 |  |  |
| University of Alexandri |  | The corro | abd-el-nabey b.a. 2.pdf |  |  | 2 |  |  |
| Egyptian Government |  | Selected | abd-el-nabey b.a. 3.pdf |  |  | 0 |  |  |
|  |  | In April 20 | abedi s.sh.p | www.elsevi | API 5L X52; | 1 |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  | The incre | agarwal a.k. | www.elsevi | Biofuels; Alc | 3 |  |  |
| Environment Protectio |  | Stress co | alawi h.pdf | www.elsevier.com/locat |  | 1 |  |  |
|  |  | The objec | alexandrian m. abstract.doc |  |  | 0 |  |  |
| ain |  | An investi | ambrose j.r.pdf |  |  | 1 |  |  |
|  |  | The effec | ameri m.pdf |  | Bioethanol; | 0 |  |  |
|  |  | Methanol | anderson j.e. abstract.doc |  |  | 2 |  |  |
|  |  | Luminosit | anderson j.e. 2 abstract | FLAME RES |  | 0 |  | ISSN: 0010-2202 |
|  |  | Experime | anderson j.e | www.informaworld.com |  |  |  |  |

# 5. Alphabetized List of Most Relevant References

There are 34 documents of highest relevance 3. See Appendix A for full summary information.

1. Agarwal, Avinash Kumar, Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines, Progress in Energy and Combustion Science, vol. 33, 2007, pp. 38, Elsevier Ltd.
2. ASTM Standard D4806-07, Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel
3. ASTM Standard D1152-06, Standard Specification for Methanol (Methyl Alcohol)
4. ASTM Standard D304-05, Standard Specification for n-Butyl Alcohol (Butanol)
5. Bellucci, F., The Behaviour of Iron and Low Alloy Steels in Anhydrous Organic Solvents – Methanolic Solutions, Corrosion Science, vol. 28, no. 4, 1988, pp. 13, Pergamon Press Plc.
6. Bologna, D.J., Corrosion consideration in design of automotive fuel systems, SAE Technical Paper Series, no. 780920, 1978, SAE
7. Bravinder, Jennifer L., State Water Resources Control Board's Advisory Panel on the Leak History of New and Upgraded UST Systems: Oxygenate Compatibility and Permeability Report, California State Water Resources Control Board, 1999
8. Brossia, C. Sean, The Effects of Impurities on the Corrosion Behavior of Iron in Methanolic Solutions, SAE Technical Paper Series, no. 932342, 1993, pp. 10, Society of Automotive Engineers
9. Brossia, C. Sean, The Electrochemistry of Iron in Methanolic Solutions and Its Relation to Corrosion, Corrosion Science, vol. 37, no. 9, 1995, pp. 16, Pergamon
10. Cavalcanti, E., The effect of water, sulphate and pH on the corrosion behaviour of carbon steel in ethanolic solutions, Electrochimica Acta, vol. 32, no. 6, 1987, pp. 2
11. Cerquett, A., Electrochemical Behaviour and Stress Corrosion Cracking of Titanium in Alcoholic Solutions, Corrosion Science, vol. 13, 1973, pp. 12, Pergamon Press
12. de Anna, P.L., The Effects of Water and Chloride Ions on the Electrical Behaviour of Iron and 304L Stainless Steel in Alcohols, Corrosion Science, vol. 25, no. 1, 1985, pp. 10, Pergamon Press Ltd.
13. de Magalhaes Avelar, Heluza, Conductometric determination of total acidity and chloride content in automotive fuel ethanol, Fuel, vol. 86, 2007, pp. 3, Elsevier
14. Ethanol Fuel Dispensing Operations in Brazil, Underwriters Laboratories Inc., 2007
15. French, Raymond, Phase equilibria of ethanol fuel blends, Fluid Phase Equilibria, vol. 228-229, 2005, pp. 13, Elsevier
16. Galante-Fox, Julie, E-85 Fuel Corrosivity: Effects on Port Fuel Injector Durability Performance, SAE Paper, no. 2007-01-4072, 2007, SAE
17. Handbook for Handling, Storing, and Dispensing E85, no. DOE/GO-102006-2303, 2006, DOE
18. Hansen, Alan C., Ethanol-Diesel Blends: A Step Towards a Bio-based Fuel for Diesel Engines, ASAE Meeting, no. 01-6048, 2001, ASAE
19. Hansen, Alan C., Ethanol–diesel fuel blends—a review, Bioresource Technology, vol. 96, 2005, pp. 8, Elsevier
20. Identification, Repair, and Mitigation of Cracking of Steel Equipment in Fuel Ethanol Service, API Draft Standard, April 2007

21. Jeuland, N., Potentiality of Ethanol as a Fuel for Dedicated Engine, Oil & Gas Science and Technology, vol. 59, no. 6, 2004, pp. 11, Institut français du pétrole
22. Johnston, Robert L., Stress-Corrosion Cracking of Ti-bA1-4V Alloy in Methanol, NASA, no. TN D-3868, 1967, NASA
23. Kane, Russell D., Stress Corrosion Cracking of Carbon Steel in Fuel Grade Ethanol: Review, Experience Survey, Field Monitoring, and Laboratory Testing, Second Edition, API Technical Report 939-D, no. C939D2, 2007
24. Kane, Russell D., Summary of Activities on Ethanol SCC – Tanks and Facilities: Failure Documentation, Survey Results, Guidelines Development, Presentation, October 25, 2007, Honeywell
25. Miller, Ron, Production of Ethanol & Update on Ethanol Current Events, Presentation, April 10, 2001, Williams Bio-Energy (now Aventine REI)
26. Nie, X., Corrosion Behavior of Metallic Materials in Ethanol-Gasoline Alternative Fuels, Materials Science Forum, vol. 546-549, 2007, pp. 7, Trans Tech Publications
27. Otto, K., Corrosion Produced By Burning Layers of Methanol and Ethanol, Corrosion Science, vol. 26, no. 6, 1986, pp. 11, Pergamon Journals Ltd.
28. Otto, K., Steel Corrosion by Methanol Combustion Products, Corrosion Science, vol. 25, no. 2, 1985, pp. 14, Pergamon Press Ltd.
29. Sridhar, Narasi, Stress corrosion cracking of carbon steel in ethanol, Corrosion, vol. 62, no. 8, 2006, pp. 15, National Assoc. of Corrosion Engineers International
30. Sridhar, Narasi, Study examines ethanol pipelines for cracking potential, Materials Performance, vol. 46, no. 12, 2007, pp. 1
31. Sridhar, Narasi, Transportation of Ethanol through Pipelines –Presentation to PHMSA, November 2007, CC Technologies
32. Weiss, M.B., Gasohol successfully pipelined; care required to maintain ethanol content, Oil & Gas Journal, 1981
33. Westbrook, Paul A., Compatibility and Permeability of Oxygenated Fuels to Materials in Underground Storage and Dispensing Equipment, California State Water Resources Control Board, 1999
34. Wolynec, Stephen, Corrosion in Ethanol Fuel Powered Cars: Problems and Remedies, Proceedings - International Congress on Metallic Corrosion, 1984, pp. 6, Natl Research Council of Canada

# Appendix A. Summaries of the Most Relevant Documents

**Last Name:** Agarwal
**First Name:** Avinash Kumar
**Title:** Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines

**Source:** Progress in Energy and Combustion Science
**Vol.:** 33
**Year:** 2007

**File Name:** agarwal a.k.pdf

**Abstract:** The increasing industrialization and motorization of the world has led to a steep rise for the demand of petroleum-based fuels. Petroleum-based fuels are obtained from limited reserves. These finite reserves are highly concentrated in certain regions of the world. Therefore, those countries not having these resources are facing energy/foreign exchange crisis, mainly due to the import of crude petroleum. Hence, it is necessary to look for alternative fuels which can be produced from resources available locally within the country such as alcohol, biodiesel, vegetable oils etc.

This paper reviews the production, characterization and current statuses of vegetable oil and biodiesel as well as the experimental research work carried out in various countries. This paper touches upon well-to-wheel greenhouse gas emissions, well-to-wheel efficiencies, fuel versatility, infrastructure, availability, economics, engine performance and emissions, effect on wear, lubricating oil etc. Ethanol is also an attractive alternative fuel because it is a renewable bio-based resource and it is oxygenated, thereby providing the potential to reduce particulate emissions in compression-ignition engines. In this review, the properties and specifications of ethanol blended with diesel and gasoline fuel are also discussed. Special emphasis is placed on the factors critical to the potential commercial use of these blends. The effect of the fuel on engine performance and emissions (SI as well as compression ignition (CI) engines), and material compatibility is also considered.

Biodiesel is methyl or ethyl ester of fatty acid made from virgin or used vegetable oils (both edible and non-edible) and animal fat. The main resources for biodiesel production can be non-edible oils obtained from plant species such as Jatropha curcas (Ratanjyot), Pongamia pinnata (Karanj), Calophyllum inophyllum (Nagchampa), Hevca brasiliensis (Rubber) etc. Biodiesel can be blended in any proportion with mineral diesel to create a biodiesel blend or can be used in its pure form. Just like petroleum diesel, biodiesel operates in compression ignition (diesel) engine, and essentially require very little or no engine modifications because biodiesel has properties similar to mineral diesel. It can be stored just like mineral diesel and hence does not require separate infrastructure. The use of biodiesel in conventional diesel engines result in substantial reduction in emission of unburned hydrocarbons, carbon monoxide and particulate. This review focuses on performance and emission of biodiesel in CI engines, combustion analysis, wear performance on long-term engine usage, and economic feasibility.

**Review:**

- Section addresses materials compatibility in automobile engines (compression-ignition engines)

- Experience in Brazil:
  - a. The tin and lead coating of the fuel tank was changed to pure tin.
  - b. The fuel lines (zinc steel alloy) were changed to cadmium brass.
  - c. The valve housings, made of cast-iron, were changed to an iron-cobalt synthetic alloy. This also compensated for the lack of lubrication resulting from the absence of lead in the fuel.

- Brink et al. divided ethanol carburetor corrosion into three categories: general corrosion, dry corrosion and wet corrosion
- General corrosion was caused by ionic impurities, mainly chloride ions and acetic acid.
- Dry corrosion was attributed to the ethanol molecule and its polarity.
- Wet corrosion is caused by azeotropic water, which oxidizes most metals.
- Freshly formulated blends containing pH neutral dry ethanol would be expected to have relatively little corrosive effect.
- However, if a blend has been standing in a tank for sufficient time to allow the ethanol to absorb moisture from the atmosphere, it may tend to be more corrosive as it passes through the fuel injection system
- Elastomeric components such as seals and O-rings in the fuel injection system [are susceptible]. These seals tend to swell and stiffen.
- Resin-bonded or resin-sealed components also are susceptible to swelling and seals may be compromised.

**References:** a. Hardenberg HO, Ehnert, ER. Ignition quality determination problems with alternative fuels for compression ignition engines. SAE paper no. 811212, 1981.
b. Brink A, Jordaan CFP, le Roux JH, Loubser NH. Carburetor corrosion: the effect of alcohol–petrol blends In: Proceedings of the VII international symposium on alcohol fuels technology, vol. 26 (1), Paris, France, 1986. p. 59–62.

---

**Title:** Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel

**No.:** D4806-07

**File Name:** ASTM D4806-07.pdf

**Review:** • See document

---

**Title:** Standard Specification for Methanol (Methyl Alcohol)

**No.:** D1152–06
**Year:** 2006

**File Name:** ASTM D1152-06.pdf

**Review:** • See document

---

**Title:** Standard Specification for n-Butyl Alcohol (Butanol)

**No.:** D304–05
**Year:** 2005

**File Name:** ASTM D304-05.pdf

**Review:** • See document

---

**Last Name:** Bellucci
**First Name:** F.
**Title:** The Behaviour of Iron and Low Alloy Steels in Anhydrous Organic Solvents – Methanolic Solutions

**Source:** Corrosion Science
**Vol.:** 28
**No.:** 4
**Year:** 1988

**File Name:** bellucci f. 3.pdf

**Abstract:** The data supplied by electrochemical methods such as potentiodynamic polarization curves and potentiostatic anodic transients show that in methanolic solution a region of unstable passivity for Armco iron and Ni-Cr-Mo low alloy steels results from the overlapping of certain ranges of solution composition (e.g. acidity up to 10 -3 M as sulphuric acid, chlorides 10 -4 tO 10 -3 M, water 0.01-0.5%). Slow strain rate tests indicated that the instability of the protective oxide films can induce susceptibility to stress corrosion cracking in the presence of applied stresses.

**Review:**

- In methanolic solution a region of unstable passivity for Armco iron and Ni-Cr-Mo low alloy steels results from the overlapping of certain ranges of solution composition (e.g. acidity up to 10 -3 M as sulphuric acid, chlorides 10 -4 tO 10 -3 M, water 0.01-0.5%).
- Susceptible to stress corrosion cracking in the presence of applied stresses:
  (a) acidity as sulphuric acid 10 -4 M
  (b) chlorides 10-4-10 -3 M
  (c) water 0.01-0.5%.

- Passivity and water content:
  (a) Below 0.1%, water passivity cannot occur and the metal surface is in the active state. As a consequence, only general corrosion takes place.
  (b) Above 0.5%, passivity is stable and no corrosion can occur.

- Chloride-acidity combination is really a necessary condition for the occurrence of stress corrosion cracking
- Source document cuts off before end of conclusions

---

**Last Name:** Bologna
**First Name:** D.J.
**Title:** Corrosion consideration in design of automotive fuel systems

**Source:** SAE Technical Paper Series
**No.:** 780920
**Year:** 1978

**File Name:** bologna d.j. abstract.doc

**Abstract:** Metals, plastics, and rubber components are used effectively in the fuel system. This paper presents some of the material limitations and corrective measures required to minimize corrosion or materials degradation. For example, the use of zinc chromate coating, petroleum base coating, and/or polyurethane foam barriers may be required to minimize the effects of road de-icing salt and mud. Fuel tank electrical connections may require sealed connections and the use of water resistant grease. Zinc coated armor wire protection of the metal fuel lines and optimum material selection of the rubber components of the fuel lines are also discussed. New legislative proposals to add increasing amounts of alcohols to gasoline may dictate further materials design optimizations as suggested by a review of some selected references dealing with this subject.

**Review:**

- Some of the material limitations and corrective measures required to minimize corrosion or materials degradation
- Zinc chromate coating, petroleum base coating, and/or polyurethane foam barriers may be required to minimize the effects of road de-icing salt and mud
- Fuel tank electrical connections may require sealed connections and the use of water-resistant grease
- Zinc coated armor wire protection of the metal fuel lines and optimum material selection of the rubber components

---

**Last Name:** Bravinder
**First Name:** Jennifer L.
**Title:** State Water Resources Control Board's Advisory Panel on the Leak History of New and Upgraded UST Systems: Oxygenate Compatibility and Permeability Report

**Source:** California State Water Resources Control Board
**Year:** 1999

**File Name:** bravinder j.l.pdf

**Abstract:** Literature seach and company survey of ethers and alcohol compatibility in UST, focusing on corrosion and permeability of polymers, metals, ceramics, pipe dope, and organic coatings.

**Review:**

- Extensive literature search and survey of materials compatibility and underground storage tanks (UST)
- For both ethers and alcohols, greater permeability in gasoline blends is observed in elastomers (e.g., hoses, seals, gaskets, packing) than in thermoplastics (e.g., flexible piping, sumps, vapor recovery tubing).
- Only permeation standard applicable to UST systems is intended to ensure safe operation of the equipment, not necessarily environmental protection
- Gasoline, oxygenated or not, does not absorb into or permeate through metals: the phenomenon of permeation is, thus, limited to certain non-metals and will typically vary greatly depending on the material
- Considered tank, piping, turbine sump, fittings, dispenser pan and hoses, and vapor recovery equipment
- Nonmetallics classified: elastomers, thermoplastics, and thermosets
- Metals commonly found: steel, brass, aluminum, copper, and zinc
- Others: ceramics, pipe dope, and organic coatings

- Corrosion and pitting in metals:
  - a. Ethers: two studies on MTBE and one on ETBE - No strong corrosion threat
  - b. Alcohols: many studies
    - Six ASTM standards: ASTM G1, G31-95, G46-94, G71-81, G119-93, G133-95

        - Includes general and localized corrosion of active metals, galvanic corrosion, electrolytic corrosion, wear, and aqueous phase separation
        - Methanol with tertiary butyl alcohol mitigates some concerns

- Corrosion and pitting in non-metals:
    a. Ethers: swelling and retention of mechanical properties are primary concerns
        - No incompatibility up to 15% by volume
        - 20+%, swelling of flurorelastomers
    b. Alcohols:
        - ASTM C 581: chemical resistance for composites (thermosetting resins, etc.)
        - ASTM D 4021-92 and Underwriters Lab 1316: safety for glass-fiber-reinforced plastic USTs
        - UL 971: plastic pipe
        - UL 567: pipe connectors, hoses, and seals
        - Swelling of polymeric materials, alternatives available

- Permeability (non-metals):
    a. Methanol most permeable blend component
    b. No standard protocol for testing

- Compatibility and Permeability (others):
    a. Ceramics: no data showing corrosion, safe
    b. Pipe dope: subject to washing out by gasohol (some pipe dope contains alcohol)
    c. Organic coatings: gasohol extracts epoxy coatings, urethane-based coatings and ethylene acrylic acid polymer coatings recommended as superior

**References:** a. "Compatibility and Permeability of Oxygenated Fuels to Materials in Underground Storage and Dispensing Equipment: A Technical Assessment of the Literature circa 1975-1997," prepared by Paul A. Westbrook, Ph.D., Shell Oil Company, October 1998. [westbrook p.a.pdf]
b. "Oxygenate Compatibility/Permeability Survey," California Water Resources Control Board, April 21, 1998. [form only]

---

**Last Name:** Brossia
**First Name:** C. Sean
**Title:** The Effects of Impurities on the Corrosion Behavior of Iron in Methanolic Solutions

**Source:** SAE Technical Paper Series
**No.:** 932342
**Year:** 1993

**File Name:** brossia c.s. 2.pdf

**Abstract:** The electrochemical and corrosion behavior of metals in aqueous environments has received substantial attention. However, relatively little work has been devoted to the electrochemistry and corrosion of metals in non- aqueous environments. Now, with greater pressures to increase fuel efficiencies and decrease exhaust emissions, alternatives and additives to gasoline (including methanol and ethanol) are receiving increased attention from government agencies and automobile manufacturers. Unfortunately, fundamental studies of the corrosion behavior of metals in these solutions are scarce.

The objective of the present work is to investigate the electrochemical and corrosion behavior of iron in methanolic solutions containing Cl, H\u+, SO\d4\u2\u-, and H\d2O. To accomplish this, a full factorial design test matrix was developed to systematically evaluate the effects of these impurities on the corrosion behavior of iron. This test matrix enabled the determination of effects due to the impurities alone, as well as synergistic effects.

Corrosion testing of pure iron samples was performed using cyclic polarization measurements. Post-test surface morphology was evaluated with optical microscopy. Four main types of polarization behavior for iron in stagnant methanol were found, each dependent upon the nature of the aggressive species present (i.e. H\u+, Cl\u-, or both). It was also found that the pitting potential is decreased by 700 mV when 10\u-\u3M chloride was present. By increasing the acidity of the solution to 10\u-\u3M, the corrosion rate of iron increased by over 15 mpy. When the water content was increased, the corrosion rate tended to decrease. Pitting was the predominant form of corrosion attack observed in all tests.

**Review:**
- Study of the corrosion behavior of iron in methanol solutions containing various amounts of Cl-, H+, SO42-, or H2O
- Adding Cl- decreased the pitting potential (breakdown potential)
- Decreasing the pH to 10-3 M increased the corrosion rate by 15 mpy
- Adding just water decreased the corrosion rate
- Pitting was the leading type of corrosion seen
- Second order effects with water were more complicated

---

**Last Name:** Brossia
**First Name:** C.S.
**Title:** The Electrochemistry of Iron in Methanolic Solutions and Its Relation to Corrosion

**Source:** Corrosion Science
**Vol.:** 37
**No.:** 9
**Year:** 1995

**File Name:** brossia c.s.pdf

**Abstract:** The corrosion behavior of iron in methanol, its dependence on the presence of low levels of aggressive species, and an interpretation of these dependencies on the basis of the electrochemical reactions occurring have been determined. A quantitative analysis of the phenomenology of the corrosion behavior due to low (mM) levels of acid, chloride and sulfate has shown that the dominant first order effects are the increase in corrosion rate and elevation in corrosion potential due to the addition of acid. The dominant second order interaction between species is the inhibition of the acid effect on corrosion rate by the simultaneous addition of water. A study of the nature and kinetics of the cathodic reactions relevant to the corrosion of iron in methanol showed that inhibition of corrosion by water is primarily due to the decrease in the mobility of the proton with increasing water content. This inhibition of corrosion occurs by hindrance of the proton hopping mechanism due to preferential protonation of water vs methanol.

**Review:**
- Inhibition of corrosion by water is primarily due to the decrease in the mobility of the proton with increasing water content. This inhibition of corrosion occurs by hindrance of the proton hopping mechanism due to preferential protonation of water vs. methanol.
- Methanol has been found to be corrosive towards the materials used for fuel

tanks, lines and injectors, especially when contaminated with impurities such as acid, chloride and water.
- In accordance with the literature, it was found that acidity increases the corrosion rate of iron in methanol, and water inhibits the corrosion, with the largest degree of inhibition observed in acidified solutions.
- Most important effects observed are the large increases in corrosion rate and corrosion potential with the addition of 1 mM H+, and the inhibition of this effect by the addition of 0.5% water.
- Water is not electro-active in the potential range relevant to iron corrosion.
- The inhibition of iron corrosion by water is primarily due to the decrease in the mobility of H+ with increasing water content

**References:**

a. R.J. Lash, Proc. of the 6th Automotive Corrosion and Prevention Co& p. 153. Society of Automotive Engineers, Warrendale, PA (1993).
b. S.P. Davis, L.A. Roudabush and Y. Adonyi, Proc. of the 6th Automotive Corrosion and Prevention Conf., p. 427. Society of Automotive Engineers, Warrendale, PA (1993)
c. P.L. de Anna, Corros. Sci. 25, 43 (1985).
d. A Discussion of MB5 (85% Methanol) Fuel Specifications and their Significance, A Society of Automotive Engineers Cooperative Research Report, Society of Automotive Engineers, Warrendale, PA (1991).
e. F. Mazza, S. Torchio and N. Ghislandi, Int. Gong. on Metallic Corrosion, Vol. 1, p. 465. National Research Council of Canada, Ottawa (1984).
f. F. Bellucci, G. Capobianco, G. Faita, CA. Farina, G. Farina, F. Mazza and S. Torchio, Corros. Sci. 28, 371 (1988).
g. C.S. Brossia and R.G. Kelly, Proc. of the 6th Automotive Corrosion and Prevention Co, p. 173. Society of Automotive Engineers, Warrendale, PA (1993).

---

**Last Name:** Cavalcanti
**First Name:** E.
**Title:** The effect of water, sulphate and pH on the corrosion behaviour of carbon steel in ethanolic solutions

**Source:** Electrochimica Acta
**Vol.:** 32
**No.:** 6
**Year:** 1987

**File Name:** cavalcanti e.pdf

**Abstract:** The corrosion behaviour of carbon steel in ethanolic solutions containing different contents of water and sulphate has been investigated by corrosion immersion tests. The influence of pH has also been studied by adding different concentrations of sodium hydroxide to ethanolic solutions ( ethanol p.a. + water + sulphate). The results have shown the detrimental effect of water on the corrosive behaviour of the carbon steel electrodes, which have suffered localized attack in solutions with a water content 10% v/v and 4.8% v/v. Sulphate was also found aggressive to carbon steel, which showed no corrosion when immersed in ethanol p.a. In spite of the deleterious effect of these impurities, commonly found in ethanol fuels in Brazil, pH was found to be the most important factor in determining the corrosivity of ethanolic solutions. For carbon steels, a pH greater than 8.0 is required to guarantee corrosion immunity in solutions containing 1.0 mg1−1 SO2−4 and

4.8% v/v H2O

**Review:**
- Corrosion study of carbon steel in ethanol with additions of contaminants: water and suphate ions
- No corrosion seen in anhydrous ethanol
- Both additives caused increased corrosion
- Water showed corrosion at 4.8 vol %, and 10 vol %
- With water present, the addition of sulfuric acid increased the corrosion experienced
- With water and sulfuric acid present, no corrosion was seen when the pH was raised to 8.0 and 9.0 by the addition of sodium hydroxide
- Most important factor was the solution pH

---

**Last Name:** Cerquett
**First Name:** A.
**Title:** Electrochemical Behaviour and Stress Corrosion Cracking of Titanium in Alcoholic Solutions

**Source:** Corrosion Science
**Vol.:** 13
**Year:** 1973

**File Name:** cerquett a.pdf

**Abstract:** The electrochemical behaviour of titanium in neutral methanolic and ethanolic solutions containing chlorides, and corrosion tests performed with U-bend specimens in similar solutions, indicate that stress-corrosion phenomena occur on titanium when particular anodic and cathodic conditions are settled.

In neutral aerated ethanolic solutions the oxide film is stable and its electronic properties (ionic and electronic currents) are similar to the ones observed in aqueous solutions. Exception is made only for the breakdown potential. In ethanolic solutions, stress-corrosion occurs only in the presence of depolarizing species which can set mixed potentials more noble than the one characteristic of oxygen (i.e. FeCla).

Breakdown potential weakly depends on the chloride concentration, but the adsorption of chlorides on the oxide surface, in ethanolic solutions shifts the steady state potential of the metal to more active potentials so that, from the electrochemical point of view the more concentrated NaCI solutions, appear to be less effective in promoting stress-corrosion, the corrosion potentials settled at the higher Cl- concentrations, being less noble than the potentials settled at the lowest Cl- concentrations. In this case the role of C1- in the dissolution of titanium in ethanolic solution seems to be restricted to the formation of complex ions. The stability of titanium oxide films in methanolic solutions is very weak and, in the anodic sense, is restricted to a very narrow range of potentials. Presence of oxygen can create mixed potentials more noble than the breakdown potentials and thus the stress-corrosion occurrence.
The beneficial effect of cathodic polarization in neutral alcoholic environment can be due to the establishment of corrosion potential less noble than breakdown potential of the oxide film.

**Review:**
- Presence of oxygen can create mixed potentials more noble (anodic) than the breakdown potentials and thus the stress-corrosion occurrence.
- The beneficial effect of cathodic polarization in neutral alcoholic environment can be due to the establishment of corrosion potential less noble than breakdown potential of the oxide film.
- In general, the electron acceptor species in alcoholic solutions can play a double role: (i) they can ennoble the corrosion potential up to or over the breakdown potential; (ii) they can supply the cathodic reaction of the corrosion process.

---

**Last Name:** de Anna
**First Name:** P.L.
**Title:** The Effects of Water and Chloride Ions on the Electrical Behaviour of Iron and 304L Stainless Steel in Alcohols

**Source:** Corrosion Science
**Vol.:** 25
**No.:** 1
**Year:** 1985

**File Name:** de anna p.l.pdf

**Abstract:** The electrochemical behaviour of pure iron and 304L stainless steel in protic organic media has been characterized by determination of current-potential potentiodynamie curves. The media studied was methyl, ethyl, isopropyl, n-butyl and 2-chloroethyt alcohols. The influence of water and chloride ion concentration on the cathodic and anodic electrochemical reactions has been investigated. The presence of water, even at a very low concentration, strongly influences the passivation of iron in protic alcoholic solutions. The kinetics of the oxidation reactions, when water and/or chloride ions were present, are a function of the specific alcohol. This has been interpreted in terms of the different protic and stereochemistry properties of the alcohols considered.

**Review:**
- Iron passivates in all of the anhydrous alcohol media studied, with the exception of methanol.
- The water concentration at the metal-solution interface differs from the bulk. In principle, solvent mixtures of alcohol and water behave such that the less water-like alcohols (of lower dielectric constant) show a stronger dependency on water concentration. In these instances, the diffusion of water to the metal-solution interface is enhanced and therefore the passive film is more stable.
- Chlorides have a detrimental effect on corrosion in iron and 304L stainless steel, particularly for concentrations above 10 -3 and 10 -2 M, respectively.
- Additions of water to HCl-containing alcohols have a slightly passivating effect on iron in methanol, but are detrimental in higher and/or chioro-substituted alcohols.
- On 304L stainless steel, additions of water have a passivating effect in HCl-containing alcohols independent of the chain length.

---

**Last Name:** de Magelhaes Avelar
**First Name:** Heluza
**Title:** Conductometric determination of total acidity and chloride content in automotive fuel ethanol

**Source:** Fuel
**Vol.:** 86
**Year:** 2007

**File Name:** de magalhaes avelar h.pdf

**Abstract:** The use of conductometric titration in the determination of corrosive agents in automotive fuel ethanol has been studied. The methodology proposed is simple, fast, and sensitive and affords a larger repeatability and sensitivity in the analysis of total acidity and chloride content than the reference methods specified in the directives of ANP (National Petroleum Agency).

**Review:**
- Main factors that induce ethanol corrosion are the free acidity, the dissolved oxygen, and the presence of chloride, sulfate, and metallic ions. The presence of these agents results from both fermentation and distillation processes, and from contaminations [see reference a.]

**References:**
a. Trabanelli G, Mantovani G, Zucchi F., Sugar Technology Reviews, 1988;14:1–27.
b. Portaria no 2, 16 de Janeiro de 2002, Ageˆncia Nacional do Petro´ leo.

---

**Title:** Ethanol Fuel Dispensing Operations in Brazil

**Source:** Underwriters Laboratories Inc.
**Year:** 2007

**File Name:** UL Brazil 1.pdf

**Abstract:** Report of trip to Brazil fuel operations relating visual examination of compatibility issues as well as empirical data from operators. Covers general compatibility issues as well as a few ways to mitigate problems.

**Review:**
- Manufacturers noted some material compatibility issues in the thirty years
- Dynamic synthetic rubber components, such as nitrile rubber, experience swelling or deteriorate.
- Materials were replaced with more resistant ones like fluoroelastomers
- No modifications were made to static seals.
- As for corrosion, some minor corrosion and a build-up of bio residue in hydraulic components.
- Manufacturers addressed these issues by:
  a. Eliminating the use of zinc alloys.
  b. Keeping fluid-confining cavities “full” - keeps materials wet and eliminates air
  c. Redesigning meters to keep them “flushed” - the flow of fuel come through the top of the meter and leaves through the bottom.
- It was indicated or observed that aluminum (plated and unplated), iron, steel, brass and copper dispenser parts are in use in Brazil in ethanol fuel dispensers

---

**Last Name:** French
**First Name:** Raymond
**Title:** Phase equilibria of ethanol fuel blends

**Source:** Fluid Phase Equilibria
**Vol.:** 228-229

**Year:** 2005

**File Name:** french r.pdf

**Abstract:** The blending of ethanol into fuels is expected to increase significantly in the coming years. In some regions of the United States, ethanol has already replaced MTBE as the oxygenate blended into gasoline. Biofuel blends, such as blends of gasoline with ethanol made from biomass, can play an important role in helping governments and corporations meet sustainability targets. However, the introduction of ethanol fuel blends into the market place requires addressing several issues related to phase equilibria. The highly non-ideal mixing of ethanol with hydrocarbons has a dramatic impact on phase behavior, with consequences for the production, storage, distribution, and use of ethanol-blended fuels. In this paper, we will (a) illustrate the impact of ethanol use on the transportation fuels industry, (b) use thermodynamics as a unifying theme to understand these phenomena, and (c) review available data and the state-of-the-art in modeling these effects. Topics will include (a) volatility characteristics (e.g. Reid vapor pressure, ASTM D-86 Distillation, vapor–liquid ratio, and evaporative emissions), (b) phase separation effects (e.g. water tolerance and enhanced solubility of aromatic fuel components in groundwater), (c) commingling of ethanol and non-ethanol fuels, and (d) materials compatibility (e.g. increased swelling and permeation).

**Review:**
- Key property for a polymeric material exposed to a solvent is the degree of solvent absorption by the material. As little as 20% volume swell can reduce physical properties such as hardness, strength, and tear resistance by 60%
- In some cases, materials that are compatible with both neat gasoline and neat ethanol are incompatible with ethanol–gasoline blends.
- Study on materials compatibility show maxima in swelling between 5 and 25 vol.% ethanol in the blend.
- Swelling of polymeric materials in solvents has been addressed using solubility parameters of one or higher dimension
- Westbrook and French demonstrated that swelling of an elastomer in a solvent mixture can be estimated from the swelling of the elastomer in the pure solvents and the activities of the solvents in the mixture

**References:**
a. M. Nulman, A. Olejnik, M. Samus, E. Fead, G. Rossi, SAE Technical Paper No. 2001-01-1999.
b. R.L. Dickerman, J.R. Dunn, G. Rossi, J.C. Wagner (Eds.), Elastomer Technology: Fuels, Oils, Fluids and Thermoplastics, SP-1611,, Society of Automotive Engineers, Warrendale, PA, 2001.
c. A. Wilson, C.B. Griffis, J.C. Montermoso, Rubber World 138 (1958) 92.
d. I.A. Abu-Isa, Rubber Chem. Technol. 56 (1983) 169–196.
e. P.A. Westbrook, R.N. French, Rubber Chem. Technol. 72 (1999) 74–90.

---

**Last Name:** Galante-Fox
**First Name:** Julie
**Title:** E-85 Fuel Corrosivity: Effects on Port Fuel Injector Durability Performance

**Source:** SAE Paper
**No.:** 2007-01-4072
**Year:** 2007

**File Name:** galante-fox j. abstract.doc

**Abstract:** A study was conducted to investigate the effects of commercial E-85 fuel properties on Port Fuel Injector (PFI) durability performance. E-85 corrosivity, not lubricity, was identified as the primary property affecting injector performance.

Relatively high levels of water, chloride and organic acid contamination, detected in commercial E-85 fuels sampled in the U.S. in 2006, were the focus of the study. Analysis results and analytical techniques for determining contaminant levels in and corrosivity of commercial E-85 fuels are discussed.

Studies were conducted with E-85 fuels formulated to represent worst-case field fuels. In addition to contamination with water, chloride and organic acids, fuels with various levels of a typical ethanol corrosion inhibitor were tested in the laboratory to measure the effects on E-85 corrosivity. The effects of these E-85 contaminants on injector durability performance were also evaluated.

Corrosion test ratings from NACE TM0172-2001 ("Determining Corrosive Properties of Cargoes in Petroleum Product Pipelines") were determined for the test fuels. This corrosion test was found to be sensitive to the presence of low levels of typical corrosive E-85 contaminants. A recommendation for adding a corrosivity requirement to ASTM D 5798 ("Standard Specification for Fuel Ethanol (Ed75 - Ed85) for Automotive Spark-Ignition Engines") will be presented.

**Review:**

- E-85 fuel properties on Port Fuel Injector (PFI) durability
- Corrosivity, not lubricity, was identified as the primary property affecting injector performance
- Relatively high levels of water, chloride and organic acid contamination, detected in commercial E-85 fuels sampled in the U.S. in 2006, were the focus of the study
- Represent worst-case field fuels
- Found to be sensitive to the presence of low levels of typical corrosive E-85 contaminants

---

**Title:** Handbook for Handling, Storing, and Dispensing E85

**No.:** DOE/GO-102006-2303
**Year:** 2006

**File Name:** EERE Handbook for E85.pdf

**Review:**

- General handbook for E85
- Materials applicability includes avoiding the following: Zinc, brass, lead, and aluminum, terne (lead-tin-alloy)-plated steel, and lead-based solder
- Instead use: Unplated steel, stainless steel, black iron, and bronze
- Avoid: natural rubber, polyurethane, cork gasket material, leather, polyvinyl chloride (PVC), polyamides, methyl-methacrylate plastics, and certain thermoplastic and thermoset polymers.
- Instead use: thermoset reinforced fiberglass, thermoplastic piping, and thermoset
- Reinforced fiberglass tanks, Buna-N, Neoprene rubber, polypropylene, nitrile, Viton, and Teflon
- Goes into a little more detail on the specific materials to avoid/use and reasons why, for specific elements of the storage/dispensing system (pipes, hoses, nozzles, etc.)

---

**Last Name:** Hansen
**First Name:** Alan C.
**Title:** Ethanol-Diesel Blends: A Step Towards a Bio-based Fuel for Diesel Engines

**Source:** ASAE Meeting
**No.:** 01-6048
**Year:** 2001

**File Name:** hansen a.c. 2.pdf

**Abstract:** The global fuel crises in the 1970's generated awareness amongst many countries of their vulnerability to oil embargoes and shortages. Considerable attention was focused on the development of alternative fuel sources, with particular reference to the alcohols. Blends of ethanol and diesel fuel were investigated and found to be technically feasible, however, the high costs of ethanol production meant that the fuel could only be considered in cases of fuel shortages. In the last two decades of the 20th century, major advances in engine technology have occurred, leading to greater fuel economy in vehicles. The reduction of emissions from engines has become a major factor in the development of new engines and manufacturers are trying to meet the requirements specified by EPA. As a result the use of alternative fuels as a means of meeting these requirements has generated much attention.

Today the economics are much more favorable in the production of ethanol and it is able to compete fairly well with standard diesel. Hence there has been renewed interest in the ethanol-diesel blends with particular emphasis on emissions reductions. When considering an alternative fuel for use in diesel engines, a number of issues are important. This purpose of this paper is to review these issues with particular reference to safety and distribution, integrity of the fuel being delivered to the engine, emissions, engine performance and durability.

**Review:**
- Same background information and other Hansen reference, not as much detail

---

**Last Name:** Hansen
**First Name:** Alan C.
**Title:** Ethanol–diesel fuel blends—a review

**Source:** Bioresource Technology
**Vol.:** 96
**Year:** 2005

**File Name:** hansen a.c.pdf

**Abstract:** Ethanol is an attractive alternative fuel because it is a renewable bio-based resource and it is oxygenated, thereby providing the potential to reduce particulate emissions in compression–ignition engines. In this review the properties and specifications of ethanol blended with diesel fuel are discussed. Special emphasis is placed on the factors critical to the potential commercial use of these blends. These factors include blend properties such as stability, viscosity and lubricity, safety and materials compatibility. The effect of the fuel on engine performance, durability and emissions is also considered. The formulation of additives to correct certain key properties and maintain blend stability is suggested as a critical factor in ensuring fuel compatibility with engines. However, maintaining vehicle safety with these blends may entail fuel tank modifications. Further work is required in specifying acceptable fuel characteristics, confirming the long-term effects on engine durability, and ensuring safety in handling and storing ethanol–diesel blends.

**Review:**
- Repeat of Agarwal info
  - a. Brink et al. (1986) divided ethanol corrosion into three categories: general corrosion, dry corrosion and wet corrosion.
  - b. General corrosion was caused by ionic impurities, mainly chloride ions and acetic acid.
  - c. Dry corrosion was attributed to the ethanol molecule and its polarity.
  - d. de la Harpe (1988) reviewed reports of dry corrosion of metals by ethanol and found that magnesium, lead and aluminum were susceptible to chemical attack by dry ethanol.
  - e. Wet corrosion is caused by azeotropic water, which oxidizes most metals (Brink et al., 1986). Freshly formulated blends containing pH neutral dry ethanol would be expected to have relatively little corrosive effect.
  - f. Non-metallic components have also been affected by ethanol with particular reference to elastomeric components such as seals and O-rings in the fuel injection system. These seals tend to swell and stiffen. Resinbonded or resin-sealed components also are susceptible to swelling and seals may be compromised

- Tests with blends containing approximately 10% and 15% dry ethanol indicated no abnormal wear in engines correctly adjusted for injection timing
- Meiring et al. (1983b) no abnormal deterioration of the engine or fuel injection system was detected after 1000 h of operation on a blend containing 30% dry ethanol,
- Many tests with ethanol-diesel combinations showed no extra wear except on the fuel injection system, which showed some interaction with the ethanol
- Long time tests (1000+ hours) are still needed to confirm to diesel specifications

**References:**

a. Hardenberg, H.O., Schaefer, A.J., 1981. The use of ethanol as a fuel for compression–ignition engines. SAE Technical Paper 811211.
b. Brink, A., Jordaan, C.F.P., le Roux, J.H., Loubser, N.H., 1986. Carburetor corrosion: the effect of alcohol–petrol blends. In: Proceedings of the VII International Symposium on Alcohol Fuels Technology, Paris, France.
c. de la Harpe, E.R., 1988. Ignition-improved ethanol as a diesel tractor fuel. Unpublished MSc. Eng. Thesis, Department of Agricultural Engineering, University of Natal, Pietermaritzburg, South Africa.
d. Bosch, 2001. VP44 endurance test with E diesel. Internal Report No. 00/47/3156, Robert Bosch Corporation, Farmington Hills, MI, USA.
e. Hansen, A.C., Vosloo, A.P., Lyne, P.W.L., Meiring, P., 1982. Farmscale application of an ethanol–diesel blend. Agric. Eng. S. Afr. 16 (1), 50–53.
f. Hashimoto, I., Nakashima, H., Komiyama, K., Maeda, Y., Hamaguchi, H., Endo, M., Nishi, H., 1982. Diesel–ethanol fuel blends for heavy duty diesel engines—a study of performance and durability. SAE Technical Paper 820497.
g. Meiring, P., Allan, R.S., Hansen, A.C., Lyne, P.W.L., 1983a. Tractor performance and durability with ethanol–diesel fuel. Trans. ASAE 26 (1), 59–62

---

**Title:** Identification, Repair, and Mitigation of Cracking of Steel Equipment in Fuel Ethanol Service

**Source:** API
**Year:** 2007

**File Name:** api ballot 939e.pdf

**Review:**
- Time ethanol remains in transportation varies according to demand, destination, point of origin, etc
- Same time variance in storage tanks
- Sited examples of SCC:
  - a. Welds and adjacent metal in tank bottoms, floating roofs and associated seal components (e.g. seal springs);
  - b. Facility rack piping, fittings and associated equipment (e.g. air eliminators);
  - c. Vertical seam and nozzle welds in lower tank shells located off bottom;
  - d. Pipeline used to transport fuel ethanol from terminal to end user facility.
- No examples of SCC seen here:
  - a. Ethanol manufacturer facilities (storage tanks, piping or associated equipment);
  - b. Intermediate supply chain equipment, barges, tanker cars or tank trucks;
  - c. Blending or transportation facilities handling products containing fuel ethanol after it has been fully blended with gasoline.
- A survey of five major end users in North America, determined that approximately 100 tanks were in ethanol service (of which 75 were currently coated). It was reported that the average age of the tanks was approximately 3 years and represented 120 tank years in fuel ethanol service. The number of reported SCC events was 19 with some including multiple occurrences per event which increases the number to approximately 24.
- Factors related to SCC: high applied or residual tensile stresses, high local concentration of strain, or local cold working, variable stress loading, air absorption, a galvanic connection to corroded (mill-scaled) steel, presence of chloride, presence of inhibitors, and corrosion potential (water content not examined beyond Ethanol standard limits, 1 vol. %)
- Provides some guidance to materials fabrication for SCC prevention/protections (see below)
- Steel grade has not been a factor, but working methods and stresses are
- Design tanks to minimize or resist (tensile) stress
  - a. Use butt welding instead of lap seam welds
  - b. Minimize cold working and plastic deformation
  - c. Use fully penetration welds and stitch welds
  - d. Use post weld heat treatment (PWHT)
  - e. Apply polymeric coatings
  - f. Avoid tank subsidence
- See appendix for cases of SCC

---

**Last Name:** Jeuland
**First Name:** N.
**Title:** Potentiality of Ethanol as a Fuel for Dedicated Engine

**Source:** Oil & Gas Science and Technology
**Vol.:** 59
**No.:** 6
**Year:** 2004

**File Name:** jeuland n.pdf

**Abstract:** One of the major challenges of the automotive industry is to reduce the greenhouse gases, and especially CO2 emissions. Many research programs are currently being led on this subject, aiming at reducing the fuel consumption of vehicles, but also at optimizing the fuel composition. The overall process must indeed be taken into account, from the fuel production to the vehicle emissions, and a "well to wheel" balance has to be calculated for each technology.

Ethanol seems to have important assets to comply with these new constraints: it is extracted from the biomass and consequently has a good "well to tank" CO2 emission balance. Moreover, its properties, especially in terms of octane number and latent heat of vaporization allow a large improvement of the engine.

The present paper aims at taking stock of the ethanol path. The main production ways are tackled, especially concerning their energy balances. The main advantages and drawbacks of the use of such a fuel are then summarized. Finally, an example of the gains that can be obtained by an optimization of the engine using pure ethanol is presented. A small supercharged engine has already been modified to benefit from the potential of ethanol, especially in terms of knock resistance. The performances of this engine have been compared with those of the initial gasoline engine, showing that important gains can be obtained with such a technology.

**Review:**

- High oxygen content of ethanol and its ability to oxidize into acetic acid induce compatibility issues with some materials used in the engine, such as metals or polymers.
- Ethanol blends can lead to the formation of azeotropes. Azeotropes are defined as any liquid mixture having constant minimum and maximum boiling points and distilling off without decomposition and in a fixed ratio.
- Impact of these azeotropes is important when blending ethanol with fuels, by leading to an increased vapor pressure, which can lead to leaks and higher losses
- Once absorbed into rubber, the oxygen of the alcohol breaks the rubber's carbon-carbon double bonds
- Swelling and component breakdown can all be solved by the use of compatible materials such as highly fluorinated rubbers (Viton®). Nylon can also be resistant, but only at low temperature (< 30°C).
- oxidation of ethanol into acetic acid induces a rapid increase in electrical conductivity
- Acetic acid can consequently enhance galvanic corrosion and chemical attack. The metals recommended for use with ethanol include carbon steel, stainless steel and bronze. Metals such as magnesium, zinc casings, brass and copper are not recommended
- Ethanol with very high water content has been found in the past (up to 5%vol), with ion concentrations that make it much more aggressive than pure ethanol. The use of anhydrous ethanol is consequently mandatory to avoid engine corrosion.

**References:**

a. Hammel-Smith, C., Fang J., Powders, M. and Aabakken J. (2002) Issues Associated with the Use of Higher Ethanol Blends (E17-E24). NREL Technical Report NREL/TP-510-32206.

b. Bechtold, R.L. (1997) Alternative Fuels Handbook. SAE Press, ISBN 0-7680-0052-1.

c. Mueller Associates, Inc. Status of Alcohol Fuels Utilization Technology for Highway Transportation: a 1986 Perspective, Spark-Ignition Engines (1985) Report N°ORNL/Sub/85-22007/4, National Technical Information Service, Springfield, Va

**Last Name:** Johnston
**First Name:** Robert L.
**Title:** Stress-Corrosion Cracking of Ti-bA1-4V Alloy in Methanol

**Source:** NASA
**No.:** TN D-3868
**Year:** 1967

**File Name:** johnston r.l.pdf

**Abstract:** The report presents the results of an investigation to determine if an incompatibility exists between methanol and Ti-6A1-4V solution-treated and aged alloy. The test specimens were obtained from virgin solution-treated-and-aged sheet material and from the remnants of two Apollo service propulsion system fuel tanks which failed while containing methanol under pressure. The investigation shows that methanol and stressed Ti-6A1-4V alloy are incompatible and result in tank failure because of a stresscorrosion mechanism.

**Review:**
- Test results indicated that the alloy is highly notch-sensitive in methanol
- There is evidence that moisture (as little as 1 percent) in methanol appreciably inhibits the adverse reaction
- Cathodic protection prevented the failure

---

**Last Name:** Kane
**First Name:** Russell D.
**Title:** Stress Corrosion Cracking of Carbon Steel in Fuel-Grade Ethanol: Review, Experience Survey, Field Monitoring, and Laboratory Testing

**Source:** API Report
**No.:** 939-D
**Year:** 2007

**File Name:** api tr 939-d.pdf

**Review:**
- SCC of steel in fuel ethanol can be mitigated by strictly limiting access to oxygen
- Summaries of corrosion rates of ethanol, methanol, water, etc on zinc, copper, steel
- Includes a survey of SCC in pipelines, storage, and distribution systems, as seen in other API reference
- Most data repeat of data in other references (see Westbrook, P.A.)

---

**Last Name:** Kane
**First Name:** Russell D.
**Title:** Summary of Activities on Ethanol SCC – Tanks and Facilities: Failure Documentation, Survey Results, Guidelines Development

**Year:** 2007

**File Name:** kane r.d. 2.pdf

**Review:**
- Presentation covers API survey (seen in API Ballot 939e document)
- Provides broad conclusions about presence or lack of SCC
    a. No problems at manufacture point
    b. No problems in first tier distribution (barges, cars, trucks)
    c. Problems at or after first holding point (terminal, storage tanks, blending

facitilites)

d. No SCC after blending with gas, none in E85, none in Europe (little use until recently), or Brazil(uses hyrdrated ethanol with more water content)

**References:** a. R.D. Kane and J.G. Maldonado, Stress Corrosion Cracking of Carbon Steel in Fuel Grade Ethanol: Review and Survey, Publication 939D, American Petroleum Institute, Washington, D.C., November 2003.

b. Bulletin 939E, Identification, Repair, and Mitigation of Cracking of Steel Equipment in Fuel Ethanol Service, API, Washington, D.C.,

c. R.D. Kane and J.G. Maldonado, "Stress Corrosion Cracking In Fuel Ethanol: A Newly Recognized Phenomenon", Corrosion/2004, Paper No. 04543, NACE International, Houston, TX, April 2004.

d. R.D. Kane, N. Sridhar, M.P. Brongers, J. A. Beavers, A.K. Agrawal, L.J. Klein, "Stress Corrosion Cracking in Fuel Ethanol: A Recently Recognized Phenomenon", Materials Performance, NACE International, Houston, TX, December, 2005.

e. N. Sridhar, K. Price, J. Buckingham and J. Danti, "Stress Corrosion Cracking of Steel in Ethanol", Corrosion Journal, NACE International, Houston, Texas, July, 2006, pp 687-702.

f. J. Maldonado, N. Sridhar, "SCC of Carbon Steel in Fuel Ethanol Service: Effect of Corrosion Potential and Ethanol Processing Source", Paper No. 07574, Corrosion/2007, NACE International, Houston, Texas, March 2007

g. R.D. Kane, Stress Corrosion Cracking in Fuel Ethanol, Paper IBP 1357_07, RioPipeline, Rio de Janeiro, Brasil. October 2007.

---

**Last Name:** Miller
**First Name:** Ron
**Title:** Production of Ethanol & Update on Ethanol Current Events

**Year:** 2001

**File Name:** williams presentation.pdf

**Review:**
- Williams Bio-fuel (now owned by Aventine) conducted ethanol transportation in pipeline study in early 1980's
- 4,600 barrels shipped in 8 inch line from Kansas City to Des Moines
- Gasoline was transported in pipe 10 days prior
- Batch composition was tested at points along the way and in final holding tank
- Good aspects: water content, proof, interfaces
- Concerns: color, gum, interface handling
- Suggestions: use of pigs to clean/inspect pipeline often, used closed floater storage tanks to prevent rainwater infiltration
- Likely test was similar to Wiess, M.B. experience

---

**Last Name:** Nie
**First Name:** X.
**Title:** Corrosion Behavior of Metallic Materials in Ethanol-Gasoline Alternative Fuels

**Source:** Materials Science Forum
**Vol.:** 546-549
**Year:** 2007

**File Name:** nie x.pdf

**Abstract:** Corrosion performances of several metallic materials (Al6061 and Al319 alloys, 304 stainless steel and grey cast iron) in the ethanol-gasoline alternative fuels were investigated. Cyclic potentiodynamic polarization tests were used to study their corrosion behavior. Anodizing and plasma electrolytic oxidation (PEO) techniques were used to produce oxide coatings on the Al6061 and Al319 alloys, and the corrosion properties of these coating sin the alternative fuel environments were also evaluated. The results showed that the 304 stainless steel, A16061 and the coating materials are compatible with the alternative fuels. The oxide coatings on both Al alloys provided effective corrosion protection in the alternative fuel environments.

**Review:**
- Gasoline oxygenated with ethanol is used in engines, the metallic fuel-line components may suffer corrosion problems
- National Ethanol Vehicle Coalition (NEVC) and the Petroleum Equipment Institute have demonstrated that aluminum is sensitive to corrosion from ethanol. However, the use of corrosive ethanol can be accommodated through the use of appropriate coatings, gasket materials, adhesives, and fuel additives
- Ethanol corrosion behavior tests showed the presence of a film on the surface of the tested material, which is less permeable and can even obstruct the metal dissolution reaction but still permits an electrochemical reaction to occur
- In the ethanol fuel environment, the Al6061 might have a similar or even lower corrosion rate than 304 stainless steel.
- The corrosion performance of the stainless steel is the most stable amongst all the tested materials. Little change in corrosion potential and corrosion resistance was observed in the different ethanol content fuels. This means that the ethanol content has little effect on the corrosion properties of 304 stainless steel.
- With increasing ethanol content, the corrosion resistance of the Al319 alloy decreases, while the corrosion resistance of the Al6061 alloy increases
- Previous works reported that the main factor affecting the corrosion rate of a mild steel in the ethanol/water/sulphuric acid system is the conductivity of the medium, and the conductivity increased when the water percentage in the ethanol-water mixture increased
- Increasing absolute water content, the ethanol-gasoline fuel becomes increasingly corrosive from E30 to E100, because of the increased conductivity
- When the ethanol-gasoline blend fuel is used, the main issue for the selection of materials is the consideration of galvanic corrosion.

**References:**
a. L.M. Wing, G.L. Evarts, SAE Technical Paper Series, 930447, 1993.
b. Handbook for Handling, Storing, and Dispensing E85, DOE/GO-102006-2303, April 2006.
c. C. Sean Brossia, R.G. Kelly, SAE technical paper series, Society of Automotive Engineers, Inc., 932342 (1993) 173-183.
d. M. Kabasakaloğlu, Íkram Kalyoncu, Tülin Kiyak, Applied Surface Sci. 135(1998)188–192

---

**Last Name:** Otto
**First Name:** K.
**Title:** Corrosion Produced By Burning Layers of Methanol and Ethanol

**Source:** Corrosion Science
**Vol.:** 26
**No.:** 6

**Year:** 1986

**File Name:** otto k. 1.pdf

**Abstract:** Burning methanol and ethanol generate formic acid and acetic acid, respectively, as reaction products. These acids, concentrated in the liquid during the fires, cause electrochemical corrosion and rust formation on metal substrates. In these experiments, small amounts of alcohol were burnt on 1020 steel coupons. Corrosion products were analysed by FT-IR spectroscopy and by microscopy.

Rates of rust formation were measured gravimetrically for various alcohol solutions, then compared with rates of deposit formation beneath fires of iso-octane. In other experiments, acidity changes in liquid methanol and ethanol were measured as larger volumes of these fuels were burnt in beakers. Observed acidity increase during the pool fires is consistent with acid concentrations necessary to produce metal corrosion.

**Review:**

- It was recently established that 1020 steel coupons develop extraordinary rust when they are exposed to gaseous methanol combustion products.
- This finding along with extensive chemical analyses indicated rust formation, caused by formic acid, produced by partial oxidation together with water and oxygen
- Acid concentrations, produced by partial alcohol oxidation, are small. When combined with the large ionic conductivity of the liquid alcohols, compared to gasoline, these acid levels suffice to generate significant metal corrosion.
- Deposits produced in experiments with a pulsating flame, where corrosion was linked to extensive cylinder wear found in engines operating on methanol.
- The rust formation is caused by partial fuel oxidation to formic acid and acetic acid, respectively, followed by electrochemical corrosion of the metal surface. Differences in both the quantity and the morphology of the rust deposit depend strongly on acid strength and on water concentration.
- As a rule, rust formation resulting from methanol exceeds that from ethanol by one order of magnitude.

**References:**

a. K. OTTO, L. BARTOSIEWICZ and R. O. CARTER III, Corros. Sci. 25, 117 (1985). [see other Otto, K. reference]

b. H. W. MARaACH JR, E. A. FRAME, E. C. OWENS and D. W. NAEGEEI, SAE (Soc. Autom. Engng) Paper 811199 (1981).

c. J. E. ANDERSON and M. W. MAGYARI, Comb. Sci. Technol. 37,193 (1984).

d. H. SOREK, J. E. ANDERSON, W. O. SIEGE and K. Oyro, Comb. Sci. Technol. 41,203 (1984).

e. H. SOREK and J. E. ANDERSON, Comb. Sci. Technol. 43,321 (1985).

f. J. E. ANDERSON, M. W. MAGYARI and W. O. SIEGE, Comb. Sci. Technol. 43,115 (1985).

g. G. K. CHt~I, E. T. KING and W. GROFF, SAE (Soc. Autom. Engng) Paper 830239 (1983).

h. R. NICHOLS "Field experience with US-methanol vehicles: future design considerations." Co-ordinating European Council Second International Symposium on the Performance Evaluation of Automotive Fuels and Lubricants, Wolfsburg, West Germany, June 5-7 (1985).

i. H. W. MARaACH JR, E. A. FRAME, E. C. OWENS and D. W. NAEGEEI, SAE (Soc. Autom. Engng) Paper 811199 (1981).

---

**Last Name:** Otto
**First Name:** K.
**Title:** Steel Corrosion by Methanol Combustion Products

**Source:** Corrosion Science
**Vol.:** 25
**No.:** 2
**Year:** 1985

**File Name:** otto k. 2.pdf

**Abstract:** Rust on 1020 steel, caused by methanol combustion products, was studied with a pulse flame combustor. Rust formation is triggered by formic acid in the exhaust which produces ferrous formate. The formate, in turn, reacts with liquid water and oxygen from the gas phase to produce FeOOH and Fe304. Rust formation decreases sharply when the steel temperature is raised above the dew point at which moisture condenses from the exhaust gas. Rust formed on a steel surface after exposure to formic acid vapor and liquid water is comparable in structure to that produced by burnt methanol.

**Review:**
- Formic acid byproduct of methane combustion produces Fe ions, reduced in an aqueous environment forms rust products, these rust products induce wear on the engine components they contact

**References:**
a. J. C. INGAMELLS and R. H. L1NDQUIST, SAE (Soc. Autom. Eng.) Paper 750123, February 1975.
b. E.C. OWENS, H. W. MARBACH, Jr., E. A. FRAME and T. W. RYAN IlI, SAE (Soc. Autom. Eng.) Paper 800857, June 1980.
c. H.W. MARBACH, Jr., E. A. FRAME, E. C. OWENS and D. W. NAEGELI, SAE (Soc. Autom. Eng.) Paper 811199, October 1981.
d. T. W. RYAN lII, D. W. NAEGELI, E. C. OWENS, H. W. MARBACH and J. G. BARBEE, SAE (Soc. Autom. Eng.) Paper 811200, October 1981.
e. W. H. BAISLEY and C. F. EDWARDS, SAE (Soc. Autom. Eng.) Paper 811202, October 1981.
f. S, CHAIBONGSAI, B. J. HOWLETT and D. H. T. MILLARD, SAE (Soc. Aurora. Eng.) Paper 830240, March 1983.
g. S. J. LESTZ, letter report 05-6800-270, to U.S. Department of Energy, November 20, 1983.

---

**Last Name:** Sridhar
**First Name:** Narasi
**Title:** Stress corrosion cracking of carbon steel in ethanol

**Source:** Corrosion
**Vol.:** 62
**No.:** 8
**Year:** 2006

**File Name:** sridhar n.pdf

**Abstract:** This paper presents the results of a study on the effects of water, acetic acid (CH3COOH), oxygen, corrosion inhibitor, chloride, methanol (CH3OH), denaturant, and corrosion product on the stress corrosion cracking (SCC) of steel in ethanol (C2H5OH). The factor that was found to have the greatest effect on causing SCC was corrosion potential, as influenced by oxygen. The lower critical

potential for SCC ranges from 25 V vs. saturated calomel electrode (SCE) to 300 mVSCE, depending on the presence of chloride and methanol as impurities. Galvanic contact with precorroded steel appeared to exacerbate SCC by increasing the corrosion potential. Within the fuel ethanol specification limits, chloride had a less significant effect than oxygen. SCC was intergranular when the chloride concentration in ethanol (both laboratory and field samples) was low (less than 1 ppm) and it was transgranular when the chloride concentration was high (32 mg/L). A denaturant, a corrosion inhibitor, and acidity, within the specification limits of fuelgrade ethanol, did not appear to have a significant effect on SCC. Water content ranging from 170 ppm to 1% by weight did not have any significant effect on SCC. Thermodynamic calculations of iron in ethanol with a few hundred ppm water showed that iron oxide is stable over a wide range of pH. Electrochemical measurements indicated significant hysteresis in the polarization behavior of steel in ethanol under SCC conditions

**Review:**

- Effects of water, acetic acid (CH3COOH), oxygen, corrosion inhibitor, chloride, methanol (CH3OH), denaturant, and corrosion product on the stress corrosion cracking (SCC) of steel in ethanol (C2H5OH).
- Greatest effect on causing SCC was corrosion potential, as influenced by oxygen. Steel suffered cracking when oxygen concentration was greater than 1 ppm.
- Critical potential for SCC ranges from 25 V vs. saturated calomel electrode (SCE) to 300 mVSCE, depending on the presence of chloride and methanol as impurities.
- Galvanic contact with precorroded steel appeared to exacerbate SCC by increasing the corrosion potential.
- Within fuel specification limits, chloride had a less significant effect than oxygen. SCC was intergranular when the chloride concentration in ethanol (both laboratory and field samples) was low (less than 1 ppm) and it was transgranular when the chloride concentration was high (32 mg/L).
- A denaturant, a corrosion inhibitor, and acidity, within the fuel specification, did not significantly affect SCC.
- Water from 170 ppm to 1% by weight did not have any significant effect on SCC. Thermodynamic calculations of iron in ethanol with a few hundred ppm water showed that iron oxide is stable over a wide range of pH. Electrochemical measurements indicated significant hysteresis in the polarization behavior of steel in ethanol under SCC conditions

---

**Last Name:** Sridhar
**First Name:** Narasi
**Title:** Study examines ethanol pipelines for cracking potential

**Source:** Materials Performance
**Vol.:** 46
**No.:** 12
**Year:** 2007

**File Name:** sridhar n. 1 abstract.doc

**Abstract:** As the use of ethanol-blended gasoline rapidly increases in the United States, existing pipelines are considered the most cost-effective method of transporting this more environmentally friendly fuel. Currently ethanol is transported in tanker trucks and ships. But known technical issues regarding the effect of ethanol on steel prompted the Pipeline Research Council International (PRCI) to initiate a study on the reliable and safe transportation of ethanol through existing pipelines

**Review:** • As the use of ethanol-blended gasoline rapidly increases in the United States, existing pipelines are considered the most cost-effective method of transporting this more environmentally friendly fuel. Currently ethanol is transported in tanker trucks and ships. But known technical issues regarding the effect of ethanol on steel prompted the Pipeline Research Council International (PRCI) to initiate a study on the reliable and safe transportation of ethanol through existing pipelines.

---

**Last Name:** Sridhar
**First Name:** Narasi
**Title:** Transportation of Ethanol through Pipelines – Presentation to PHMSA

**Year:** 2007

**File Name:** sridhar n. 2.pdf

**Review:**
- Review of SCC (and other corrosion problems) involving ethanol on steel
- SCC seen in downstream pipeline components
- Includes some of the same information as the API study
- Key factor is oxygen content, with additional effect from Cl-
- Variability of SCC depending on ethanol batch
- Previous work showed water content and pH had little effect on SCC

- Gaps in current efforts:
  - a. Lack of a practical method for ethanol testing
  - b. Lack of “ASTM-like” specifications for FGE tailored for reliable transportation rather than just for end-use
  - c. Challenges in ensuring product quality when products from different producers get commingled
  - d. Lack of standardized ethanol source mixtures
  - e. Incomplete knowledge of real oxygen concentrations in pipelines nor where stream is picking up oxygen
  - f. Lack of understanding of how product composition changes during aging (time, head, length of travel, etc.)
  - g. Gaps in knowledge of why different ethanol sources differ in their effect on materials of construction
  - h. Avoiding oxygen contamination
  - i. Mixing ethanol from different sources
  - j. Understanding how to prevent SCC
  - k. Understanding which blends cause SCC
  - l. Understanding of consequences of SCC on pipeline, environment, repair, safety
  - m. Understanding of how fast SCC develops
  - n. Swelling and permeation in seals and gaskets
  - o. Understanding the impact of inhibitors on the consumer
  - p. Prioritizing locations of greatest integrity concern for inspection and mitigation
  - q. Lack of understanding of mechanism of ethanol SCC
  - r. Understanding differences between sugar-based and corn-based ethanol

- SCC mitigation:
  - a. One inhibitor and one oxygen scavenger identified in recent PRCI research: Di-ethanol amine (DEA), and Hydrazine, respectively
  - b. Three non chemical means of oxygen scavenging identified: Mechanical

---

**Last Name:** Weiss
**First Name:** M.B.
**Title:** Gasohol successfully pipelined; care required to maintain ethanol content

**Source:** Oil & Gas Journal
**Year:** 1981

**File Name:** weiss m.b.pdf

**Abstract:** Amoco Oil Co. successfully pipelined three 10,000-bbl batches of gasohol from Kansas City to Des Moines, Iowa. This article describes details of these shipments and addresses concerns about product quality and materials compatibility.

**Review:**
- Amoco test pipelining of gasoline with 10 vol% ethanol (gasohol)
- Pipe: line are made of seamless, Grade B, welded steel pipe with a 0.25-in. wall. Maximum operating pressure of the system is 1,440 psi, and maximum gasoline pumping rates are 2,000 bph and 750 bph in the 8 in. and 6-in. lines,
- Major concerns: phase separation (water contamination), particulates (scouring the pipe)
- The test showed that pipelining of gasohol is feasible. Water was not a big problem, contamination was not excessive, and, at least short term, materials compatability appear reasonable.
- Although some hazing occurred at the head of gasohol batches during the tests, there were no cases of phase separation, and only about 2% of the gasohol had to be slopped because of particulate contamination or discoloration.
- Contaminants in flags and gasohol were iron rust, iron and lead sulfides, and dirt. This was not surprising in a line which routinely moves light oils product, including leaded gasoline. Gum found after evaporation of gasohol samples was classified as "typical gasoline gum" including oxidation products
- There was no evidence of materials which would indicate deterioration of "pipeline" seals or gaskets.
- Was no evidence that gasohol strips corrosion inhibitors from a pipeline.

---

**Last Name:** Westbrook
**First Name:** Paul A.
**Title:** Compatibility and Permeability of Oxygenated Fuels to Materials in Underground Storage and Dispensing Equipment

**Source:** California State Water Resources Control Board
**Year:** 1999

**File Name:** westbrook p.a.pdf

**Abstract:** Literature search of ethers and alcohol compatibility in UST, focusing on corrosion and permeability of polymers, metals, ceramics, pipe dope, and organic coatings.

**Review:**
- Trace (1000 ppm) amounts of water passivates some metal systems
- Close to this passivation limit water causes phase separation
- Eectrical conductivity is also increased leading to galvanic and electrolytic corrosion
- Loss of lubricity is also observed at this limit
- Corrosion and wear products can be suspended in the fuel

- Non-metals
  a. Presence of oxygenates enhances permeation of hydrocarbons into elastomers

and thermoplastics

- b. Incorporation of thermoplastic liner in hoses may cut down on permeation
- c. Three categories on non-metallics: elastomers, thermoplastics, and thermosets
- d. In some cases liquid phase may be more active (will see more permeability and swelling) than the vapor phase
- e. High permeability is seen with small, volatile solvents, or solvent that strongly associates with the material, or both
- f. Swelling of up to 20% can affect hardness, strength, and tear resistance by 60%
- g. Elastic buckling of membrane materials between the ribs of USTs is critical to design
- h. Plasticizers can also migrate out of polymers (generally low molecular weight)
- i. Environmental stress cracking (ESC) not often reported in literature
- j. Increased fluid resistance (fluoroelastomers) often have compromised low temperature sealing characteristics
- k. Two ASTM standards for testing fuel stability: D-381-94, D-873-94

- Metals
  - a. Cathodic reduction of ethanol has been proposed to be ½ O2 + C2H5OH + 2 e- -> OH- + C2H5O- ; combined with a decomposition reaction of the metal produces CH2=CH2 + H20, thus ethanol fuels cannot stay dry in contact with an active metal
  - b. 0.1 to 0.2 percent water can passivate aluminum and ferritic stainless steels metals
  - c. Presence of water increases conductivity to the point where other corrosion is possible
  - d. Conductivity of 40-70 microsiemens per meter is sufficient for galvanic corrosion
  - e. Galvanic corrosion may occur without oxygen present
  - f. Electric potential of about 1 volt will cause corrosion, improperly grounded pumps can have currents in the tens of microamperes
  - g. Water content above 0.1 percent (MeOH) and 0.5 (EtOH) will cause phase separation
  - h. Presence of water and an aqueous phase increases the concentration of oxygen and other contaminants due to increased solubility
  - i. Wear as seen in engines is unlikely to occur because it is largely a product of combustion, but increased wear is seen in solution where water content is just below that of phase separation – this is attributed to microdomains of the aqueous phase which has not coalesced
  - j. Erosion-corrosion as a combined mechanism is a product of the above mechanisms and the flow of the alcohol
  - k. T. Powell (SAE 750124), and S. Wolynec (see references) shows experience with microcontaminants from the fermentation process etc in the final fuel
  - l. Brossia and Kelly showed systematically the effects of microcontaminants on iron alloys
  - m. Alloying can affect the stability of the oxide layer on the metal (copper or aluminum in steel)
  - n. ESC again not a major factor, generally occurs at t >140 F
  - o. Corrosion rate can increase or decrease with time depending on the inhibitor used, mono-, di-, and tri-ethanolamines have been used with the smaller ones performing better, amine-based corrosion inhibitors also work on steel

- Results
  - a. Tables A1-A6, and B1-B6 summarize swelling and permeability data for a

variety of solutions and materials
b. Data for composites and thermoplastics is limited
c. Maximum swelling in polymers with EtOH at 15%
d. Fluoroelastomers are more resistive (about 2 orders of magnitude to standard fuel blend C)
e. USTs, rigid fiberglass piping, and flexible plastic piping all have little permeability
f. Table 12 shows corrosion rates of MeOH on various metals (from Lash, et al.),
g. Other materials: no problems expected or found with ceramics; problems with uncured alcohol-including pipe dope; problems with epoxy; urethane coatings are recommended by some but may not be suitable for liquid immersion (just splashing); ethylene acrylic acid copolymer showed good performance over two years on steel substrates; sacrificial coatings are not recommended; steel, nickel plate, pre-painted zinc-nickel, cadmium plate, and anodized alloys 319 and 356 are recommended by some

**References:**

a. Davidson, J.M., LUST Line Bulletin 28 pg. 18 (1998). "MTBE and data on Underground Storage Tank Systems: A Question of Compatibility"
b. Bologna, D.J., and Page H.T., SAE 7800920 (1978) "Corrosion consideration avoid magnesium, terneplate, bare aluminum, brass, zinc, zinc alloys, and cadmium in design of automotive fuel systems"
c. Titchener, A.L., Metals and Energy vol. 19-23, (1980), pg. 112-125, (new Zealand), "Compatibility of Vehicle Materials with Unconventional Fuels"
d. McCallum, P.W., Timbario, T.J., Bechtold, R.L., and Ecklund, E.E., Chemical Engineering Progress, (1982), pg. 52-59, "Alcohol Fuels for Highway Vehicles"
e. Alternative Fuels Committee of the Engine Manufacturers Association, SAE Tech 820261 (1982). "A Technical Assessment of Alcohol Fuels"
f. Harvey, C.A., EPA-AA-TSS-PA-8601, US EPA, Office of Mobil Sources, Ann Arbor, MI, August (1990). "Materials Compatibility with Gasoline/Alcohol Blends."
g. Keller, J.L., US DOE Contract EY-76-C-04-3683, NTIS Document HCP/W3683-18, Washington, DC, July, (1978). "Methanol Fuel Modification for Highway Vehicle Use – Final Report."
h. Nakaguchi, G.M., US DOE Contract EY-76-C-04-3683, NTIS Document ALO-3683-T1, Washington, DC, July, (1978). "Ethanol Fuel Modification for Highway Vehicle Use – Final Report."
i. API Recommended Practice: 1626 (1993) "Storing and Handling Ethanol and Gasoline-Ethanol Blends at Distribution Terminals and Services Stations"
j. API Recommended Practice: 1627 (1986) "Storing and Handling Gasoline-Methanol/Cosolvent Blends at Distribution Terminals and Services Stations"
k. API Publication 1132 (1994). "Effects of Oxygenated Fuels and Reformulated Fuels on Elastomers and Polymers in Pipeline/Terminal Components."

---

**Last Name:** Wolynec
**First Name:** Stephen
**Title:** Corrosion in Ethanol Fuel Powered Cars: Problems and Remedies

**Source:** Proceedings - International Congress on Metallic Corrosion
**Year:** 1984

**File Name:** wolynec s. abstract.doc

**Abstract:** A review of corrosion problems found in ethanol cars using the same components as those of gasoline cars is presented. All metallic components in contact with liquid ethanol, such as terneplate or phosphated steel fuel tanks, zinc plated fuel pumps and zamak carburetors suffer some degree of corrosion. Hot corrosion was observed to occur on exhaust valves due to deposition of lead oxides. To control this corrosion the ethanol cars are using tin plated fuel tanks, cadmium plated fuel pumps, electroless nickel coated zamak carburetors and aluminized exhaust valves. Some corrosion inhibitors were tried to control corrosion but with limited success

**Review:**
- Test of corrosion on automotive components in an ethanol-powered car
- Some corrosion inhibitors were tried to control corrosion but with limited success
- Metals seemed to be a variety of materials already identified as susceptible to corrosion: Al, Zinc, and brass

# Appendix B. Deliverables

Copies of all search documents
Excel spreadsheet of bibliographical information of all search documents
Excel spreadsheet of key review information for all search documents
Test database of bibliographical and review information
Copy of first month’s progress report
Copy of raw notes of document reviews
Copy of final report presentation (summarizing this document)