

## STRESS CORROSION CRACKING IN FUEL ETHANOL: A NEWLY RECOGNIZED PHENOMENON

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### ABSTRACT

During the past decade, there has been evidence of stress corrosion cracking of steel storage tanks and associated piping used in fuel ethanol service. While SCC has not been wide spread, it has produced failures in some user facilities. No failures have been identified in facilities that produce fuel ethanol. This paper describes a review and survey conducted under an API funded study of this newly recognized phenomenon. It summarizes the basis of SCC in fuel ethanol and related environments and documents service experience. Further, more detailed information and survey results can be found in API publication 939D. It includes over 70 pages, 22 figures, 17 tables, 42 references, a bibliography of 15 related references, and a comprehensive summary table detailing 16 case histories involving ethanol SCC and non-SCC experiences.

### INTRODUCTION

An extensive survey of published literature, service experience and previously unpublished studies on stress corrosion cracking (SCC) of carbon steel in fuel grade ethanol and related topics was conducted by InterCorr International, Inc. (Houston, Texas) for The American Petroleum Institute and a consortium of fuel ethanol producers which includes the Renewable Fuels Association. The results of this study along with detailed information and survey results can be found in API publication 939D. [1] It includes over 70 pages, 22 figures, 17 tables, 42 references, a bibliography of 15 related references, and a comprehensive summary table detailing 16 case histories involving ethanol SCC and non-SCC experiences.

### BACKGROUND

Ethanol has been used in automobile fuels to a certain extent for more than 25 years. In the early 1990's the U.S. Congress passed the Clean Air Act that required an oxygenate in gasoline supply in specific regions of the country. Oxygenates used are either ethanol or MTBE. Recently, MTBE has been found

as a contaminant in groundwater and 17 states have banned its use. Additionally, the federal government is considering new energy legislation that among other things, would phase out the use of MTBE, eliminate some oxygenate requirements and phase in a modest but increasing requirement to use renewable fuels like ethanol and biodiesel. Consequently, the use of ethanol as an additive/extender to gasoline is expected to increase.

The present study was the first part of a multi-part plan developed by the API Refining Committee, Subcommittee on Corrosion and Materials, to address the needs of industry regarding potential problems associated with SCC of carbon steel in fuel ethanol. The initial direction taken was to expeditiously develop a white paper to provide a concise and accurate review of the currently available information on SCC in fuel grade ethanol. This work also included documentation of the experience from companies involved in fuel ethanol supply, transportation, storage and distribution, and an initial assessment of the potential economic impact of this problem to the petroleum industry.

#### What is Fuel Ethanol vs. Ethanol?

Ethanol is an alcohol that can be produced from a variety of sources. In the United States the most common source is from corn and grain. However, ethanol can also be produced naturally (fermented) from any carbohydrate source, such as wheat, cane, beet and fruits like grapes and apples. While grain and synthetic alcohols are technically the same (the molecule is identical), there are differences in the amounts of contaminants (butanol, acetone, methanol, organic acids) in each.

Fuel ethanol is not sold with zero water content, where it would be referred to as anhydrous ethanol. Denatured alcohol typically contains up to 1 percent water and other constituents. Fuel ethanol with less than 0.5 percent water is considered “anhydrous ethanol”. Ethanol with higher water contents is usually referred to as “hydrated ethanol”. Such hydrated ethanol is uncommon in the United States but is used as a fuel in Brazil.

In the United States, denaturants are also added to fuel alcohol in accordance with the Bureau of Alcohol, Tobacco and Firearms. According to Federal Regulation Title 27 Parts 19, 20 and 21 (including CFR 19.1005, 27CFR 21.24 and C.D.A. 20), a denaturant is to be added to alcohol in order to make it unfit for beverage or internal human medical use. The API research report 936D provides more background related to the manufacturing processes and range of denaturants used in fuel ethanol.

There are several standards that govern fuel grade alcohol, related analyses and its use as a fuel. The primary standard for fuel ethanol can be found in ASTM D4806 – Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel – which gives the compositional and physical limits for fuel ethanol. [2] These are summarized in Table 1.

A parameter that is used in evaluation of fuel ethanol is the pHe as defined by ASTM D6423. [3] The pHe value is a measure of the acid strength of high ethanol content fuels. It is applicable to fuels containing nominally 70 volume percent or more ethanol, or higher. pHe is similar to the pH parameter used in aqueous solutions. An extremely important point is that pH 7 is considered neutral for aqueous solutions, whereas a pHe value of 9.55 is the neutralization point for ethanol. Therefore, environments that have a pH of 6 in aqueous solutions may be considered only mildly acidic, whereas in ethanol pHe 6 represents a solution of significantly higher acidity (as defined as the magnitude of the reduction from the neutralization value).

Table 1 – Quality Specification for Fuel Ethanol per ASTM D4806

Property	Units	Specification	ASTM Designation
Ethanol	%v min	92.1	D5501
Methanol	%v max	0.5	--
Solvent-Washed Gum	mg/100 ml max	5.0	D381
Water Content	%v max	1.0	E203
Denaturant Content	%v min	1.96	D4806
	%v max	4.76	
Inorganic Chloride Content	ppm (mg/L) max	40 (32)	E512
Copper Content	mg/kg max	0.1	D1688
Acidity as acetic acid	%m (mg/L)	0.007 (56)	D1613
pHe	--	6.5-9.0	D6423
Appearance	Visibly free of suspended or precipitated contaminants (e.g. clear & bright)		

## CORROSION AND SCC IN ALCOHOLIC MEDIA

### Corrosion in Alcoholic Environments

Most engineers and researchers are more familiar with corrosion chemistry of aqueous solutions. For the most part, the similarities between organic and aqueous media dominate. Figure 1 shows that the electrode potentials of various materials in water, ethanol and methanol are very similar and the potential for the hydrogen electrode is similar, as well. It is primarily in the region of Hg and Ag, which have a very high electrode potential in water, where a significant reduction in the electrode potential is observed. Additionally, water, methanol and ethanol are all protic media capable of sustaining electron transfer and ionization of the hydrogen atom. Therefore, in most cases, corrosion processes and galvanic interactions would be expected to be thermodynamically similar in water, methanol and ethanol. [4]

Comparison of the physical properties of water, methanol and ethanol are also revealing. Ethanolic solutions have lower conductivity than either methanol or water. The oxygen solubility in methanol and ethanol are similar; however, they are both an order of magnitude higher than that of water. Therefore, the availability of oxygen for participation in the corrosion reaction is expected to be generally greater in ethanol and its solutions as well. Another important aspect of ethanol with potential relevance to its corrosivity is its hygroscopic nature relative to other fuels. Data show a radical increase in water content of ethanol after 30 days exposure to a humid environment. [5]

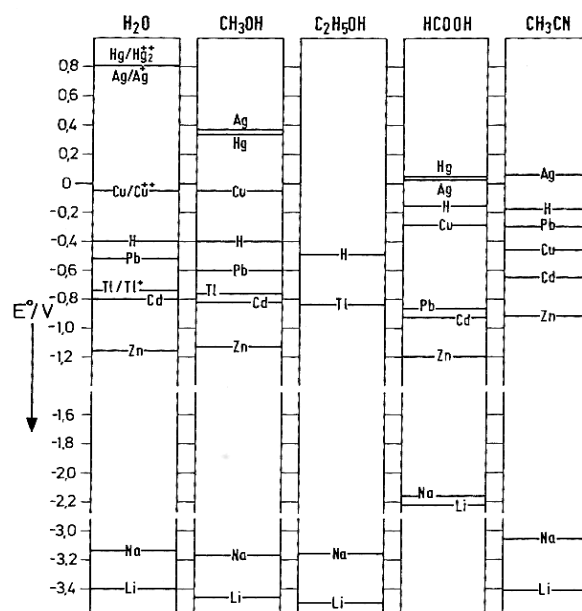


Figure 1 – Comparison of electrode potentials of metals in different solvents:  
Including water, methanol and ethanol. [1']

Figure 2, shows the corrosivity of zinc, iron and nickel in water and in alcohols versus their chain length (for C<sub>1</sub> through C<sub>8</sub>) [4]. The relationship displayed indicates that there is an increase in aggressivity going from water to methanol (C<sub>1</sub>) which then decreases with increasing carbon number. This relationship leaves ethanol with approximately the same general corrosivity as water. The reason for the increase in corrosivity going from water to methanol is generally considered to be the effect of the increased oxygen solubility in methanol. Since it has been shown that the oxygen solubility of methanol and ethanol is similar (both higher than that of water), the decrease in corrosion rate from C<sub>1</sub> through C<sub>8</sub> is likely to be the result of the increased chain length and, in turn, its impact on molecular or ionic mobility in the media.

### SCC in Ethanol

A major finding of this study was that only limited data existed in the published literature on SCC of steel in ethanol. [5, 6] The first of the two references cited indicate that SCC of steel may be possible in ethanolic solutions as evidenced by examination of surface features of slow strain rate (SSR) test specimens exposed to ethanol with additions of LiCl and H<sub>2</sub>SO<sub>4</sub>. The cracking in ethanol appeared qualitatively to be less severe than found for methanol but no ductility loss data (elongation or reduction in area versus air properties) was presented. The cracking of steel in methanolic and ethanolic environments was comparable in many ways to SCC of steel in liquid ammonia where susceptibility can be affected by minor impurities of water.

The second reference describes the SSR testing of steel in ethanolic solutions with formic and acetic acids, and water at 60 C. Additions of 0.10 to 25 percent formic and 0.1 percent water in ethanol did not produce SCC. However, steel bend specimens produced SCC in a solution of 0.01 percent acetic acid and 0.1 percent water that was less severe than found in methanolic solutions. Cracking was basically surface fissuring of less than 0.01 mm in depth.

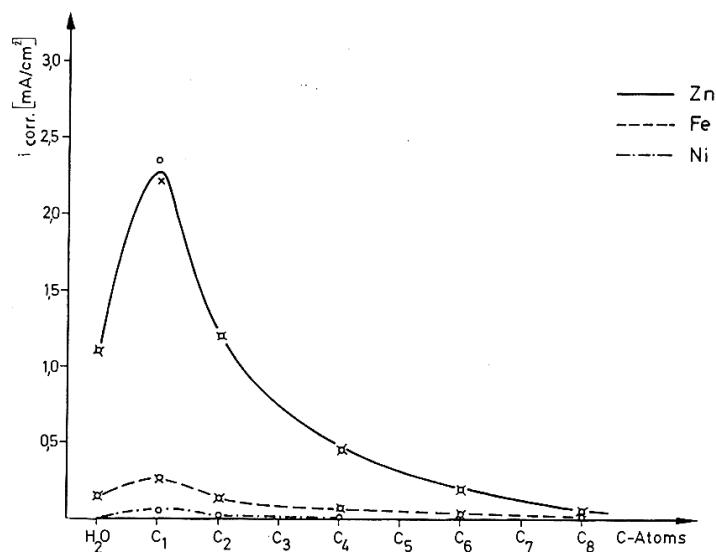


Figure 2 – Corrosion rate ( $i_{corr}$ ) of zinc, iron and nickel in primary alcohols  
Plotted versus carbon number of solvent: Methanol (C =1); Ethanol (C = 2)

### Corrosion and Pitting in Ethanolic Environments

Despite the limited data on SCC of steel in ethanolic solutions, there was, in fact, substantial information found on the general and pitting corrosion behavior of steel in ethanol and ethanolic solutions that were relevant to the present concerns for corrosion of steel tanks and piping in fuel ethanol. Since SCC of steel likely involves corrosion to a certain degree and, in particular, the initiation of local anodic sites, it was felt that this review should attempt to characterize corrosion in ethanolic solutions.

In overview, the literature was found to be consistent in the representation that ethanol solutions are generally less corrosive than those of methanol. Many of these studies were conducted on fuel grade hydrated ethanol in Brazil with the impurities shown in Table 2. [7]

Table 2 – Characteristics of Brazilian Fuel Grade Ethanol

Characteristics	Result
Specific Gravity at 20 C	$0.8093 \pm 0.0017$
Alcohol (%)	$93.6 \pm 0.6$
Total Acid (mg/100 ml), max.	3.0
Aldehydes (mg/100 ml), max.	6.0
Esters (mg/100 ml), max.	8.0
Higher alcohols (mg/100 ml), max.	6.0

The literature also indicates that ethanol containing certain impurities can sustain corrosion in carbon steel and other materials. Furthermore, these impurities and other additives can quite commonly promote tendencies toward localized corrosion, as shown in Table 3.

Table 3 – Corrosion in Brazilian Fuel Ethanol

Test	Fuel Ethanol		Ethanol	
	Morphology	Corrosion	Morphology	Corrosion
1	Pitting	Density – 35 pits/inch <sup>2</sup> Rate – 1.9 mpy	General	0.006 mpy
2	General	Rate – 0.36 mpy	General	0.009 mpy
3	Pitting	Rate – 0.09 mpy		

Table 4 – Parametric Study of Selected Variables on Corrosion in Hydrated Ethanol

Solution	Variables				Mass Loss	
	Ethanol (%)	SO <sub>4</sub> <sup>-2</sup> (mg/L)	Cl <sup>-</sup> (mg/L)	pH	(g/m <sup>2</sup> )	(g/m <sup>2</sup> )
ABCD	92.6	4	2	4	13.600	12.500
ABD	92.6	4	0.5	4	11.000	11.300
ACD	92.6	1	2	4	10.200	8.000
BCD	93.8	4	2	4	9.710	11.200
CD	93.8	1	2	4	9.010	9.530
BD	93.8	4	0.5	4	8.750	9.200
AD	92.6	1	0.5	4	5.800	4.120
D	93.8	1	0.5	4	5.130	4.580
ABC	92.6	4	2	8.5	1.470	1.270
B	93.8	4	0.5	8.5	1.010	0.958
A	92.6	1	0.5	8.5	0.955	1.00
AB	92.6	4	0.5	8.5	0.950	1.110
BC	93.8	4	2	8.5	0.928	0.960
Base	93.8	1	0.5	8.5	0.885	0.744
C	93.8	1	2	8.5	0.870	0.900
AC	92.6	1	2	8.5	0.724	1.090

The results in Table 4 from a corrosion study in hydrated ethanol were sorted in descending order based on the extent of mass loss corrosion during the exposure. Most notable is the influence of pH. All of the environments in the top half of the listing (most corrosive) were run at low pH (pH 4). These environments have about an order of magnitude higher mass loss than those at pH 8. The next most important factor in producing high corrosivity appears to be high sulfate level as evidenced by the

position in the top two slots at the top of the list. However, the actual effect of this variable has not been independently evaluated. The three most corrosive environments (at the top of the list) were those with the higher amount of water (lower ethanol). Additionally, high chloride concentrations existed in all but one of the top five most corrosive environments. One shortcoming of the abovementioned study, however, was that it did not measure susceptibility to localized pitting attack on the steel coupons. Still, while these studies do not match directly with compositional range for fuel ethanol (per ASTM), they do indicate that pH (pHe), sulfate (sulfur) and chloride may also be important variables and may also be involved in the SCC process as well.

In another Brazilian study involving additions of a 20 percent HCl solution to ethanol, the corrosion rate and morphology were found to change according to Table 5. [7]

These data indicate a change in corrosion rate from high to low to high, and a change in corrosion morphology from uniform to pitting back to uniform, over the range of 1 to 80 percent water content. This illustrates the complex relationship of acidic water in ethanol. At low concentrations, it leads to a dramatic reduction in the general corrosion and the onset of pitting at around 4 percent water in ethanol. However, the trend is reversed with supplementary additions of acidic water.

Table 5 – Impact of additions of 20% HCl to Ethanol on Corrosion Rate

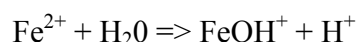
Water (%)	Duration (hrs)	Corrosion Rate (mmpy)	Corrosion Morphology
0	44	4.5	Uniform
1	300	2.5	Uniform
4	300	0.53	Pitting
6	300	0.01	Slight Pitting
32	140	0.01	Uniform
64	140	2.5	Uniform
80	140	2.8	Uniform

No comprehensive conclusions of corrosion and SCC in fuel ethanol have been reported in the published literature. In general, the tendency expected in purer ethanol solutions typical of fuel grade ethanol may be similar to that found for steel in methanolic solutions where the steel tends to exhibit passivity or very low corrosion rates (pseudo-passivity) in very mild environments. With increasing aggressivity of the environment, there is an initiation of local anodic attack (local loss of passivity), followed by general corrosion at still higher levels of solution aggressivity.

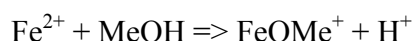
Most of what can be inferred has come from investigations involving steel in methanolic solutions with the assumption that these environments are mechanistically similar. In solutions of methanol and water in the range of 200 to 460 ppm, the natural (air-formed) oxide film on the surface is not stable and partially dissolves leading to the following reaction in the protic medium [8]:



The oxide free areas on the steel surface will rapidly dissolve according to the following reaction:

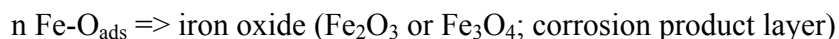
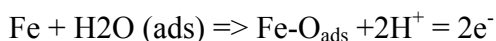


followed under aerated conditions by:



This leads to local anodic attack under aerated conditions which, in turn, sets up the conditions conducive for SCC. If sufficient corrosive causing agents are added to the system, the local anodic attack changes to a more generalized form of corrosion over the complete surface thus reducing susceptibility to SCC.

The role of acidity in partially hydrated methanolic environments has also been evaluated in terms of its role in the corrosion mechanism. The presence of  $\text{H}^+$  in methanol contributes to destruction of the normally protective oxide film. An anodic Tafel slope of 30-35 mV per current decade has been measured. At higher currents, loss of linearity in the potential versus log current relationship was also observed as a result of diffusion controlled transport of the  $\text{Fe}^{2+}$  ions. At still higher anodic potentials, absorbed oxygen is formed and the growth of a passive oxide layer takes place as



The region of potential that corresponds to this transition from active (anodic) to passive behaviors is precisely where pitting and SCC can occur. However, these processes depend on the level of acidity and water content in the environment through specific (and possibly competitive) adsorption on the metal surface. Therefore, there may be differences in the exact behavior of water and acidic species in other alcohols such as ethanol.

#### SCC in methanol

Studies have been conducted to evaluate the phenomenon of SCC of steel in methanolic environments. [6, 9, 10] Typically, these studies have included the use of plastically deformed and/or dynamically strained tests such as found in U-bend (ASTM G30) and slow strain rate (ASTM G129) specimens. In aerated solutions at 20 C, it has been shown that there is a critical amount of water that produces SCC in steel that ranges from somewhere above 0 but less than 0.05 volume percent to just below 1 percent water by volume, based on reported trends in multiple tests (See Figure 3). The highest probability of failure by SCC was reported to be around 0.20 percent water in methanol.

Studies of iron and a low alloy steel (Fe-0.94Cr-0.98Ni-0.16Mo) with a yield strength of 932 MPa, [10] showed that conditions of slow oxide growth were observed in methanolic solutions containing impurities in the following range: acidity (0 to  $10^{-3}$  M with formic acid), chlorides ( $10^{-4}$  to  $10^{-3}$  M) and water (0.01 to 0.5 percent) when the potential was held between -200 and +100 mV SCE. By comparison, SCC of steel was observed in the more controlled range of conditions indicated as follows:  $10^{-4}$  M formic acid,  $10^{-4}$  to  $10^{-3}$  M chloride, 0.1 to 0.5 percent water, and -100 to 0 mV SCE applied potential

The absence of dissolved oxygen in the environment decreases the potential of the metal outside of the abovementioned range for SCC, thus eliminating SCC failure.



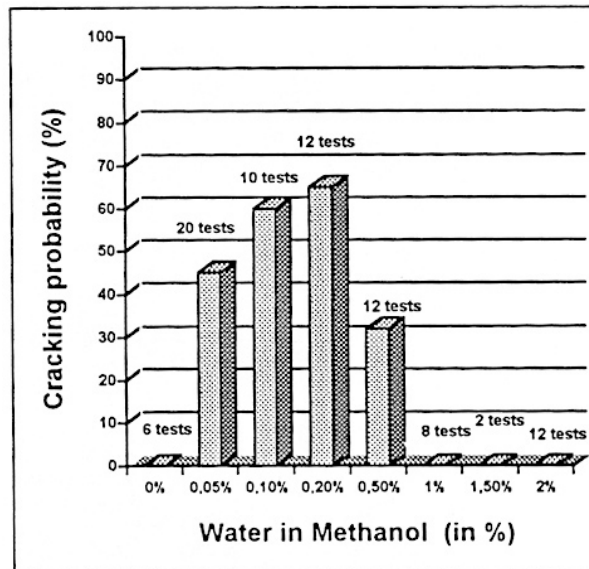


Figure 3 – Susceptibility to SCC in methanol versus water content.

The influence of other variables on methanol SCC was also evaluated. The concentration of formic acid in methanol between 0.005 and 0.04 wt. percent produced SCC in steel with a minimum time to failure occurring between 0.01 and 0.02 wt. percent at a solution water content of 0.1 percent added to the methanol and tested at 60 C.

#### INDUSTRY EXPERIENCE WITH SCC IN FUEL ETHANOL

The API report documents evidence provided by multiple fuel ethanol users showing occurrences of SCC of steel components (e.g. tanks, piping, roof hanger springs) exposed to fuel ethanol in user's storage and transportation equipment. Examples of SCC produced in fuel grade ethanol at user facilities are shown in Figure 4 through 6.

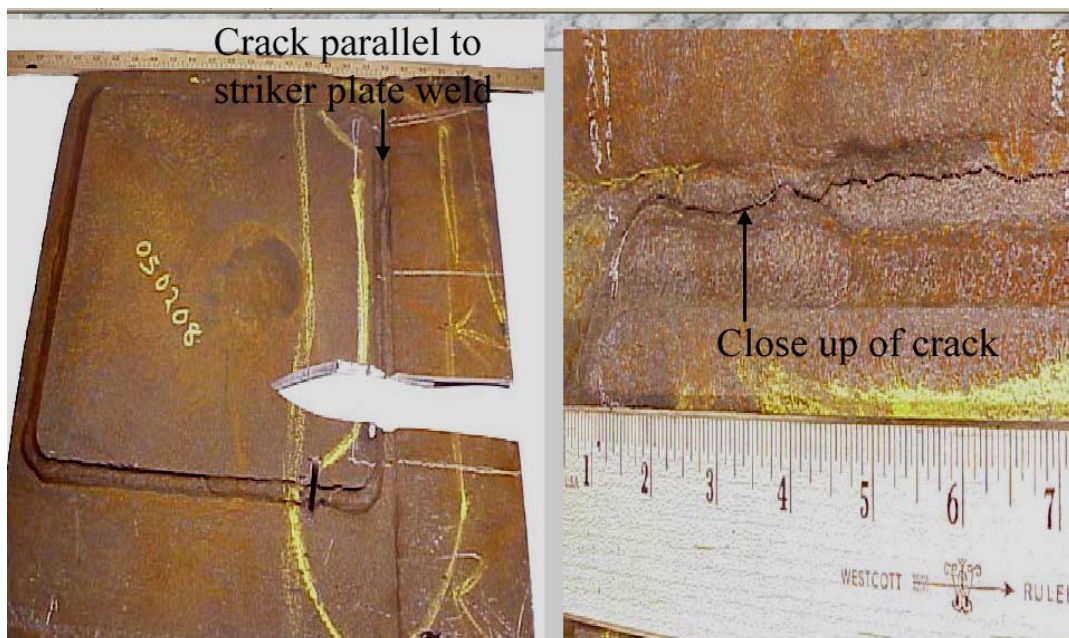


Figure 4 – SCC in steel tank bottom. Note crack running parallel to fillet weld in striker plate.

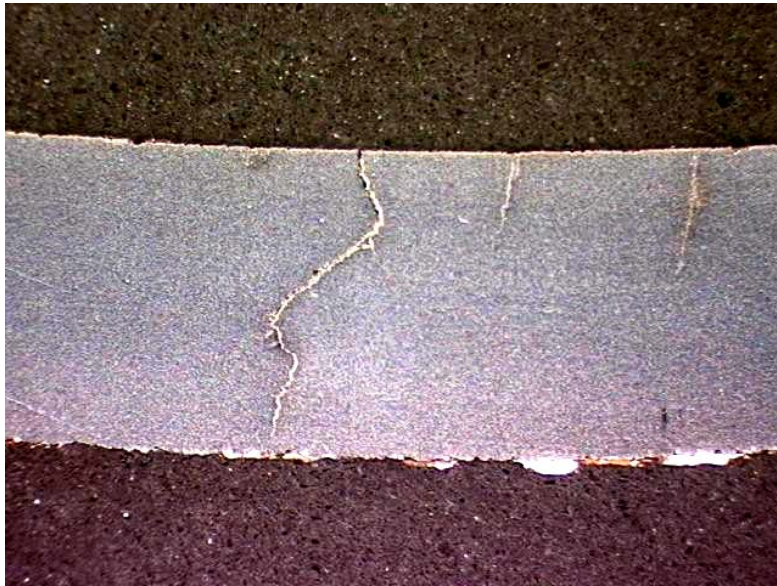


Figure 5 – Characteristics of SCC in steel exposed to fuel ethanol, showing multiple crack initiations and through-thickness propagation in piping.

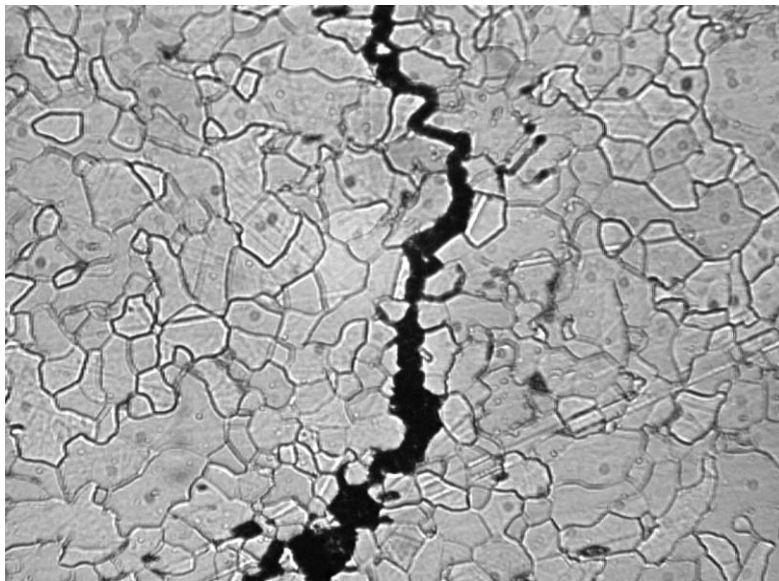


Figure 6 – SCC (produced in Fuel ethanol) in steel metallographically prepared with grain boundary etch at 500X. Note intergranular cracking features.

SCC failures were found in steel tank bottom plates, transfer piping and components (air eliminator), and tank roof springs. Figure 5 indicates the through thickness nature of the cracking and the intergranular character of the cracking is shown in Figure 6.

In some cases, the failed equipment had seen prior non-ethanol service. A summary of all documented SCC failures/leaks in fuel grade ethanol and some SCC-free service experience found by this study was included in the API report. A summary table was assembled that includes results of reports and related documents and correspondences which include plant experiences, metallurgical and chemical analyses, and laboratory corrosion studies.

In general, it should be noted that all SCC failure in fuel grade ethanol failures were experienced by users of fuel ethanol. An interesting point documented was that no ethanol manufacturers have reported failures or leaks from SCC. Furthermore, a major inspection program of tanks located at a particular manufacturing facility has reported no evidence of SCC. Just as interesting is that some end users have not experienced any SCC in fuel ethanol service.

#### RECENT UNPUBLISHED LABORATORY STUDIES IN FUEL ETHANOL

Several limited studies were conducted by various investigators to evaluate corrosion and SCC of steel in ethanol environments. At the time of this study, the results of these investigations had not as yet been published. Due to the extreme importance of this apparent new cracking phenomenon, these results were included in the API research report to further define the nature of SCC in fuel grade ethanol and help guide future studies that may be funded by API or other parties. These cases are only briefly summarized below:

Study #1. A study [11] was conducted using coupons and electrochemical methods. The mass loss corrosion rates for various ethanol environments were very low (typically all less than 1 mpy). Excess water additions had only a minor influence on the corrosion rate which was still very low. An additional part of this investigation included the exposure of carbon steel U-bend SCC specimens, as well as welded AISI 4130 steel at HRC 30 and 55. The environment was an ethanol that reportedly had produced SCC in the field. The test temperature was progressively increased from room temperature to 130 F over a period of 60 days. No SCC was observed in these tests. Additional SCC tests were conducted with additions of acetic acid and sulfate. Again, no SCC was observed.

Study #2. Welded U-bend SCC specimens of a carbon steel were placed in a commercial sample of fuel grade ethanol. [12] All U-bend specimens cracked at (uncontrolled) room temperature. The failures occurred in an exposure period of between 5 to 6 months from initiation.

Study #3. A sample of fuel ethanol was provided for slow strain rate testing per ASTM G129 at room temperature. [13] The sample was reported to be denatured but non-inhibited ethanol derived from corn. The tests were conducted on carbon steel specimens at an initial strain rate of  $1 \times 10^{-6} \text{ sec}^{-1}$ . The specimens were taken from the base metal adjacent to the weld, oriented with their axis parallel to the weld. The specimen showed extensive cracking throughout the gage section (See Figure 7) which was confirmed to be intergranular in nature (similar to crack observed from in-plant leaks) by metallographic observation (See Figure 8). About five months later the same ethanol was tested again for SCC, but no cracking was observed. Analysis indicated that the water content in the later test was higher, probably as a result of the hygroscopic nature of ethanol during storage.

SSR tests were also conducted in another fuel ethanol sample reportedly derived from wine obtained from a Caribbean source. Substantial secondary cracking and susceptibility to SCC was observed in this sample. This sample was also found not to contain denaturants or inhibitors.

Study #4. A limited program was conducted that included a combination of electrochemical and SSR testing. [14] These tests were performed using synthetically prepared ethanolic environments with additions of 5 percent methanol and 1 percent water, and in a simulated fuel grade ethanol based on the specifications of ASTM D4806. These tests were conducted on specimens machined from carbon steel at room temperature at an initial strain rate of  $1 \times 10^{-6} \text{ sec}^{-1}$ . No evidence of SCC was observed in 100 percent ethanol or when 5 percent methanol or 5 percent methanol plus 0.5 percent water was added. When a simulated fuel grade ethanol was used as the test environment, fissuring was obtained in the highly strained necked region.



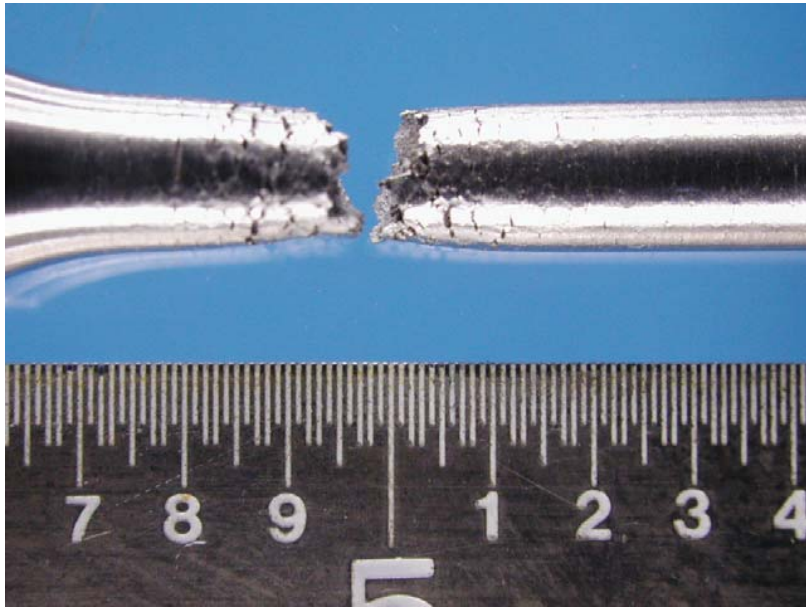


Figure 7 – SCC produced on welded carbon steel in fuel ethanol.

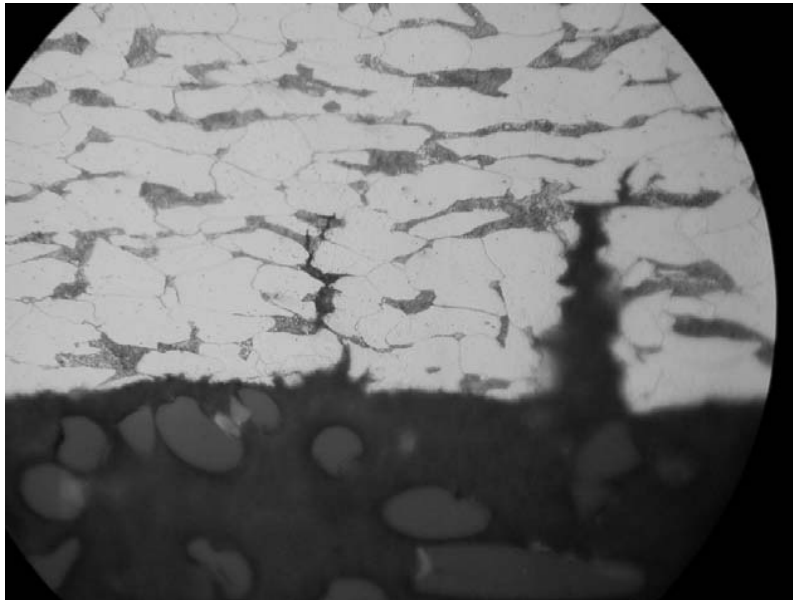


Figure 8 – Close-up of SCC from Figure 18. Cracking was a mixture of intergranular and transgranular features.

Cyclic electrochemical polarization tests were also conducted on specimens of carbon steel in the same environments used for the SSR tests. The corrosivity of the simulated fuel grade ethanol increased with increasing water content. The simulated fuel grade ethanol environments (with and without water) were the only environments found to cause pitting and the formation of a dark film after polarization.

## CONCLUSIONS

Based on the API study described herein, a comprehensive report was developed on SCC in fuel ethanol. The table of contents for this report is shown in Appendix I. It includes over 70 pages, 22 figures, 17 tables, 42 references, a bibliography of 15 related references, and a comprehensive summary table detailing 16 case histories involving ethanol SCC and non-SCC experiences. A summary of the conclusions are given below:

- SCC in fuel grade ethanol has been observed in several locations around the United States and is not limited to any one geographic location.
- Fuel grade ethanol is not a “commodity”. Fuel ethanol varies widely in composition.
- SCC in fuel grade ethanol has produced failures in less than 1 year in some cases.
- Stress is an important factor in SCC in fuel grade ethanol with SCC reported in highly stressed or dynamically stressed welds or components.
- Based on a literature review and preliminary laboratory studies, the factors that increase corrosivity of fuel ethanol appear to be increased water content and decreased pHe, and other potential factors may include sulfur, sulfate and chloride concentration.
- Based on existing information on other forms of SCC of steels and other materials, it is not expected that parameters that increase corrosivity of the fuel ethanol will have a direct correlation with susceptibility to SCC.
- Based on preliminary laboratory studies, SCC has been produced in samples of commercial fuel ethanol including some that apparently does not contain denaturants or inhibitors.
- SCC in fuel grade ethanol has been reproduced in laboratory tests in fuel ethanol samples obtained from the field. Evidence of out of specification ethanol has also been reported.
- SCC in fuel grade ethanol potentially has many aspects (including crack morphology) that are common to SCC produced in steel exposed to environments such as methanol.

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#### APPENDIX I – API RESEARCH REPORT 939D: TABLE OF CONTENTS

Section	Description	Page
--	Table of Contents	2
1	Executive Summary	4
2	Introduction	6
	Scope	6
	Technical Basis	6
	Technical Approach	6
3	Background	7
	Description of Fuel Ethanol Service	7
	Environmental and Economic Importance and Impact of Ethanol	7
	Ethanol - Description of Manufacture, Distribution, Storage and Use	7
	Description	7
	Standards	8
	Manufacture	9
	Significance of SCC Problem	10
	Potential Magnitude of Risk to Assets	11
4	Review of Published Literature	12
	Corrosive Attack in Organic Media	12

	Corrosion and SCC in Ethanolic Environments	15
	Influence of Water	16
	Influence of Impurities	20
	Corrosion and SCC in Alcoholic Containing Environments	24
	Steel	24
	Ti-Alloys	27
	Zr-Alloys	27
	Stainless Steel	28
	SCC Mechanisms of Steel in Other Environments	29
	Ammonia SCC	29
	Caustic SCC	30
	CO-CO <sub>2</sub> -water SCC	32
	Amine SCC	32
	External SCC of Steel Pipelines	34
<b>5</b>	Review of Company Reports and Experience Survey on SCC in fuel grade ethanol	36
	Materials	36
	Metallurgical & Microstructural Aspects of Cracking in Plate and Pipe	36
	Environmental Parameters	40
	Mechanical Factors	43
	Unpublished Laboratory Studies on SCC in Fuel Grade Ethanol	44
	Study #1	44
	Study #2	44
	Study #3	44
	Study #4	47
	Other Comments	48
	Nature of Ethanol	48
	Experiences with Ethanol	49
	Design and Stress Considerations	49
<b>6</b>	Other Sources of Information	50
	Information from The Materials Technology Institute (MTI) of the Chemical Process Industries	50
	NACE RefinCor Search	51

	1980	51
	1995	51
	1998	51
	1999	51
	2000	52
	2002	53
	Search of News Sources	53
<b>7</b>	Overall Findings and Results	55
	Summary of Important Findings	55
	Gaps Analysis	56
<b>8</b>	References	58
<b>A-I</b>	Appendix I – Bibliography of Literature Obtained for this Study, but not cited in References	62
<b>A-II</b>	Appendix II – Summary of Reported Incidence of SCC in fuel grade ethanol and SSC-Free Service	65
<b>A-III</b>	Appendix III – SCC in fuel grade ethanol Survey Form	70
<b>A-IV</b>	Appendix IV – Analyses of Ethanol from Various Sources	73