A comparative study on the corrosion behaviour of welded and un-welded API 5L X70 steel in simulated fuel grade ethanol

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Abstract: In a bid to mitigate global warming, fuel grade ethanol (FGE) is being increasingly used in the fuel industry. However, there are material compatibility issues. In this study, the effect of Simulated Fuel Grade Ethanol (SFGE) on welded and un-welded API 5 L X-70 pipeline was investigated via gravimetric technique. Mass loss tests showed that the lowest corrosion rate was recorded in E10, whereas the highest corrosion rate was recorded in E40 environment. Statistical analysis reveals that on the basis of two-factor analysis of variance (ANOVA) test results, exposure time, and ethanol concentration significantly affected the corrosion rates of welded and unwelded X70 steel. Morphological examination revealed increased corrosion with an increase in ethanol concentration for welded X70 steel, which compares well with the results from mass loss tests.

Subjects: Mechanical Engineering; Manufacturing Engineering; Materials Science; Chemical Engineering; Clean Tech

Keywords: API; corrosion; SFGE; ethanol

1. Introduction
Alcohol fuels have been around for years, typically mixed with gasoline in a blend (also known as gasohol). E10 (10% ethanol to 90% gasoline) can be used in any internal combustion engine, and many oil companies already blend their fuels that way (Rangel et al., 2016). E10 reduces greenhouse gases by up to 3.9% (Basanta & Ajit, 2016). The use of these fuels in higher proportion requires modification to the fuel storage and delivery systems on cars and trucks. E85, a mixture of 85% ethanol to 15% gasoline, can be used in flex-fuel vehicles. Car enthusiasts have modified their vehicles to run on ethanol or methanol alone, with mixed results. This E85 can reduce the net emissions of greenhouse gases by as much as 37.1%, which is a significant amount. Ethanol, when
used as a gasoline additive, serves both as an octane enhancer and oxygenate to promote complete combustion and reduce harmful emissions (Maldonado & Sridhar, 2007).

However, carbon steel which is a predominant material used in the transportation of fuel ethanol, is highly susceptible to ethanol corrosion and stress corrosion cracking. A significant number of accidents have been reported relating to this failure particularly at end-user terminals and at weld regions (Kane et al., 2005; Lou et al., 2009; Sridhar et al., 2006). A number of investigations have been carried out vis-à-vis this problem (Baena et al., 2012; Beavers et al., 2011; Cao et al., 2013; Goodman & Singh, 2012; Lou et al., 2009).

Breitenbach et al. (2015) evaluated the susceptibility of the API 5 L X70 steel stress corrosion cracking in corn and sugar cane ethanol environments using slow strain rate testing (SSRT). From the research results, it was shown that the carbon steel is susceptible to stress corrosion cracking in corn ethanol environment. However, in sugar cane ethanol environment, the SSRT showed carbon steel’s immunity to stress corrosion cracking. Sridhar (Sridhar et al., 2006) studied the effects of water, acetic acid, oxygen, corrosion inhibitor, chloride, methanol, denaturant, and corrosion products on the stress corrosion cracking (SCC) of carbon steel in ethanol. It was discovered that oxygen produced the greatest effect on causing SCC in the carbon steel. Galvanic contact with pre-corroded steel abated SCC. Also, within the fuel-grade ethanol specification limit, chloride had a less significant effect than oxygen. Electrochemical measurements indicated significant hysteresis in the polarization behaviour of steel in ethanol under SCC conditions.

Joseph, Loto, Sivaprasad, Ajayi, Tarafder et al. (2016) evaluated the influence of sodium chloride (NaCl) on the degradation of micro-alloyed steel (MAS) in E80 simulated fuel grade ethanol environment (SFGE). It was discovered that chloride caused pitting in the MAS after immersion in E80 with chloride. In the absence of chloride, there was no pitting. Also, the fracture resistance of MAS reduced in E80 with an increase in chloride after starting the experiment with a control environment (i.e., E80 with no chloride).

Kane et al. (2004) studied the stress corrosion cracking of API steel in fuel ethanol. It was discovered that the factors that increase corrosivity of fuel ethanol appear to be increased water content and decreased pH, and other potential factors may include sulphur, sulphate, and chloride concentration. Samusawa and Shiotani (2015) investigated the influences of organic acids, chloride, and water on the corrosion behaviour of carbon steel by immersion testing in simulated fuel grade ethanol (FGE) environments. It was discovered that the pitting corrosion factors of the minor contents of ethanol are acetic acid, chloride, and H₂O, whereas formic acid promoted general corrosion. An increase of the chloride ion concentration in the solution promotes pitting corrosion, but its effect is enhanced by an increased amount of coexistent acetic acid. Joseph, Loto, Sivaprasad, Ajayi, Fayomi et al. (2016) investigated the degradation of micro-alloyed steel in E20 and E80 simulated fuel-grade ethanol (FGE) environment. The corrosion rate was determined through mass loss tests and electrochemical measurements. It was discovered that the micro-alloyed steel sample immersed in E20 suffered from crevice and pitting corrosion, whereas when immersed in E80, it uniformly corroded. Also, corrosion rate increased with an increase in the ethanol concentration. It is important to note that surface cracks, holes, and other surface defects can also aggravate corrosion resistance of materials, especially in high-temperature oxidation environment (Abbas, 2006; Abbas & Marin, 2017; Hoby & Abbas, 2018; Zhang et al., 2020, 2017). Hence, the aim of this study is to comparatively investigate welded and un-welded X70 steel for their corrosion behaviour in E10—E40 simulated fuel grade ethanol.
2. Experimental procedure

2.1. Material preparation

The materials used for the work were machined out of a pipeline API 5 L X70 steel of diameter (160 mm) under as received conditions. The chemical composition of the X70 steel includes: 0.162 C, 0.061 Si, 0.266 Mn, 0.011 P, 0.004 S, 0.001 V, <0.002 Nb, <0.001 and the balance Fe. The metal was cut into strips, using a power saw. In order to prepare welded samples, strips were welded in pairs via butt welding using 2.3 mm (upset), 5 V (voltage), and 2 s (flashing time). Mild steel electrode was used for the welding. Afterwards, the welded strips were cut into required dimensions for the immersion test. The samples were dry-abraded using different grades of emery paper (60, 220, 320, and 600 µm).

2.2. Preparation of test environment

The test environments of this study are E10, E20, E30, and E40 simulated fuel grade ethanol environment, which was prepared in accordance with the ASTM (American Society for Testing and Materials International) standard (ASTM-D-4806-01a, 2001) for fuel grade ethanol. The reagents used for the fuel blends include: 5 vol.% of 1 L pure methanol; 1 vol.% of 1 L distilled water; 5.6 vol. % of 1 L acetic acid with purity of 99.8%, 88.4 vol.% of 1 L ethanol and 8 g of sodium chloride (NaCl) with purity >99%.

Figure 1. Variation of corrosion rate with exposure time for welded X70 steel.

Figure 2. Variation of corrosion rate with exposure time for unwelded X70 steel.
2.3. Immersion test

Before immersion, the initial weight of the polished samples was taken via the weighing balance and their dimensions, respectively. The surfaces of the samples were cleaned with acetone, before immersion using a clean cotton wool to avoid scratching the samples. After preparation of material and test environment, the corrosion media were poured into bottles, and the samples
were suspended in the solution for varying days (i.e. 10, 20, 30, and 40 days). Duplicate samples were suspended in solution in order to determine the reproducibility of the experiments. After exposure to the test environment for each test period, the samples were removed from the corrosion media. They were cleaned, allowed to dry, and the final weight of the samples were taken. Corrosion rate was calculated via Equation (1) (Joseph, 2017).

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CR = \frac{(K \times W)}{(A \times T \times D)}
\]

(1)

Where CR is corrosion rate in mils per year (mpy), K is 534, W is mass loss in milligrams, A is sample area in square inches, T is exposure time in hours, and D is density in g/cm³.

3. Results and discussion

3.1. Effect of exposure time and ethanol concentration on corrosion rates

Figure 1 shows an increase in corrosion rate with an increase in exposure time for all the ethanol concentrations. There was a linear progression, which indicates that exposure time had a significant effect on the corrosion rates. A possible inference is that the longer the duration the fuel ethanol mixture spends in storage tanks made of X70 steel, the more the possibility of corrosion of the steel. Corrosion rates are typically low (ranges between 1.5E-05 and 4.0E-05 mpy) for the un-welded pipe steel (Figure 2) as compared with the welded steel (in the range of 2E-05 and 14E-05 mpy). An explanation for this lies in the susceptibility of weld regions to ethanol corrosion and ethanol stress corrosion cracking as explained in the literature (Torkkeli et al., 2013).

Figure 3 shows that an increase in the ethanol concentration of the fuel grade ethanol mixture, resulted in an increase in the corrosion rate of the welded samples relative to exposure time.

| Table 1. ANOVA data for welded X70 steel |
|-----------------------------------------|
| Source of Variation | SS     | Df  | MS    | F     | Significance F (95% confidence) |
| Ex. Time            | 6.73E-09 | 3   | 2.24E-09 | 41.02 | 3.5  |
| Ethanol Conc.       | 5.03E-09 | 3   | 1.68E-09 | 30.67 | 3.5  |
| Residual            | 6.02E-10 | 11  | 5.00E-11 |       |      |
| Total               | 1.237E-08 | 17 |       |       |      |

| Table 2. ANOVA data for un-welded X70 steel |
|---------------------------------------------|
| Source of Variation | SS     | Df  | MS    | F     | Significance F (95% confidence) |
| Ex. Time            | 1.75E-10 | 3   | 6.00E-11 | 4.14  | 3.5  |
| Ethanol Conc.       | 6.3E-11   | 3   | 2.00E-11 | 1.49  | 3.5  |
| Residual            | 1.55E-10  | 11  | 1.00E-11 |       |      |
| Total               | 3.9E-10   | 17 |       |       |      |
A different trend was observed for the un-welded sample scenario (Figure 4) where fluctuations are seen. The statistical significance of this experimental data was determined via the two-factor Analysis of Variance (ANOVA) test also known as the F-test. The aim was to determine if the effect of varying exposure time and ethanol concentration was significant. Tables 1 and 2 show the ANOVA test result. The ANOVA data for welded X70 steel (Table 1) shows that with 95% confidence, exposure time, and ethanol concentration significantly affects the corrosion rate of the steel. On the other hand, Table 2 shows that with the same confidence level, exposure time significantly affects the corrosion rate of un-welded steel, while the effect of ethanol concentration is insignificant when the variation in corrosion rate due to chance is considered.
3.2. Effect of ethanol concentration on surface morphology

For the morphological examination, the tested welded samples were examined under the scanning electron microscope, a TESCAN instrument equipped with Vega TC software and the results are presented in Figures 5–7. Figure 5 shows the morphology of X70 steel in the absence of ethanol. No corrosion is seen which compares well with corrosion rate results. (Figure 6a) shows the surface morphology of X70 in E10 SFGE, mild corrosion is observed. (Figure 6b) shows the surface morphology of X70 in E20. There is increased corrosion on the sample surface. (Figure 7a,b) show severe general corrosion. On the whole, morphological examination revealed increased corrosion with increase in ethanol concentration, which supports the results from mass loss tests.

4. Conclusion

The corrosion behaviour of welded and un-welded samples of X70 pipe steel has been investigated and compared. Corrosion rate of the welded steel was found to be dependent on ethanol concentration and exposure time, whereas corrosion rate of the un-welded steel was dependent on exposure time only. The results were confirmed with 95% confidence via ANOVA F-test. Morphological examination revealed increased corrosion with increase in ethanol concentration, which compares well with the results from mass loss tests.

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