Ethanol Corrosion in Pipelines

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Transportation of ethanol (ethyl alcohol) as a fuel is increasing. This article examines the properties of ethanol, its corrosive properties, and possible pitfalls in identifying them. It also provides general guidelines on the selection of pipeline material to ensure the integrity of the ethanol transport system.

The increasing need for alternative energy has propelled the search for new resources, and one of these is ethanol. The Renewable Fuels Association (RFA), the trade association for the U.S. ethanol industry, promotes the use of fuel-grade ethanol. This includes E-10 (90% gasoline/10% ethanol), reformulated gasoline (RFG), and E-85 (15% gasoline/85% ethanol). The RFA is also developing fuel cell applications and E diesel.

A number of farmers in the U.S. Midwest have started corn-based ethanol plants. This has prompted engineers to think about laying pipelines to transport ethanol.

Pipelines require selecting suitable materials. This necessitates understanding what ethanol is and how it reacts with its environment. This article discusses the reaction of ethanol to commonly used pipeline materials.

Properties of Ethanol

Table 1 shows typical properties of ethanol, including chemical formula, gravity, and vapor pressure.

Corrosion Mechanism

Ethanol carries up to 0.003% vol. acetic acid ($CH_3COOH + H_2O$). Organic acids are corrosive in the presence of moisture, but, in the pure state, do not attack steel. However, plastic and rubber are vulnerable.[1] The acid-forming molecules react with water molecules to create hydrogen ions, which attach to the available electrons on the oxygen atom of water. This is shown in Equation (1).

$$H^+ + \begin{array}{c}\mathrm{H}\\ :\mathrm{O}:\\ \mathrm{H}\end{array} \rightarrow \left[\begin{array}{c}\mathrm{H}\\ \mathrm{H}:\mathrm{O}:\\ \mathrm{H}\end{array}\right]^+ \qquad (1)$$

The product is H_3O^+ or H^+. H_2O is called a hydronium ion.

Acetic acid is monoprotic (containing one ionizable hydrogen atom per molecule). Only one of the hydrogen atoms that is attached to the O atom breaks away from CH_3COOH (hydrogen acetate) as a hydronium ion. The rest of the hydrogen atoms attached to C atoms remain united with the C atoms. The reaction is similar to that described in Equation (2).

$$CH_3COOH + H_2O \rightarrow H_3O^+ + CH_3COO^- \text{ (acetic acid)} \quad (2)$$

The acetic acid in ethanol is not pure. Moisture and other impurities are present, hence it is reactive to most metals. Acetic acid is protic (having a hydrogen atom bound to an oxygen as in a hydroxyl group, or a nitrogen as in an amine group) so it donates the hydrogen ions to the material it contacts. The corrosion reaction is that of low pH solvent, shown in Equation (3).

$$2H^+ + 2e \rightarrow H_2 \quad (3)$$

The pH Factor

Most water (moisture) other than seawater has a pH range between 4 and 10. In this range, the corrosion rate is independent of the pH, and depends solely on the speed of oxygen diffusion on the metal surface. The barrier to this diffusion is the metallic oxide, which is continuously renewed by the corrosion process. As long as the oxygen diffusion is controlling the formation of a diffusion product (corrosion product), any further corrosion is controlled. Oxygen concentration, temperature, and velocity of the flow are the major factors that determine the corrosion rate within this pH range. Several laboratory observations have proven this fact.[2]

At a pH <4, oxygen diffusion is no longer controlling. The corrosion reaction is established in part by the rate of hydrogen evolution. Hydrogen evolution in turn depends on hydrogen overvoltage of various impurities or phases present in specific steels. The rate becomes sufficiently high in this pH range to make anodic polarization a possible contributing factor. Because cementite (Fe_3C), a corrosion product, is a phase of low hydrogen overvoltage, a low-carbon steel (CS) corrodes in acid at a lower rate than does a high-carbon or a low-alloy steel.

The corrosion morphology is little different for weaker organic acids such as carbonic and acetic acid. In these acids, the dissolution of oxide occurs at relatively higher pH levels and the corrosion rate increases, accompanied by hydrogen evolution at pH 5 or 6.[3] The pH is not a good indicator of acid concentration for a weak acid, so overall corrosion rates might be higher than the pH alone might suggest. At a given pH, there is more evolved hydrogen (H^+) to react with and dissolve the barrier oxide film with a weak acid compared to a strong acid.

In practice, the oxide film dissolves, the surface pH falls, and the metal is more or less in direct contact with the acid solution. This may not happen uniformly across the metal surface. In localized areas of small concentrations, the corrosion reaction could be sporadic, causing pitting corrosion in place of the general corrosion that is commonly associated with ethanol.

Ethanol containing acetic acid with little moisture reacts similarly to the reaction of weak acids with a pH level of 5 or 6. Since that pH level is in the alkaline range, the possibility of stress corrosion cracking (SCC) increases, especially if the material is in high tensional stress. Failure of steel from SCC in an ethanol environment is not uncommon.[4]

TABLE 1

Typical properties of ethanol

Chemical Formula	Specific Gravity of Pure Alcohol	Specific Gravity of Ethyl Alcohol at 20 °C	Vapor Pressure
C_2H_5OH	0.789	0.8073	1.59 psi at 70 °F (21°C)

Corrosion Prevention

Prevention of the corrosion in ethanol is possible by creating a barrier between the steel surface and the ethanol. The selection of the proper inhibitor must be done carefully because the selected inhibitor may emulsify and/or foam. The inhibitor should have adequate properties to adsorb to the steel surface to form a strong barrier film.

Another preventive action could be the use of inhibitors that change the properties of the fluid in the carrier pipe. This is achieved by application of the passivation inhibitor to the steel surface. The commonly used passivation compound is a class of poly alkaline polyamines; 5% solution of tetraethylenepentamine is also used as inhibitor as a passivation agent to prevent ethanol corrosion.

Film-forming inhibitors can cause pitting corrosion if adequate dosing is not used. Economizing on these inhibitors could be dangerous.

The subject of selection of the inhibitor is complex and requires several data. Hence the subject is not discussed in detail at this point.

Factors to Consider While Selecting Suitable Line Pipe Material

Ethanol at temperatures up to 200 °F (93 °C) is corrosive to nearly all the known engineering materials.[5] CS can be effectively used with a proper inhibition program. Stainless steel does not have any special edge over CS with good inhibitors.

SCC is another possibility that needs to be considered. The following five characteristics of SCC, identified by Revie,[6] must be kept in mind when selecting material for an environment that is susceptible to SCC:

- Pronounced specificity of damaging chemical environments

- General resistance to or immunity of all pure metal. Pure alloys, however, are susceptible
- Successful use of cathodic polarization to avoid the initiation of SCC
- Inhibiting effect of various extraneous anions added to a damaging environment[7]
- Effect of the metallurgical structure

Steel for new ethanol pipelines should be ductile to minimize the possibility of SCC. API 5L PSL 2 requirements should be specified. The pipeline specification should include requirements for the supply of line pipe; both longitudinal submerged arc welding (LSAW) and helical submerged arc welded seam (HSAW) line pipe could be specified depending on the project requirements.

The line pipe specification should include additional requirements for plate and coil material as listed below. Other specific controls can be added according to the needs of the project.

- Fully killed (Al-Si killed)
- Control of microalloyed elements (%Nb, %V, %Ti) and their total presence
- Low carbon
- Low sulfur, and treated for inclusion shape control
- Steel produced with continuous cast process
- Steel with segregation control
- Controlled rolling process of plates
- Using thermomechanical cooling process to achieve fine grain steel
- Ultrasonic testing (UT) of the plate and full body UT of the pipe
- Hardness testing of the pipe base metal, SAW weld, and heat-affected zone

None of the above requirements should be difficult to achieve by any good steel or pipe manufacturer.

Non-metals and ceramics are another alternative that can be considered, but apart from the handling difficulties, each one has specific properties and must be considered in detail according to the actual environment and application condition.

Conclusions

Transportation of ethanol fuels in pipelines requires knowledge and understanding of the corrosive properties of this fuel. The corrosion mechanisms described in this article need to be considered when specifying pipeline materials and operation. Various inhibitors can be used to prevent ethanol corrosion on metallic pipelines. Careful attention to the factors to consider when selecting pipeline materials will greatly assist the pipeline engineer in the design, operation, and maintenance of an ethanol pipeline.

References

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