Executive Summary

Literature Review

Impact of Gasoline Blended with Ethanol on the Long-Term Structural Integrity of Liquid Petroleum Storage Systems and Components

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EXECUTIVE SUMMARY

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sponsored by

American Petroleum Institute
Washington, DC

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Houston, Texas

Steel Tank Institute
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1. INTRODUCTION

This report summarizes the results of a literature review conducted for the American Petroleum Institute on the impact of gasoline blended with ethanol on the long-term structural integrity of liquid petroleum storage systems and components.

It is anticipated that the use of ethanol in motor fuels will continue to increase. This has generated interest about the potential long-term structural effects of ethanol on liquid petroleum storage systems, including underground storage tanks (USTs), underground piping, and associated components.

The objective of the literature review is to determine the state of industry knowledge and research on the effects of ethanol/gasoline blends on the long-term structural integrity of UST systems and components. This review is intended to assist decision-makers on further research requirements and needed changes or supplements to existing standards for underground storage systems and components used for storing and dispensing gasoline blended with ethanol.

2. LITERATURE REVIEW

Attached in Appendix A are the synopsis' and bibliographic information for all articles reviewed for the project. The report is organized by article index numbers. Reference numbers cited in this report refer to the article index number.

3. FINDINGS

3.1 Overview of Ethanol in Gasoline Fuel

Ethanol is an alcohol produced through the fermentation of biomass, typically corn, although other sources may be used. Ethanol containing some water is called "hydrated"; ethanol that is further processed to remove all water is called "anhydrous". As a fuel oxygenate, ethanol is blended with gasoline to increase the oxygen content of the fuel. The resulting mixture is typically a blend of 10% ethanol and 90% gasoline, conventionally termed "gasohol," although other mix proportions have been used. Ethanol is also used as a volume extender and octane enhancer in gasoline fuels. The term "ethanol fuel" refers to the use of ethanol as the primary

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energy containing substance. Storage systems may be called upon to store any concentration of ethanol. Therefore, while focusing on gasohol, this literature search examines all ethanol blends. Furthermore, studies pertaining to higher concentrations of ethanol are relevant when examining effects of the lower layer of a phase-separated ethanol/gasoline blend.

Methanol, an alcohol produced from natural gas, is also used as an oxygenate or fuel substitute. It has been suggested that methanol studies may be indicative of worst case limits for ethanol compatibility; however, this has not been proven for all materials. Multiple sources indicate that methanol is much more aggressive than ethanol to materials used in fuel storage (49, 97, 130).

Ethanol has been used as an oxygenate in the Midwest for over 20 years (239). Relatively few material compatibility problems have been reported with the use of 10% ethanol blends (56) and no recorded major leak or failure has been directly attributed to ethanol use (248). The most often reported problems are swelling, hardening, or minor leakage of elastomeric seals and o-rings (66). Notwithstanding this experience, there is interest to determine the long-term effects of exposure of storage system materials to ethanol/gasoline blends and to determine if there are legitimate concerns about possible leaks in the system due to shrinkage and cracking of seals and o-rings in dispensing equipment in systems that are switched from ethanol service to non-ethanol service.

3.2 Phase Separation and Water Bottoms

Water and gasoline are immiscible, and phase separation will result from almost any quantity of water in gasoline, separating into water and gasoline layers. The lower water phase is termed “water bottom” in fuel tanks. Unlike gasoline, alcohol is a polar molecule and will therefore mix readily with water, up to various levels of saturation depending on other soluble and suspended components in the mixture. Alcohol is also miscible with gasoline but has a higher affinity to water than to gasoline and will adhere preferentially to the water. If sufficient water is present, the ethanol and water will separate from the gasoline. This process is called phase separation and will occur at approximately 0.5% water content for 10% ethanol / 90% gasoline blends (58, 106). The blend separates into an alcohol/water lower phase (water phase) and an upper phase consisting of gasoline with a slightly reduced alcohol concentration (hydrocarbon phase) (186). No study reports the exact composition of each phase, but one paper states that the

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lower layer consists of 75% ethanol, cosolvents, and 25% water (124, 135).

Phase separation is a concern because it creates an alcohol rich water bottom, which can increase the potential for localized corrosion of steel tank walls (50, 124). Higher corrosivity has been attributed to increased oxygen content and increased conductivity of the ethanol/water phase (50, 73, 135). No test data are available to quantify the change in the conductivity and associated corrosion rate in alcohol-rich water bottoms. Other effects include the dissolution of corrosion by-products by the alcohol (55, 56, 58), thus exposing the metal to continued corrosive activity, and the presence of other fuel components in the ethanol/water phases (such as acetic acid) that accelerate corrosion rates (161). Conversely, one study indicates that alcohol-rich water bottoms are no more corrosive than non-alcohol water bottoms (55). However, the study did not include the effects of impurities in the solution. The higher alcohol content in water bottoms may be locally detrimental to FRP tank walls that are qualified only for low alcohol blends; however, no such problems have been reported or evaluated in the literature.

In order to reduce the likelihood of phase separation, efforts must be taken to avoid water infiltration into systems containing ethanol/gasoline blends (44). Tanks should be free of water prior to initial filling and all precautions should be taken to minimize the potential for water infiltration and condensation in the tank (58). Removal of the water layer is recommended by API (132). Manual and automatic methods are available to detect the presence of a water phase in buried tanks (177).

One article suggests that the presence of ethanol reduces the likelihood of water bottoms by maintaining the water in solution (295). The dissolved water is carried out of the system with fuel consumption. This mechanism relies on small quantities of water entry as required by current specifications such that the water quantity does not exceed the threshold for phase separation.

Microbial growth in storage tanks can be fostered by water bottoms (177, 243). Microbial contamination can affect both certain metallic and non-metallic materials. Microbes, both bacterial and fungal, can enter a storage system through fuel transfers, vents, and equipment and can grow wherever water is present, for example at the fuel/water interface in water-bottoms and on the upper walls and ceilings of tanks where condensation is prevalent.

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Microbial growth can be controlled through cleaning and use of biocides (254, 243). Existing literature suggests that ethanol may increase the occurrence of microbial attack, but provide no specifics on the extent of reported increase (243).

3.3 Fiberglass Reinforced Plastic (FRP) Tanks

FRP tank laminates are composites of thermosetting resins and glass fibers. Some thermosetting resins (e.g. orthophthalics) do not perform well in alcohols and alcohol fuels (20, 201), and are not known to have been used for this service. Resins typically used in FRP tanks (e.g. isophthalics, terephthalics, and vinyl esters) exhibit some level of swelling (with weight gain) and softening when exposed to alcohols, including ethanol (20, 50, 56). Methanol produces more pronounced effects than ethanol (148), and ethanol/gasoline mixtures may be more aggressive than pure ethanol (20, 50). Softening can be measured as reduction in hardness and material stiffness, which can be measured by mechanical tests for Barcol surface hardness and modulus of elasticity. These physical changes are a function of permeation, which can be measured by absorption and swelling tests, and are largely reversible if the laminate is allowed to dry (18, 22, 24). After desorption of alcohol, some permanent loss of mechanical properties may occur, but the mechanism is not well defined (22). Reduced stiffness, along with creep, results in a lower resistance to buckling, a key design criterion for FRP tanks. This behavior may affect the adequacy of safety factors for buckling design of FRP tanks exposed to ethanol/gasoline blends (50).

The U.S. standard governing the manufacturer of FRP underground storage tanks (UST) is Underwriters Laboratories (UL) 1316 “Glass-Fiber-Reinforced Plastic Underground Storage Tanks for Petroleum Products, Alcohols, and Alcohol-Gasoline Mixtures” (107). The standard was first published in 1983. Since 1987 this standard has required long term (180 days) immersion tests on FRP tank laminates in ethanol and ethanol/gasoline blends for tanks intended for that service. Prior to the 1987 edition, the standard did not require testing for ethanol or other alcohol exposure. The current standard does not require tanks intended for petroleum products only to be tested for alcohol immersion. For tanks intended for ethanol/fuel mixtures, after high-temperature, double-sided exposure of test specimens, the material must retain 50% of its short-term flexural strength and stiffness, and impact resistance when test results are extrapolated to 270 days (107).

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