

Ethanol-Water Phase Separation White Paper

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Background

The use of ethanol as a fuel in the United States has significantly increased over the past decade. Today, greater than 80% of all retail gas stations in the US blend gasoline with up to 10% ethanol (E10). Ethanol is a renewable fuel, and has been highlighted by the national Renewable Fuels Standard as a primary method of achieving the renewable fuels goal. Ethanol is also an octane booster, and E10 fuels rely on the ethanol content to achieve octane levels.

Water Intrusion

Fuel is typically stored in underground storage tanks (UST) and it is common for water to find its way into these tanks. Prior to the use of ethanol, water entering the tank would drop through the fuel and find its way to the bottom of the tank where it could be detected and removed before it would be picked up by the pumping system and delivered into a vehicle. Pure water is heavier, or denser, than gasoline-based fuels. The following table shows the density of various fluids at 15°C (59°F):

| Fluid | Density (kg/m³) |
|--------------|-----------------------------------|
| E10 gasoline | 690-785 |
| Pure ethanol | 789 |
| Water | 998 |

Table 1: Density of various fluids

Ethanol is a hydrophilic compound, which means it naturally attracts water. Therefore when water enters a tank containing an ethanol blended fuel, the water will eventually be absorbed by the ethanol. The amount of water that is absorbed in the fuel versus falling to the bottom is a function of the rate of water flow into the tank along with the amount of mixing that occurs. Full absorption usually requires some kind of mixing such as that provided during a fuel delivery to a UST. Table 2 highlights many common reasons for water intrusion in an underground storage tank, and the rate at which water flows into a tank.

| Source of Water Intrusion | Rate of water flow into tank |
|---|------------------------------|
| Water in delivery of fuel | Instant |
| Existing water in tank when switching from neat/pure gas to ethanol-blended gas | Instant |
| Water in delivery spill bucket released into tank | Quick |
| Delivery riser cap not replaced after delivery, rain water entry | Quick |
| Hole in vent cap / line, rain water entry | Varies |
| Leaky tanks / Groundwater entry | Slow |
| Degraded or cracked seals of sump lid | Slow |
| Condensation of water vapor | Slow |

Table 2: Sources of water intrusion in an underground storage tank

How Phase Separation forms

Water in the tank will continue to be absorbed into the ethanol-blended fuel until it reaches a saturation point. With E10 fuel at 15°C, this saturation point is at approximately 0.5% water to the volume of fuel. Once the blended fuel reaches this saturation level, the ethanol-water mixture separates from the fuel and falls to the bottom, since its density is now higher than the fuel with which it is mixed. This separated layer is commonly known as ***Phase Separation***. The phase separation layer typically contains 3-4 parts of ethanol for each part water. For a 10,000 gallon tank that is 60% full of fuel, it will take approximately 30 gallons of water to cause full phase separation of the fuel, and the resulting layer will contain approximately 120 gallons of ethanol which would be about 5 inches in height assuming a 10-foot diameter tank.

An alternate phenomenon can occur with far less water than that needed for phase separation. As previously discussed, some of the water will drop directly to the bottom of the tank as it enters. This water will pull some quantity of ethanol from the fuel as it passed through it. This water-ethanol mixture will then pull additional ethanol from the surrounding fuel over time, increasing in volume and resulting in a mixture that is very similar to phase separation. We refer to this layer as ***Partial Phase Separation***. Partial phase separation can occur with far less than 0.5% water. The resulting layer may contain less ethanol than normal phase separation, making it more dense. Additionally, this layer is somewhat temporary in nature; if the tank of fuel is thoroughly mixed (say, during a delivery), the ethanol-water will likely be reabsorbed back into the fuel, and the partial phase separation will disappear. Studies have shown that a small amount (~1”) of phase separation can be quickly remediated by scheduling a delivery of fuel; however, the resulting mixture may contain higher concentrations of absorbed water, pushing it closer to Phase Separation.

Effects of Phase Separation

There are three negative effects of phase separation:

1. Damage to petroleum equipment infrastructure
2. Damage to customer vehicles and station brands
3. Out of spec or unsellable fuel

1. Damage to petroleum equipment infrastructure

Phase separation contains a lot of ethanol, some water, and a small amount of gasoline. Let's assume a typical ratio of 75% ethanol, 20% water, and 5% gasoline. This mixture is highly corrosive compared to pure water or E10 gasoline; there are some concerns that phase separation may even be more corrosive than 100% ethanol. Some tanks may not be compatible with this ethanol-rich, corrosive liquid. Depending on the composition of the tank, phase separation sitting in the tank may slowly deteriorate the integrity of tank walls, increasing the risk of a leak into the environment.

Beyond the tank, other elements of the storage and delivery system (piping, dispenser, submersible turbine pump) may also be at risk if the phase separation levels rise to the point where it is picked up by the pumping system. Each of these can also have environmental and financial concerns, as their replacement can be expensive and damaging to the environment if not detected. Ideally, a station owner would want to know about any occurrence of phase separation as fast as possible, allowing them to quickly remediate to reduce the exposure to potential deterioration.

2. Damage to customer vehicles and station brands

As mentioned in the example described earlier, a 10,000 gallon tank with 6000 gallons of fuel that has recently had phase separation is likely to have up to 5" of the separated layer. Typically, submersible turbine pumps set their intake at around 5"-6". This leads to a significant chance that phase separation will enter the pumping system, travel through the piping, dispensers, and ultimately into customer vehicles. Phase separation in most vehicles will cause engines to stall, leaving disabled vehicles at the station. Affected vehicles will require repairs (usually at the station owner's expense). Of course, owners of the damaged vehicles are understandably upset, and typically share bad experiences with their friends and family. Thus, the station suffers a hit in their brand and customer loyalty. The problem can be much further exasperated if the local news media pick up the story. In this case, the station may lose significant business that is difficult to recover, and the fuel marketer takes a considerable hit to their brand.

Remediation of the problem at this point, beyond the damage to customer vehicles and brand, includes purging the piping system, replacing dispenser filters, and possibly disposing of the entire tank of fuel, which can easily cost thousands of dollars.

3. Out of spec or unsellable remaining fuel

The octane of pure ethanol is approximately 113, which makes ethanol an octane booster. Most companies that are blending 87-octane E10 gasoline will blend with pure gasoline that is below 87 octane, because the 10% ethanol will boost the octane level to 87. However, once phase separation occurs, the remaining fuel is depleted of ethanol, which will lower the octane. Depending on how much phase separation occurs and how much ethanol is pulled out of the fuel, the remaining fuel may be out of specification due to a reduced octane level. In this case, even if the phase separation is removed from the bottom of the tank, the remaining fuel is not legally sellable.

Current Detection Methods

Most station owners typically use one or more of the following methods to detect phase separation, each of which has limitations:

1. Automatic Tank Gauge / Monitor with water detection
2. Water-finding paste
3. Dispenser filters

1. Automatic Tank Gauge with water detection

Figure 1 shows a typical underground storage tank. The center of the tank contains a magnetostrictive probe, which is a component in an automatic tank gauge (ATG). This probe is wired to a console, which is typically mounted in the back office of a gas station. Querying the console allows the user to determine various parameters in the underground tank. In particular, there are floats for fuel and water that determine the respective levels of each. The water float is typically tuned for a density that will certainly lift in water but not in other lighter fluids (such as gasoline or diesel). Note that in this figure, there is water at the bottom of the tank, and the water float has lifted accordingly. This information is sent to the tank gauge console so that the station operator can read the height information and react as needed.

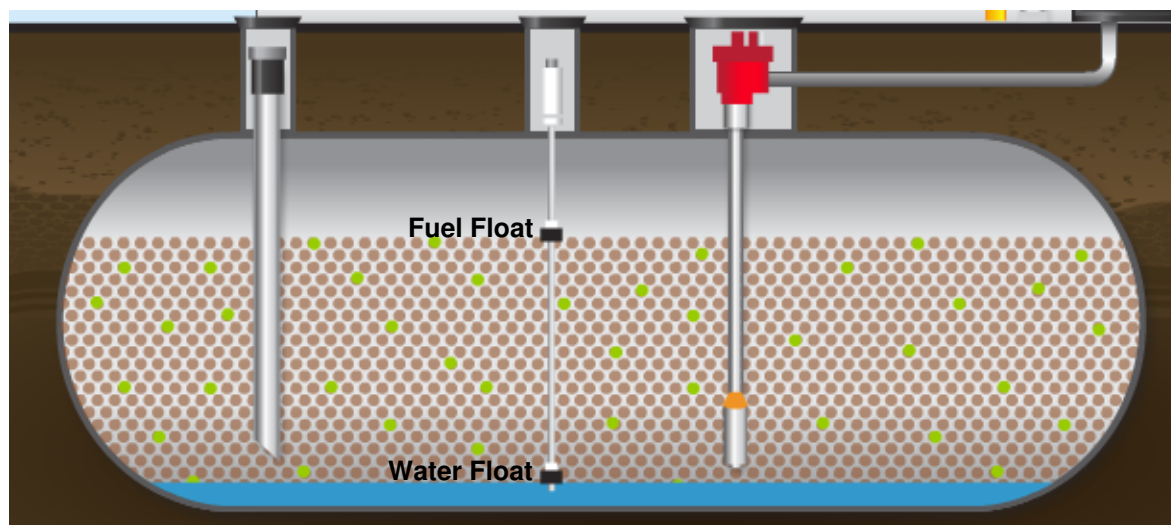


Figure 1: Underground storage tank with fuel and water floats

Phase separation has a density range of 800-850 kg/m³ at 15°C, depending on the density of gasoline, the blend of ethanol in the gasoline, and the ratio of ethanol to water. Water floats are typically tuned to a density greater than 800 kg/m³. The net effect is that while the water float will rise in water, it may not rise in a phase separation mixture. This is the fundamental problem with ATG-based solutions for the measurement of phase separation. While these solutions work extremely well for the detection of water in various fuels, the addition of ethanol causes the water to transform to a lower density mixture, which may not always be detected. The station operator that is counting on the level reading of the water float on their ATG to alarm them of an issue is effectively blind to a problem if the water float is sitting at the bottom of a tank, indicating no water when in fact there may be several inches of phase separation in the tank.

One may wonder why the water float is not tuned to a density level between the highest density of gasoline and the lowest density of phase separation. Each of these density ranges reported in Ethanol is a hydrophilic compound, which means it naturally attracts water. Therefore when water enters a tank containing an ethanol blended fuel, the water will eventually be absorbed by the ethanol. are at a nominal temperature of 15°C. As the temperature rises and falls, the densities change significantly. It is possible to see a very high density gasoline (say 820 kg/m³) under extremely cold conditions and very low density phase separation (say 780 kg/m³) under extremely hot conditions. Under these scenarios, it's impossible to select a single density for the water float that will always rise in phase separation and will never rise in gasoline.

2. Water-finding Paste

A common method of detecting water in a tank is to apply a special water-finding paste to the end of a stick and dip the stick into the tank, a process known as “sticking” a tank. A change in the color of the paste (varies based on paste manufacturer) may indicate the presence of water in the tank. In recent years, these paste manufacturers have added variations that will detect phase separation.

There are multiple issues with these pastes. The first is that they are difficult to interpret. The change in color is sometimes subtle, and operators are not always given enough training to properly interpret the changes of color. Multiple factors may affect the color change, such as the duration of exposure in the tank, thickness of the applied paste, operator training and the outdoor conditions (rain, snow, etc.), making the paste-based solutions inconsistent.

Secondly, the paste-based solution is only effective when used regularly. Some companies have policies where store operators are expected to stick the tank once or twice a week. Even if they did it at these frequencies (and many stations do not), phase separation can occur any time and can quickly grow. These stations would have to be extremely lucky to actually stick the tank at the moment that phase separation formed and before it caused damage to their customers' cars and their business.

3. Dispenser filters

Each gasoline dispenser usually has a disposable filter inside it that filters out unwanted particulates prior to the fuel reaching the nozzle and customer vehicle. Some of these filters will also filter out water, by quickly constricting once water is detected. The result is a very slow flow of fuel out of the nozzle. Therefore, slow flow is a potential indication of water reaching the dispenser. In recent years, these filter manufacturers have developed more complex filters that will also constrict with phase separation.

As with water-finding paste, there are multiple issues with dispenser filters. The first is that the filters do not work instantaneously; in other words, they do not go from a state of “full flow” to “no flow” in zero seconds. Even the quickest of filters take a minute or two to completely close up. In that time, the filters may still allow some contaminated fuel (i.e. phase separation) to pass through and enter customer vehicles. While they may reduce the damage, they do not completely eliminate the potential to get phase separation in a vehicle.

By the time phase separation is detected by a dispenser filter, it has already accumulated in significant volume, leading to much larger remediation costs. In order for phase separation to enter the dispenser, it must have gone through the tanks pumping system and piping. That also means that the tank must contain 5-6 inches of phase separation. To remediate this problem, the piping must be purged of phase separation and dispenser filters changed. The remaining fuel is significantly stripped of ethanol and much more likely to be out of spec. And the extended exposure of phase separation to tanks and piping may accelerate any potential corrosion issues in the petroleum infrastructure.

The newer filters that are rated for phase separation are more discriminating, using finer filter openings. Customer feedback indicates that many station owners that switch to this phase separation filter find that their filters get clogged more quickly, sometimes for reasons unrelated to phase separation. Thus the station owner needs to increase the frequency of filter changes, costing time and money.

Veeder-Root Solution

In an ideal world, a station would never get phase separation, or would be alerted when conditions for phase separation occurring are increasing, giving station operators the ability to preventatively react to the problem. Today, we are not aware of any predictive-based solution for phase separation.

The next best alternative to prediction is automated, continuous early detection. If a station is alerted of phase separation in a tank as soon as it occurs, it can quickly take action, which will preserve the tank infrastructure and keep phase separation far away from customer vehicles.

Veeder-Root has recently developed such a solution. Veeder-Root completed an extensive research and development program resulting in the industry’s first tank gauge based solution that identifies phase separation as it occurs in ethanol blended gasoline. Veeder-Root focused on a solution that would be compatible with existing installed equipment and would not adversely



affect the minimum detectable product height, which could cause the station to lose visibility to a large amount of fuel at the bottom of the tank.

Veeder-Root's innovative phase separation detector uses multiple densities to differentiate between heavy gasoline and light phase separation, which could have similar densities and confuse current industry solutions. The solution was designed to positively detect phase separation, while minimizing false alarms due to high density gasoline.

Conclusion

The prevalence of ethanol-blended fuels is increasing the incidence rate and awareness of the phenomena of phase separation. Proposed increases in the ethanol blend levels will further elevate a stations' risk to phase separation. These risks include damage to the petroleum infrastructure, damage to customer vehicles and station brand equity, and the potential to be left with unsellable fuel. The adoption of Veeder-Root's new detection solution will provide early detection of phase separation and allow station operators to react quickly, thereby reducing their potential risk and cost of remediation.