



Treatise on Alcohol-Blended Gasoline: Phase Separation and Alcohol Monitors

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Introduction and Phase Separation

Alcohols¹ have been added to gasoline as an octane booster, an oxygenator, a means of extending the fuel supply, and replacing ethers such as methyl tertiary butyl ether (MTBE). While these are all good things, alcohol has one major issue. Water and alcohol are fully miscible and this can cause the alcohol and water to separate from the gasoline and form two distinct layers. This is a process commonly termed *phase separation*.

During phase separation, the alcohol is partially removed from the gasoline forming a denser bottom layer composed of alcohol, water, and alcohol-soluble hydrocarbons. The upper less dense layer is gasoline rich partially depleted of alcohol and alcohol-soluble hydrocarbons (Gramajo de Doz *et al.*). This presents two problems. The first is the possibility that the bottom layer can be stirred up and pumped into a vehicle and stall the engine. The second is that the upper layer will be reduced in octane value and may no longer meet specifications (Owen and Coley).

The point of phase separation is controlled by several factors: the type of alcohol, the amount of alcohol, the presence of cosolvents, the temperature, the hydrocarbon composition of the gasoline, and the amount of water (Owen and Coley). Each of these factors will be discussed in turn. Water content and temperature will be discussed first because they are the two main variables.

Water Content

Water and alcohol are infinitely soluble in one another at room temperature (API). The alcohol in the fuel will take up water to a certain point and the alcohol, water, and gasoline will coexist. If this coexisting mixture enters a vehicle, then the water will convert to steam during fuel combustion and exit as part of the exhaust. However, if water continues to accumulate in the tank, then the point of phase separation may be reached. At this point the water, alcohol, and gasoline will no longer coexist.

Water content is the most important controlling variable. If there was no water in the fuel mixture, then the other variables would not matter. In general, as the water content increases the closer the fuel gets to phase separation. For this reason, the percent water content is placed on the horizontal axis on the generic graphs² that will follow. Since water is so important a discussion of how water can enter a tank follows.

Loose fill caps, leaky fittings and faulty gaskets are points of entry for water. For this reason, inspect gaskets and fittings at regular intervals for failures. Also ensure that fill caps are in good working order and that they are always properly closed after opening.

¹ Although other alcohols have potential to be used in fuels such as isopropanol and t-butanol, this paper is primarily concerned with methanol and ethanol.

² The graphs in this book are based upon data presented in: Owen, K. and Coley, T. (1995) Automotive Fuels Reference Book, 2nd ed., SAE, Warrendale, PA. 276-278 which uses gasoline that is 26% aromatic hydrocarbons. Also, the graphs in this book show simple straight lines whereas the actual data produces a slightly curved line.

Low points and basins are places where rain water and other types of water can accumulate. This can occur around the fill gauge manhole or in the secondary containment submersible pump pit. Care should be taken to ensure that these areas remain as dry as possible.

Vents are another area where atmospheric moisture has a potential to enter the tank. Every time the tank inhales it draws atmosphere in. If the tank is cooler than the atmosphere, then the atmospheric moisture can condense inside the tank and join the fuel. Alternatively, the hygroscopic nature of alcohol will desiccate the atmosphere that enters the tank.

A leak in the tank or the lines will allow moisture to enter the tank; this is especially true of underground storage tanks. After raining, vadose water has the potential to flow toward the tank and enter it. If the tank is below the water table, then phreatic water can enter the tank. The bad thing about this is that the fuel also has the potential to exit the tank and contaminate the surrounding soil and groundwater.

Essentially every time the tank is open, there is a potential for water to enter. Care must be taken every time the tank is opened for service or filling to ensure no water enters. Although care may be taken, atmospheric moisture still has the potential to enter through vents and every time the tank is opened.

Temperature

Temperature impacts the water tolerance of alcohol-blended fuels and as such occupies the vertical axis on the general graphs seen below. As temperature increases the amount of water needed for phase separation increases. This simple rule brings about some complicating factors that will be discussed below.

Figure 1 shows a general phase separation diagram for ethanol-gasoline blended fuel containing 10% ethanol. This fuel type is commonly referred to as E10. Please note that this is general because we are not considering the hydrocarbon content of the fuel or any cosolvents. On this diagram, water content as a percentage of total fluid volume is on the horizontal axis and is increasing to the right. Temperature is in degrees Fahrenheit and is increasing toward the top on the vertical axis. The line on the graph represents the threshold at which phase separation occurs and is termed the phase separation line. Any combination of temperature and water content that falls above the phase separation line will be a combustible motor fuel. However, any combination of temperature and water content that falls on or below the line will result in phase separation.

The internal temperature of a fuel tank can be different from the ambient air temperature. This is especially true for an underground storage tank. What this means is that some complicated scenarios are possible. One such scenario is what can happen when the storage tank temperature is different than the onboard vehicle fuel tank. Another is a fuel tank at constant temperature with an increasing moisture content. Yet another occurs in a fuel tank with a constant moisture content and variable temperature.

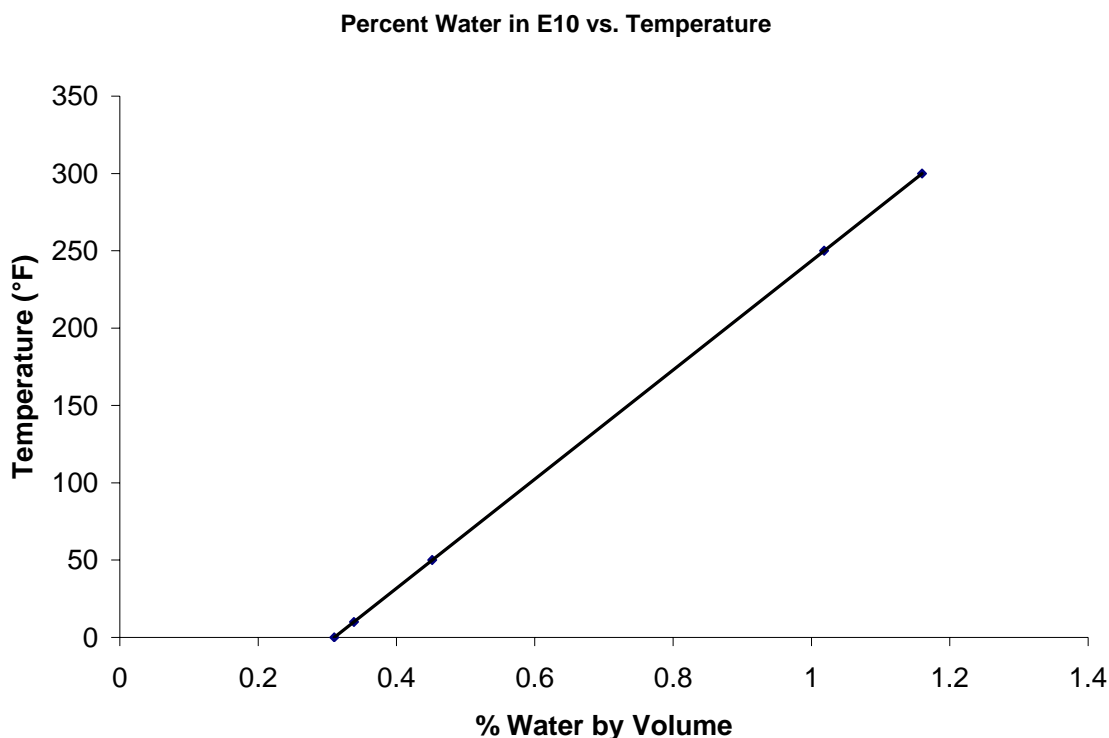


Figure 1: Graph showing the general relationship between water content and temperature³. This graph based upon Krause. All variables are unknown except for water content, temperature, and alcohol concentration.

In the first scenario we will take a tank of E10 sitting in an underground storage tank. The fuel in the underground storage tank is at 50°F and has 0.5% water content by volume. This corresponds to the red dot in figure 2. The position of the red dot is below the phase separation line and thus the fuel in this tank is not a combustible motor fuel. However, it is summer and the onboard vehicle fuel tank is at 75°F. Assuming that there is no fuel or water in the vehicle tank, then the fuel containing 0.5% water content by volume will warm to 75°F. The E10 fuel will now be at the point represented by the blue dot with coordinates of 0.5% water and 75°F. This new point is above the phase separation line and the fuel in the onboard vehicle fuel tank will remix due to the turbulence of the pumping process. Fortunately, this fuel will be combustible and the vehicle will be fine. Please realize that this is an ideal situation and that the reversal of phase separated fuel is not guaranteed in the field by this method and that the amount of mixing between the two phases may not generate the remixed fuel will have the same alcohol content or octane rating as the original tank contents.

The second scenario is much like the first except that it takes place in winter. Taking the same underground storage tank at 50°F and placing the same E10 fuel in it but with 0.4%

³ The temperature on many of the graphs in this text has been extrapolated beyond the boiling point of ethanol under standard conditions to demonstrate the fact that there is a point at which increasing the temperature will not reverse phase separation.

water content by volume we end up at the red dot on figure 3. The red dot is located above the phase separation line and this fuel is a usable motor fuel. As above, the vehicle receiving the fuel has an empty and moisture free tank but is at 25°F. The fuel in the onboard vehicle fuel tank is now at 25°F with 0.4% by volume water content. This point is represented by the blue dot on figure 3 and is below the phase separation line. When the vehicle owner goes to start the vehicle, the denser non-combustible alcohol rich phase will be injected into the engine first causing the vehicle to stall.

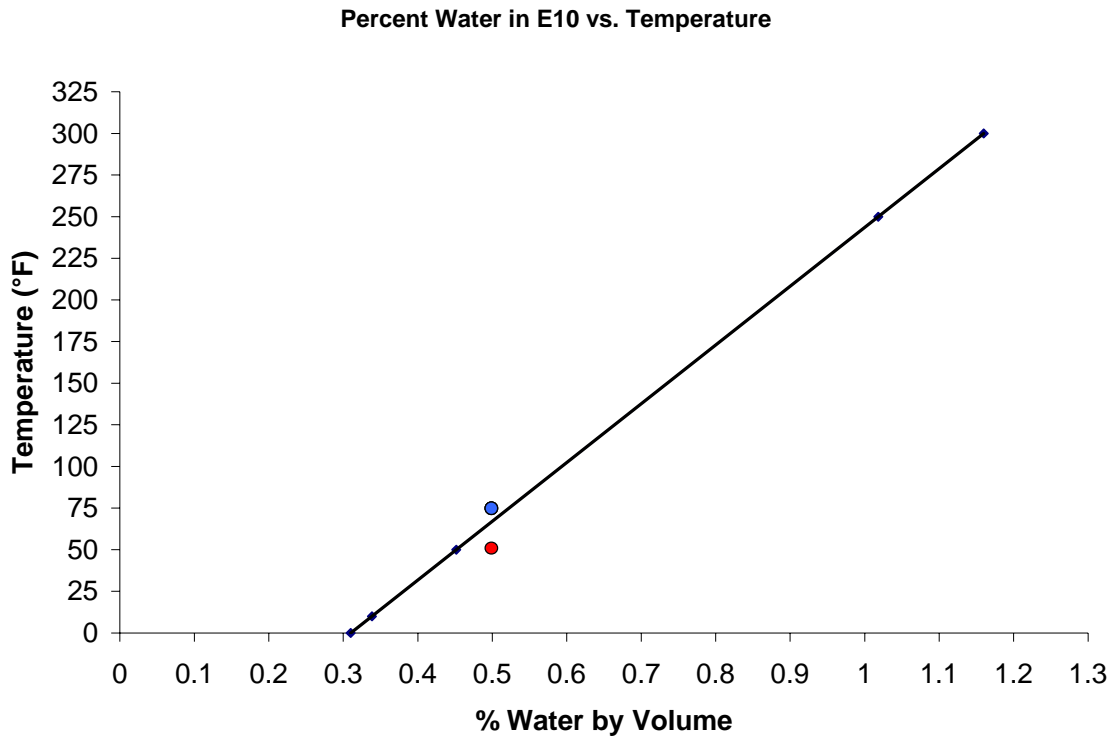


Figure 2: Graph showing an ethanol-gasoline blended fuel that contains 0.5% water by volume and what happens when the fuel is warmed from 50°F to 75°F.

The second scenario is much like the first except that it takes place in winter. Taking the same underground storage tank at 50°F and placing the same E10 fuel in it but with 0.4% water content by volume we end up at the red dot on figure 3. The red dot is located above the phase separation line and this fuel is a usable motor fuel. As above, the vehicle receiving the fuel has an empty and moisture free tank but is at 25°F. The fuel in the onboard vehicle fuel tank is now at 25°F with 0.4% by volume water content. This point is represented by the blue dot on figure 3 and is below the phase separation line. When the vehicle owner goes to start the vehicle, the denser non-combustible alcohol rich phase will be injected into the engine first causing the vehicle to stall.

A third scenario simply involves the fuel tank itself and a variable moisture content. For the purpose of simplicity the underground storage tank will be at a constant 50°F. Figure 4 shows the same general graph but has a horizontal line on it that represents 50°F.

Starting with a moisture free fuel we have a point that is clearly above the phase separation line. As the moisture content increases we must move to the right along the 50°F line. At 0.2% water, we are still above the phase separation line and the fuel is still usable as a motor fuel. By the time the moisture content reaches 0.45% the phase separation line is met and the fuel phase separates. Continuing to increase the moisture content will have no appreciable affect on phase separation but will continue to grow the volume of the phase separated layer as additional alcohol is stripped from the top layer.

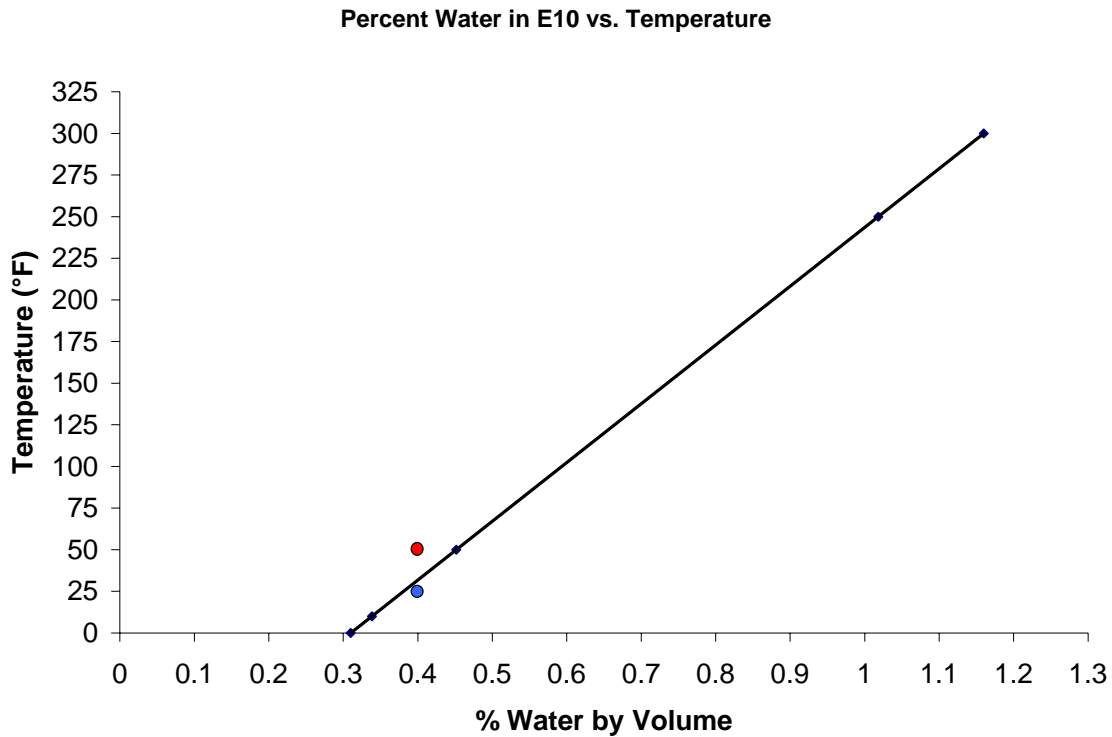


Figure 3: Graph showing an ethanol-gasoline blended fuel with 0.4% water content by volume being cooled from 50°F to 25°F.

A third scenario simply involves the fuel tank itself and a variable moisture content. For the purpose of simplicity the underground storage tank will be at a constant 50°F. Figure 4 shows the same general graph but has a horizontal line on it that represents 50°F. Starting with a moisture free fuel we have a point that is clearly above the phase separation line. As the moisture content increases we must move to the right along the 50°F line. At 0.2% water, we are still above the phase separation line and the fuel is still usable as a motor fuel. By the time the moisture content reaches 0.45% the phase separation line is met and the fuel phase separates. Continuing to increase the moisture content will have no appreciable effect on phase separation but will continue to grow the volume of the phase separated layer as additional alcohol is stripped from the top layer.

The fourth scenario to be covered is an underground storage tank with a constant moisture content and variable temperature. Figure 5 shows the same general graph but with a line that represents 0.5% water content by volume. As long as the tank

temperature remains above 67°F the contents of the tank will be a usable motor fuel. However, if the temperature falls below 67°F, then the fuel will phase separate. If the tank then warms back up to some temperature above 67°F the two layers will start to mix and reverse the phase separation.

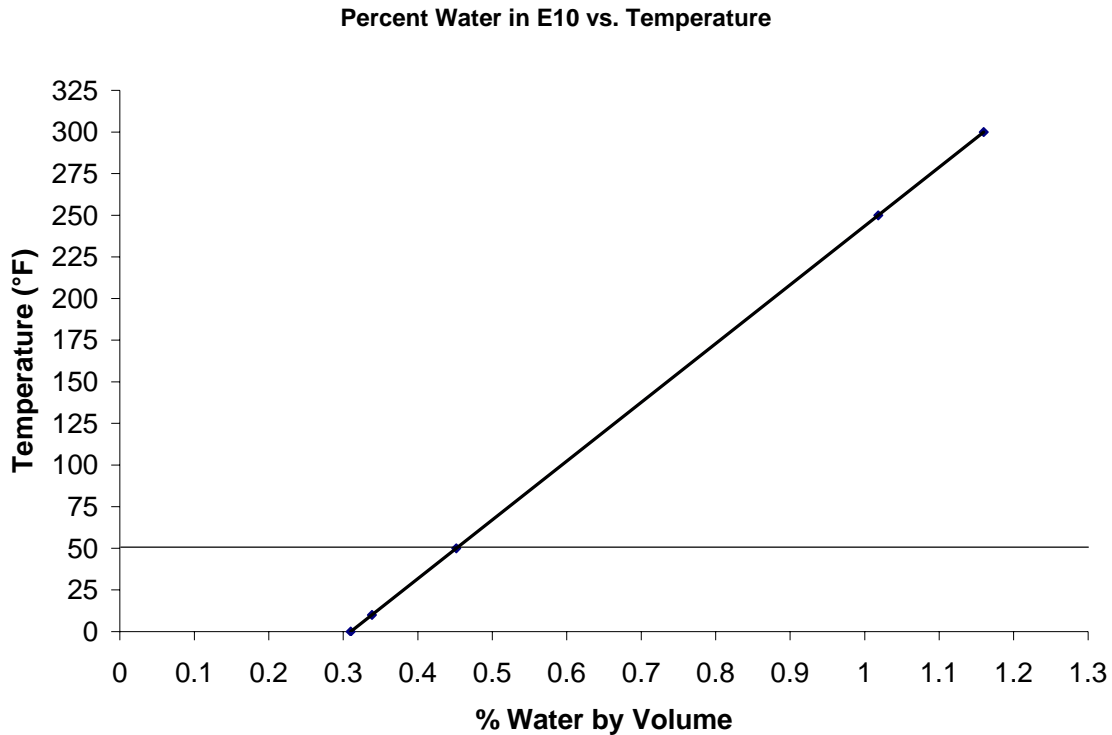


Figure 4: Graph showing how phase separation is impacted by a rise in moisture content.

The fourth scenario to be covered is an underground storage tank with a constant moisture content and variable temperature. Figure 5 shows the same general graph but with a line that represents 0.5% water content by volume. As long as the tank temperature remains above 67°F the contents of the tank will be a usable motor fuel. However, if the temperature falls below 67°F, then the fuel will phase separate. If the tank then warms back up to some temperature above 67°F the two layers will start to mix and reverse the phase separation.

Please note that these scenarios are ideal. In the field the situation will be much more complex. Vehicles will likely have fuel in their tanks when filling up and there is no guarantee that the onboard fuel tank will be moisture free. Other variables that impact phase separation also have to be considered. Cosolvents and additives, difference in alcohol concentration, hydrocarbon content of the fuels, and possible different alcohols in the fuels that exist at the filling station and in the onboard vehicle tank can result in two different phase separation lines. One phase separation line for the storage tank and one phase separation line for the onboard vehicle fuel tank should be expected due to the possible differences in fuel chemistry. It should also be expected that a third phase separation line will result due to the mixing of the fuel in the onboard vehicle fuel tank

with the fuel from the storage tank. To further demonstrate how complex phase separation is, the remaining phase separation graphs will use motor fuels that are 26% aromatic hydrocarbons; which will produce completely different graphs than what is seen above.

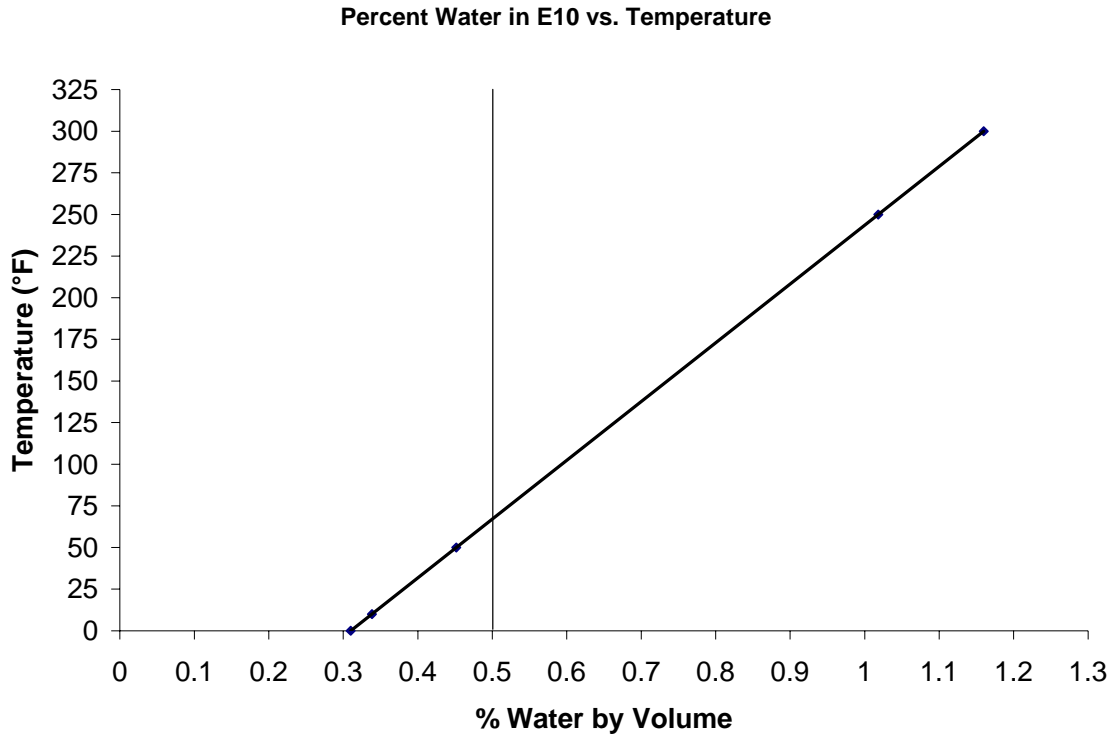


Figure 5: Graph showing the effect of temperature on phase separation when the fuel has a constant moisture content.

Alcohol Concentration

The phase separation line will move with the alcohol content of the fuel. As a general rule of thumb, for alcohol concentrations of 20% or less, the greater the proportion of alcohol the more water it will take to cause phase separation (Owen and Coley). However it is actually a little more complex than that. The phase separation line also tends to decrease in slope with increasing concentrations of alcohol (Owen and Coley). There is also a temperature at which the phase separation lines for two different concentrations of alcohol cross (Owen and Coley). At this temperature the two concentrations of alcohol will phase separate at the same concentration of water. Below this crossing point the general rule of thumb reverses.

The crossing point for two ethanol phase separation lines is generally much lower than that of two methanol phase separation lines. Figure 6 shows a generalized graph of three blends of ethanol-gasoline. The blue line represents 5% ethanol by volume or E5. A 10% blend or E10 is represented by the pink line and a 15% blend or E15 is represented by the yellow line.

The graph clearly shows that the slope gets steeper as the ethanol concentration decreases. This generates another scenario. A scenario that might take place due to ethanol shortages is worthy of discussion here.

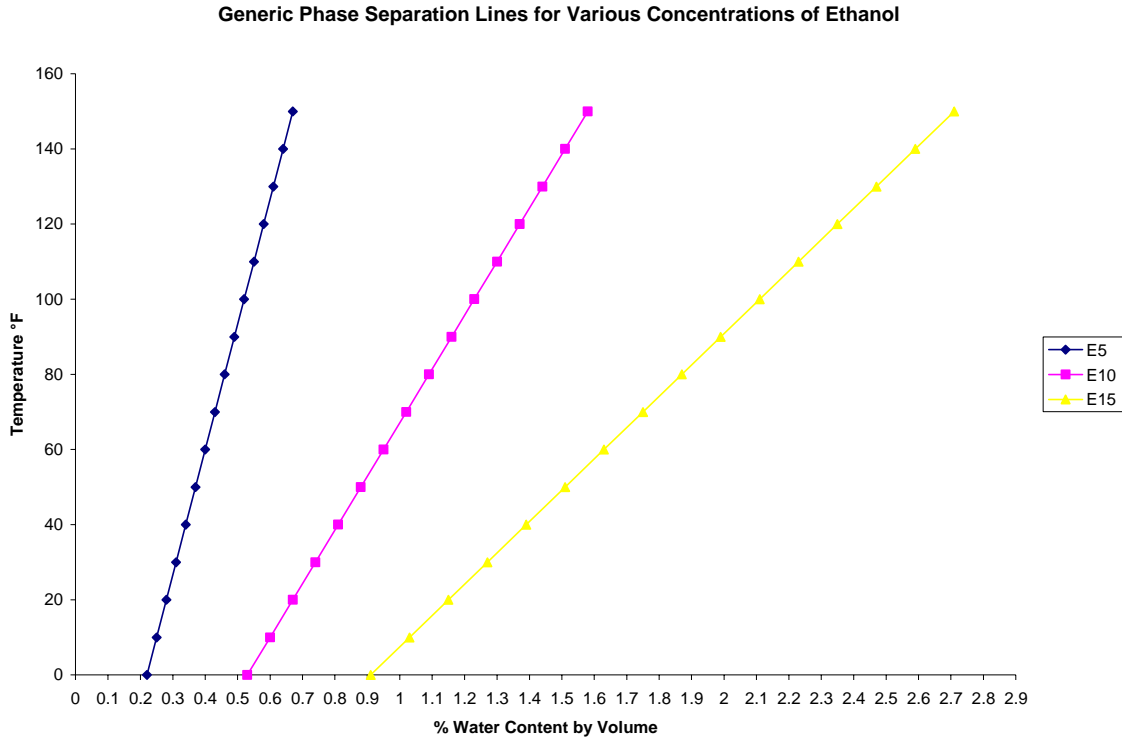


Figure 6: Graphing showing different phase separation lines for different blends of ethanol-gasoline. These phase separation lines do not take other factors into account such as the hydrocarbon content of the gasoline.

Commingling Ethanol-Blended Gasoline with Alcohol-Free Gasoline

I have received many phone calls from gas station owners to see if any issues existed if alcohol-free gasoline was placed into tanks that previously contained or currently contain E10. There are two situations that can cause issues when switching from E10 to alcohol-free gasoline and vice-versa. The first is if the tank is not completely emptied of the alcohol blended fuel. If we take a tank with a 10,000 gallon capacity and empty it to 1% volume, we will have 100 gallons of E10 left. Filling the tank to its 10,000 gal capacity with alcohol-free gasoline will result in an ethanol-gasoline blend containing 0.1% ethanol. The phase separation line for this blend will be steeper than the E5 line of figure 6. As one can see, the likelihood of phase separation will dramatically increase.

Now we will take the same scenario, but change it so that the results can be seen on a modified version of the above figure. The 10,000 gallon tank has 5,000 gallon of E10 and is filled to capacity with alcohol-free gasoline. The resulting blend is E5. If the initial water content is at 0.9% by volume in the E10 and the temperature is at 60°F we will be at the red dot on figure 7. Notice that this point is above the phase separation line for the 5,000 gallons of E10. Filling the remaining capacity with alcohol and water free gasoline will result in a water content of 0.45% by volume. If the fuel remains at 60°F

then the fuel will be in the condition represented by the blue dot. The resulting E5 will be below the phase separation line and phase separation will occur.

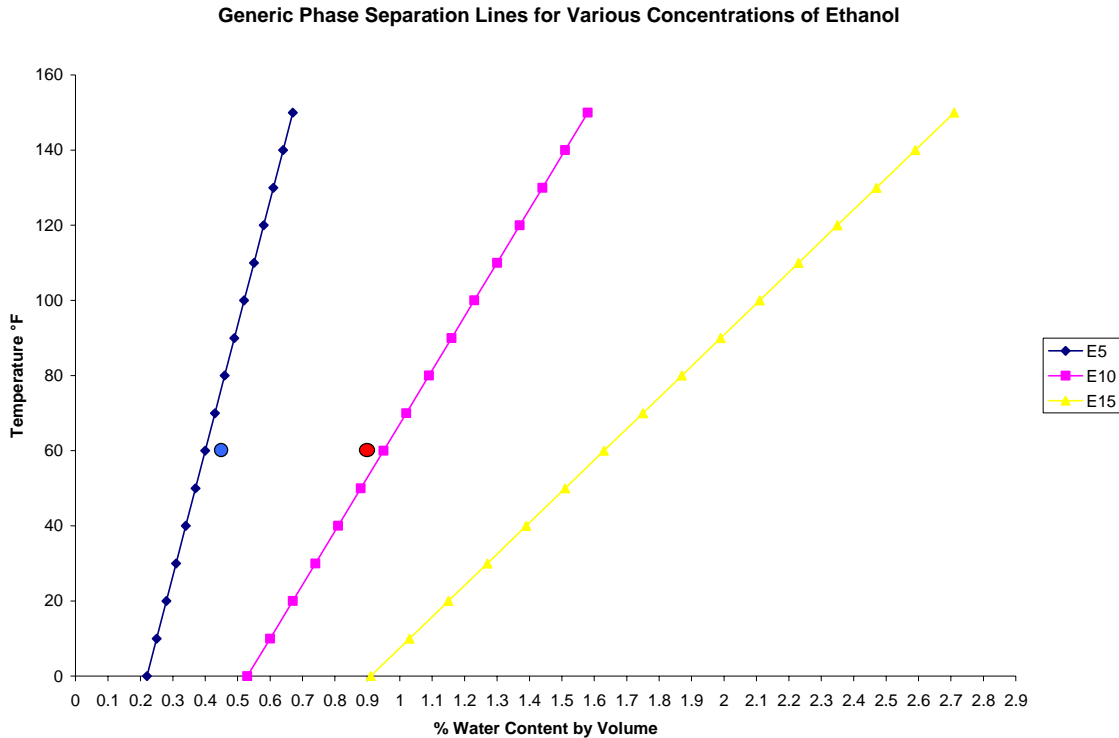


Figure 7: Graph showing what happens when alcohol blended fuel is mixed with alcohol-free fuel.

The above scenario may not play out like this. It can also end up favorably, but it all depends on conditions and a lot of variables. If we modify the above scenario by changing only the initial water content to 0.4% by volume we have a favorable outcome. The red dot on figure 8 shows the condition of the 5,000 gallons of E10. This point is located above the E10 phase separation line and also happens to be on the E5 phase separation line. If the water content were to remain constant during the mixing, then the resulting E5 would phase separate. However, since the added alcohol-free fuel is also water free, the resulting mix is 0.2% water by volume. This point is represented by the blue dot and is above the E5 phase separation line. Under these conditions the mix is still a usable motor fuel.

The first scenario illustrates why it is important to empty, as completely as possible, a storage tank of alcohol-blended fuel before adding alcohol-free fuel. The reverse is also true. The tank should be emptied as much as possible of alcohol-free fuel before adding alcohol blended fuel to avoid the same possibilities because the alcohol being blended into the gasoline may have taken up some quantity of water during transport and transfer.

A second situation that can cause an alcohol monitor to slow flow when using alcohol-free gasoline will now be discussed. However, this situation does not directly involve phase separation. Water in a storage tank will tend to settle to the bottom. When new fuel is added to the tank, the bottom water will be stirred into the gasoline. Immediately

pumping after filling can result in suspended water particles being entrained in flow. The water will then activate the alcohol monitor and slow flow.

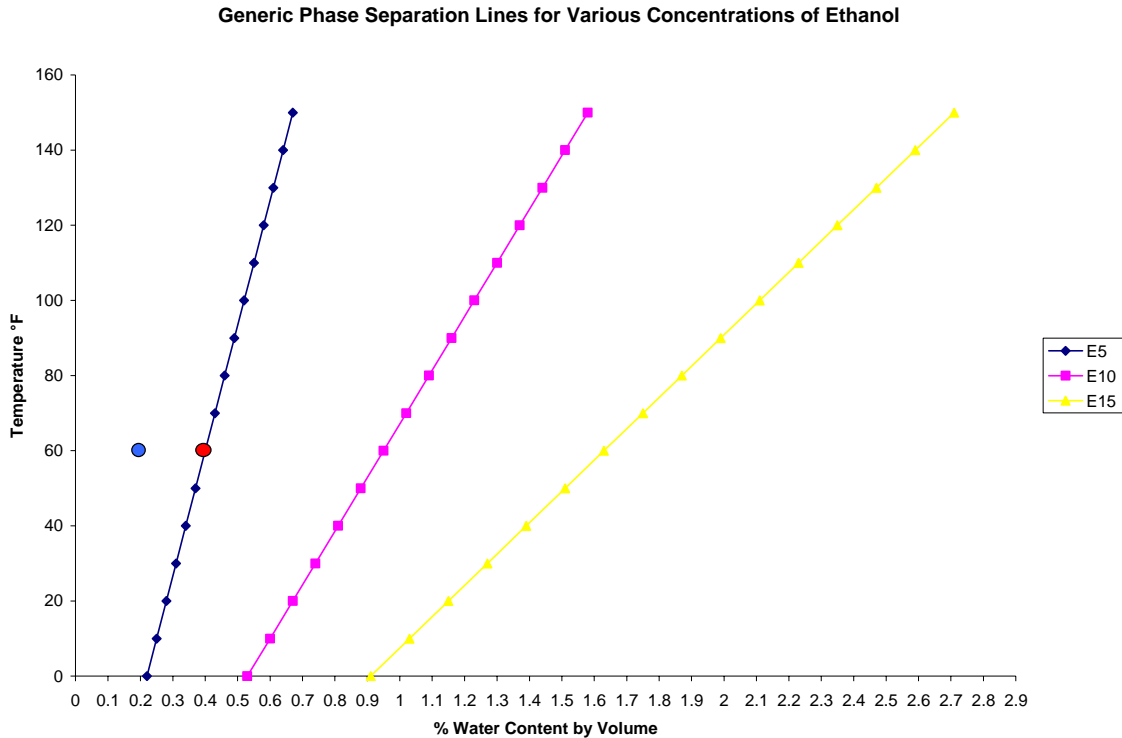


Figure 8: Graph showing that it is possible to mix alcohol-blended and alcohol-free fuels and have a usable motor fuel.

Letting the tank rest after filling to let the water settle back to the bottom is not a guarantee. The very act of pumping can agitate this bottom layer and entrain water into the flow of gasoline. This is why phase separation detecting media should not be used with straight gasoline. It should also be noted that there is no inexpensive and practical way to build a dual use filter for detecting phase separation in alcohol-blended fuels and water in alcohol-free fuels.

One additional point of commingling is the temperature of the two fuels may be different. The resulting temperature of the mix may push the mix into phase separation. Also, please note that adding a new load of ethanol-blended fuel to existing ethanol-blended fuel can result in a temperature shift.

Alcohol Type

The type of alcohol used for an alcohol-blended fuel impacts the location of the phase separation line (Owen and Coley). Figure 9 shows the same phase separation lines seen in figures 6, 7, and 8 that represent different blends of ethanol-gasoline. In addition to these phase separation lines are lines for different blends of methanol-gasoline represented by the dashed lines. A 10% methanol-blend or M10 is represented by the red dashed line; 15% methanol or M15 is represented by the orange dashed line; and 20% methanol or M20 is represented by the green dashed line on figure 9.

It is clearly shown that methanol-blended fuels will phase separate at a much lower concentration of water than ethanol-blended fuels (Owen and Coley). The graph also shows that the methanol phase separation lines cross somewhere in the vicinity of 4°F. Above this temperature and methanol will follow the general rule of thumb that increasing the concentration of methanol will result in greater water tolerance. However, below this temperature the opposite is true and increasing the concentration of methanol will result in a lesser water tolerance (Owen and Coley).

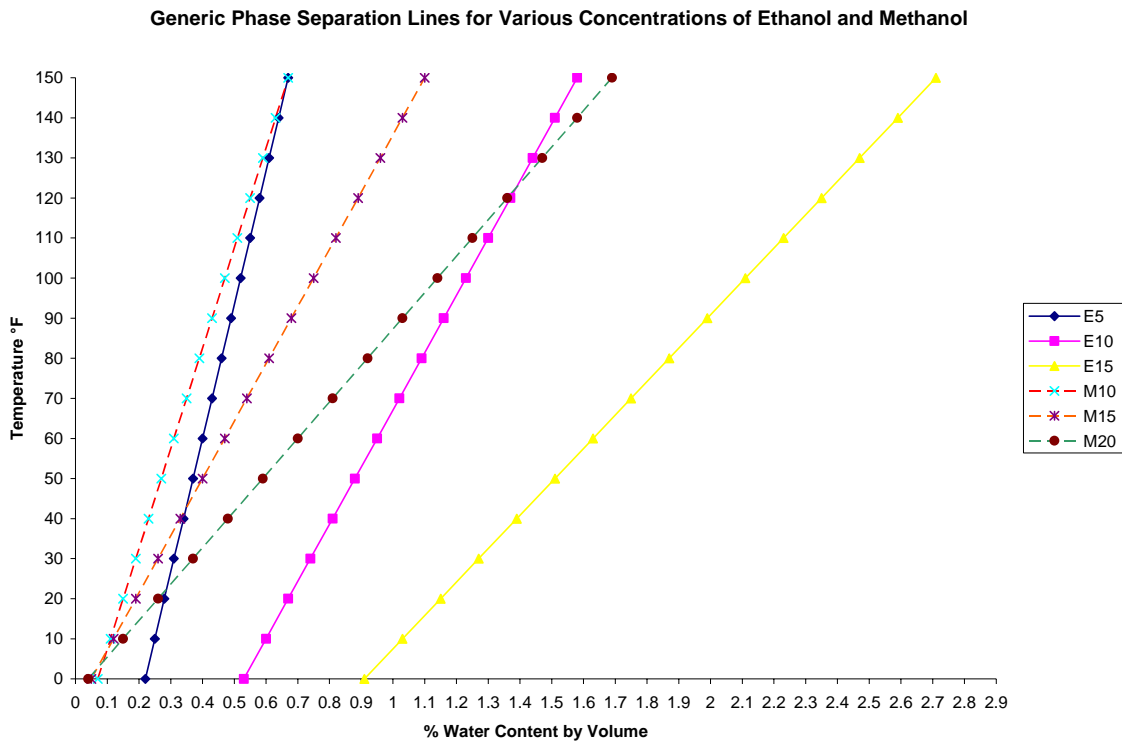


Figure 9: Graph showing phase separation lines for various concentrations of ethanol or methanol.

Cosolvents

Cosolvents are used to increase the water tolerance of an alcohol-blended fuel (Owen and Coley). For example, methanol is commonly blended with tertiary-butanol to counter methanol's poor water tolerance. Basically, what happens is that the phase separation line for the solution is somewhere between the two phase separation lines for the alcohols. The solution's phase separation line will also tend to be closer to the phase separation line of the alcohol in the greatest concentration.

Below is figure 10, which shows four generic phase separation lines for methanol with tertiary-butanol as a cosolvent and the same for ethanol. In these two alcohol systems there is definitely a positive increase in water tolerance of the blends. Methanol blended at 10% went from the red-dashed line to the yellow-dashed line when 3.2% tertiary-butanol is added. Ethanol blended at 10% went from the pink line to the blue line when 3.2% tertiary-butanol is added.

While the addition of tertiary-butanol is beneficial, the addition of methanol to ethanol-blended fuels is not. Therefore, care must be taken when adding a methanol based fuel additive to ethanol-blended fuels. Basically, if an 8 ounce bottle of methanol is added to 10 gallons of E10, then the phase separation line will be close to the straight E10 phase separation line. However, if an 8 ounce bottle of methanol is added to 1 gallon of E10, then the water tolerance of the fuel will be closer to that of methanol than that of ethanol and the chances of phase separation occurring increases.

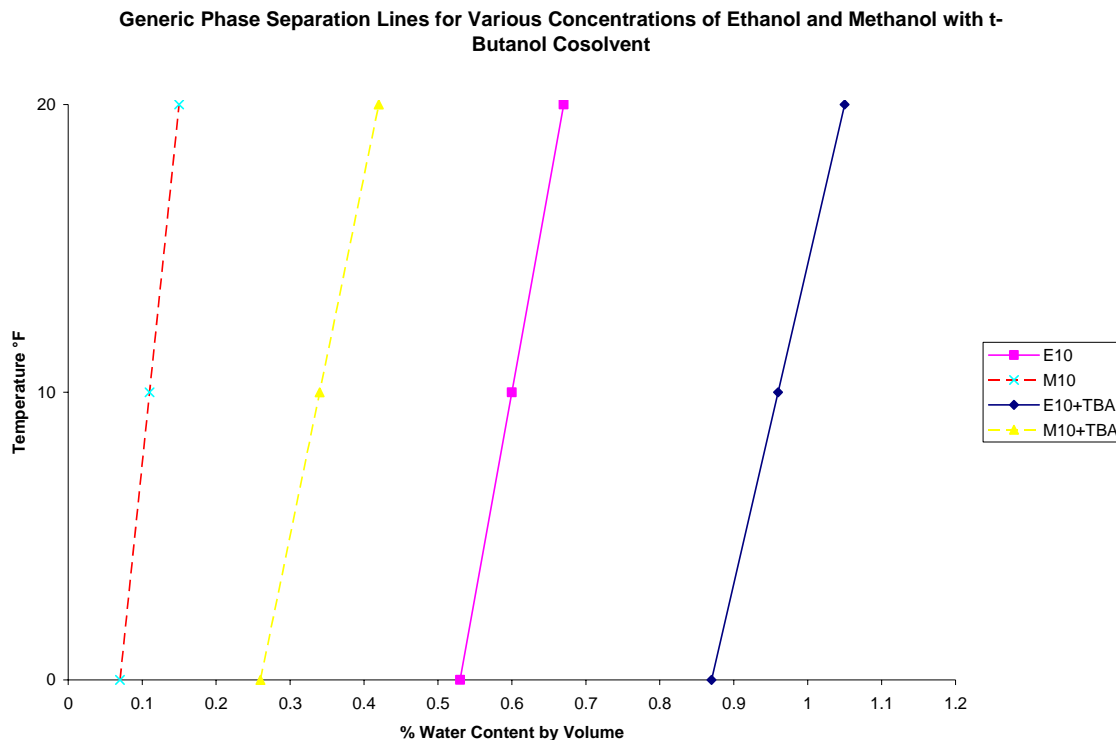


Figure 10: Graph showing the phase separation lines of M10, E10 and each with tertiary-butanol added. TBA and t-butanol both stand for tertiary-butanol.

Figure 11 shows phase separation lines for blends of the two alcohols that are 10% methanol and 0% ethanol; 10% ethanol and 0% methanol; 6.7% methanol and 3.3% ethanol; and 6.7% ethanol and 3.3% methanol. The graph shows that the phase separation lines for the mixed alcohol fuels fall between the straight E10 and M10. It is also shown that if the mixed fuel contains more ethanol than methanol then its phase separation line will be closer to the E10 phase separation line. In fact, the closer a mixed alcohol fuel gets to E10 the closer its phase separation line will get to the E10 phase separation line. This holds true for methanol as well. The closer a mixed alcohol fuel gets to M10 the closer its phase separation line will get to the M10 phase separation line.

One important thing to remember is that the total alcohol concentration will determine which phase separation lines will bound the mixed alcohol phase separation line. For example: A mixed alcohol fuel containing 9% ethanol and 6% methanol should fall between the M15 and E15 phase separation lines.

Hydrocarbon Composition

The hydrocarbon composition has bearing on the water tolerance of an alcohol-blended fuel (Owen and Coley). For aromatic hydrocarbons the water tolerance tends to increase with increasing aromatic content (Owen and Coley). Figure 12 shows the phase separation lines for E10 in which the gasoline contains either 14%, 26% or 38% aromatic hydrocarbons. It can be seen that an aromatic content of 14% is less water tolerant than the same E10 with 26% aromatic content. An interesting thing revealed is that the phase separation lines for 26% and 38% aromatic content are closer to each other than those for the 14% and 26% aromatic content despite that each fuel is different by 12% aromatic content.

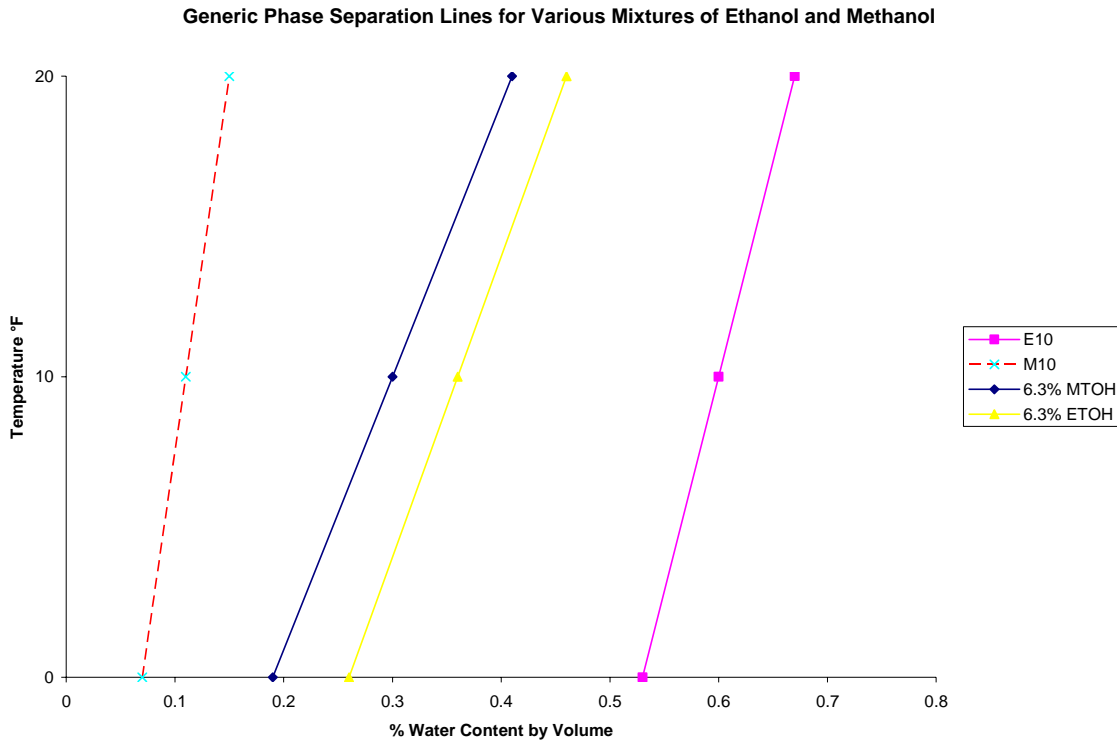


Figure 11: Graph showing how the phase separation line of mixed alcohol fuels containing ethanol (ETOH) and methanol (MTOH) fall between the phase separation lines of ethanol-blended and methanol-blended fuel.

Characteristics of the Phase Separated Bottom Layer

When phase separation occurs somewhere between 30 to 70 percent of the ethanol will drop to the bottom of the tank with the water (Muzikova *et al.*). The exact amount of ethanol is based upon many factors that are beyond the scope of this text and the amount of time the fuel has been in phase separation will result in a changing ethanol concentration as the two layers come to an equilibrium (Muzikova *et al.*) As it drops, some of the alcohol soluble hydrocarbons will be stripped from the gasoline. Because the water and alcohol that drop to the bottom are in different proportions than at the moment of phase separation, the bottom layer will be a lower proof alcohol.

Taking 100 gallons of E10 that needs 0.5% water by volume added to start dissociation will be equivalent to 190 proof ethanol at the moment of phase separation. If 30% of the ethanol leaves solution then the phase separated bottom layer will be 171 proof. The high amount of 70% of the ethanol leaving solution will result in 187 proof ethanol. However, these are just arbitrary numbers and the proof of the bottom layer can vary dependent upon how much ethanol is stripped; how much water was needed to cause phase separation; and if any previously phase separated bottom layer exists to mix with the new phase separated material. In short, the chemistry of the phase separated bottom layer and how it takes on this chemistry is beyond the scope of this text, but the idea that the proof of the phase separated alcohol is different from the proof of the gasoline dissolved alcohol is an important concept to know.

Generic Phase Separation Lines for Various Aromatic Hydrocarbon Composition

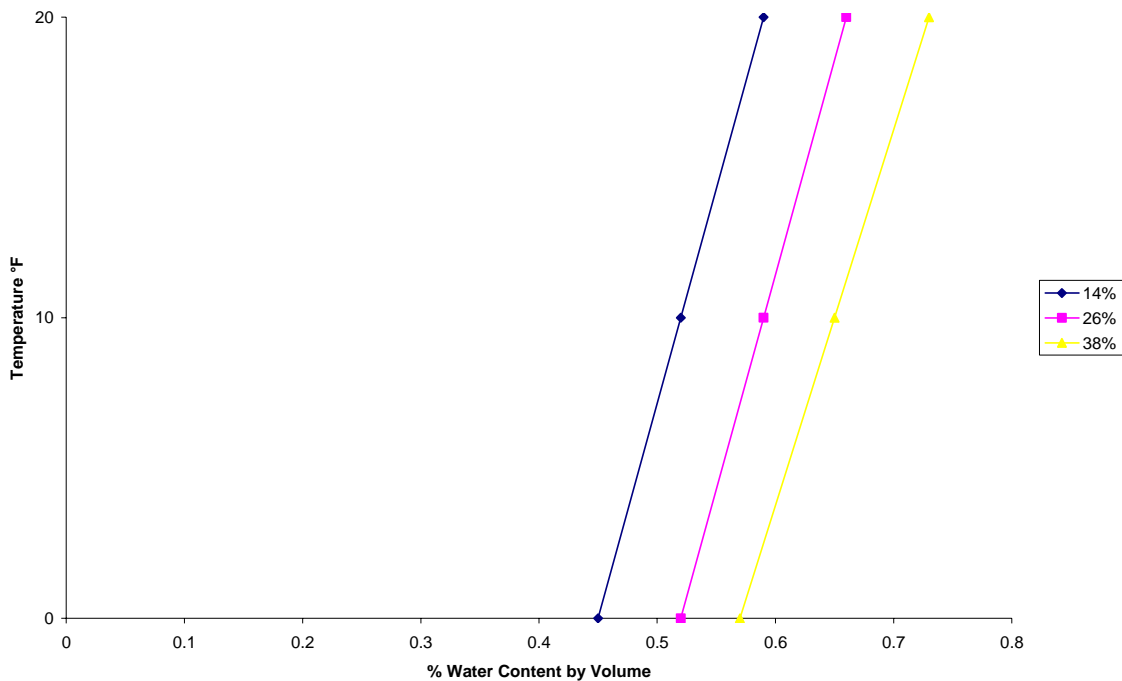


Figure 12: Graph showing how hydrocarbon content affects the phase separation line for 14%, 26%, and 38% aromatic hydrocarbon content in E10 fuel.

The Alcohol Monitor

An alcohol monitor is a filter with the special property of being able to detect alcohol-water that has phase separated from gasoline. Once phase separated alcohol-water has been detected, the alcohol monitor slows the flow of gasoline and increases the differential pressure across the filter element. The slowed flow is then used to alert the gas station attendant and the vehicle owner that there is an issue. An alarm can also be used to detect the high differential pressure and give a visual and/or audible alert.

Basic Construction

The alcohol monitor (figure 13) is basically constructed with two elements. There is an inner element that is wrapped around the filter's center core and contains the phase

separation detecting media. Around the inner wrap is an outer pleat pack containing water absorbing media.

The outer pleat pack is a pleated filter media constructed of glass microfibers and has a super absorbent polymer implanted in the matrix. Particulate removal and water retention is accomplished by the pleated glass microfiber media. Any emulsified water that might be in flow is absorbed by the super absorbent polymer while alcohol and dissolved water are allowed to pass.

The inner element is also constructed of glass microfiber media and contains a super absorbent polymer with a slightly different chemistry than the super absorbent polymer in the outer pleat pack. When phase separated alcohol-water comes in contact with the inner element, the super absorbent polymer swells and congeals to clog the porosity. This effectively slows flow to lessen the entry of phase separated material into a vehicle.

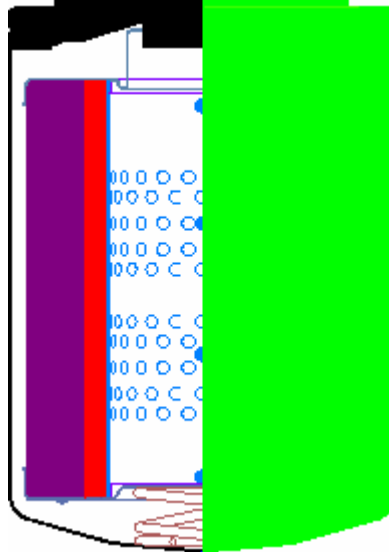


Figure 13: Cutaway view of an alcohol monitor. The red zone represents the inner phase separation detecting media that is wrapped around the core. The purple zone represents the outer pleat pack that absorbs free water.

Theory of Operation

When a water molecule is exposed to both a super absorbent polymer and an alcohol, it has two choices. The water molecule can either associate with the alcohol or with the super absorbent polymer. In the case of methanol or ethanol, the water molecule would prefer to be associated with the alcohol at sufficiently high proof. However, at higher concentrations of water in the alcohol, the super absorbent stands a greater chance of attracting and retaining a water molecule.

The super absorbent polymer in the inner element is designed to attract water if phase separated water-alcohol is present and to ignore water if the alcohol and water are coexisting with the gasoline. However, it should be noted that even if phase separation has not occurred, the super absorbent polymer will still leach what water it can from the alcohol. It is simply a matter of time.

When the water content is low and phase separation has not occurred then the flow of fuel through the alcohol monitor may be fast enough that the super absorbent polymer does not have time to take up any water. Once flow stops and there is fuel sitting in the filter housing, the super absorbent polymer has time to take some water out of solution.

As the water content increases, the amount of time needed for the super absorbent polymer to strip water from alcohol decreases. Once the alcohol phase separates it goes through a sudden decrease in proof. This is because phase separation involves a drop out of all the water and only a partial drop of the ethanol. The sudden jump in the concentration of dissolved water in ethanol causes a sudden decrease in the time it takes the super absorbent polymer to absorb the water⁴.

In short, the polymer transforms from a dry powder to a moist gel as it absorbs water. The gel swells and fills the porosity of the filtration media leaving no path open for conventional fluid flow. Unlike conventional absorbents, such as a sponge, compression does not easily liberate absorbed water (Buchholz).

Alcohol Monitor Testing

There are three important tests that an alcohol monitor must pass. These are an incremental test, a sudden addition test, and a water-alcohol test. There are also several important design considerations that must be observed when performing one of these tests. The considerations will be discussed first followed by a discussion of the three tests.

Considerations

First, the test stand should have a large reservoir for holding fuel. A larger reservoir volume has several benefits over a smaller one. There is the detraction of an increase in the test cost due to the volume of fuel needed to perform the test. Regardless of the cost increase, a larger reservoir volume is closer to reality than a smaller. More fluid volume means decreased contact time between the alcohol monitor and a cycling slug of fuel. Cycling the same smaller volume of fuel over and over through the pump will add to pump overheating, shorter pump life, and make it more difficult to control the temperature variable. Thus a larger volume helps to control the test temperature and prolong the life of the test stand's pump.

A second consideration is the control of fluid temperature to ensure that phase separation occurs at a known level of water content. As mentioned earlier, the large volume of fuel helps to regulate the fluid temperature. Additional precautions and controls may be desired. One is that the ambient temperature is not at the desired test temperature. To control and adjust temperature, a cooling / heating tube of some type may be used. It is important to make sure that the cooling / heating tube is away from the fuel reservoir so as to avoid the unintentional injection of condensation into the test fluid.

⁴ The water diffuses into the super absorbent polymer by diffusion according to Fick's Law which states that the rate of diffusion is faster when the concentration (or activity) gradient is larger (Buchholz and Graham).

Thirdly is the alcohol content of the fuel. Alcohol is usually blended at the pump and this can cause variations in the final alcohol content. An alcohol checker should be used to determine alcohol concentration. If it is below the desired concentration, then 200 proof alcohol should be added to increase the concentration. However, if the concentration is above the desired concentration, then alcohol-free fuel should be added to lower the concentration. If available, pure gasoline should be used and 200 proof ethanol added to it to produce E10.

A fourth consideration is the initial water content. Due to the hygroscopic nature of alcohol, moisture can be taken up by the fuel. It is therefore important that the initial water content be measured and taken into account when testing the functionality of an alcohol monitor.

The unimpeded flow rate should be set to a known value for all tests as a fifth consideration. This should be a number that is easily obtainable through some sort of flow reduction mechanism that is below the lowest possible value for flow through a clean alcohol monitor. A value of 10 gpm is a good value to choose.

Cleanliness of the test fluid is of utmost importance as a sixth consideration. Starting with a dirty fluid will clog the porosity of the alcohol monitor and give false result by causing premature and non-water induced shutdown. Some contamination is to be expected. To ensure the cleanest test conditions, the test rig should be constructed out of stainless steel and 200 proof ethanol should be used between each test to strip particles and free water out of the test rig. Test lines should also be laid in such a way that complete drainage of the cleaning ethanol can be accomplished.

Finally, a seventh consideration is to take all the other impacting variables on phase separation into account. These variables are mentioned above but will be briefly restated. You must take the type of alcohol, the amount of alcohol, the presence of cosolvents, the temperature, the hydrocarbon composition of the gasoline, and the amount of water into consideration. Duplicate and replicate tests are not possible and cannot give reliable data if the hydrocarbon content of the gasoline is changing from test to test. The phase separation point can move from test to test if the alcohol concentration changes from test to test. Thus all these variables should and must be accounted for and reported in order to have meaningful and reliable results.

Incremental Testing

Incremental testing is done to simulate the gradual build up of water in a fuel storage tank. It is a good idea to add the water in easy to use percentages to make plotting the data easier. About 15 data points before phase separation occurs should be used so as to define a plateau that shows that the alcohol is not reacting to any water-alcohol-fuel mixture. Data collection should continue until an S-shaped curve is defined (figure 14).

To begin the test, the initial water concentration should be determined and this point becomes the starting point. At each increment, inject the predetermined water volume

into the fuel reservoir and allow it to mix. Allow the reservoir to mix for 1 minute for every 10 gallons of fuel. Another water concentration measurement should be made after each injection is mixed to ensure that the water concentration is staying near the calculated value. Run the fuel mixture through the alcohol monitor for 1 minute for every 10 gallons of fuel. Take another water concentration measurement before the next injection to account for water stripping.

Plotted data will show that the pre-phase separation plateau has a slight negative slope (figure 14). This negative slope is a result of minute water absorption that is either being stripped as the water-alcohol-fuel is flowing through the alcohol monitor or it is water that is absorbed while the alcohol monitor sits idle during the mixing process. It is likely both processes; however testing has not been conclusive to date. The data shows that the flow rate starts reduced at the start of each increment and continues to decline during each incremental interval.

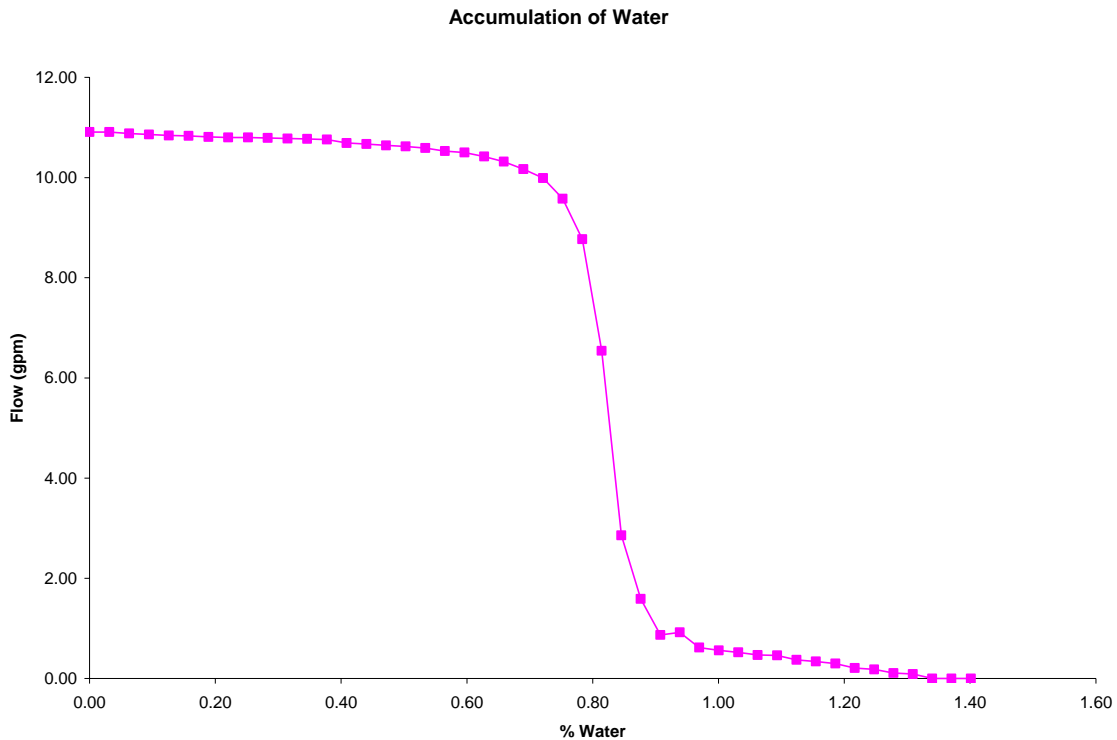


Figure 14: Accumulation of water graph. Normally this graph would start with the pump set to a fixed starting variable. However, this data was collected with the impedance of the filter element setting the initial flow rate for the purpose of showing that the alcohol monitor strips some water from the fuel before phase separation occurs.

At the point of phase separation, the flow rate goes through a sudden decrease. This is seen in figure 14 as the near vertical portion of the graph. This happens because the super absorbing polymer has swelled and gelled. After the large drop in flow rate, the rate of flow continues to decline as the gel continues to plug more porosity.

Sudden Addition Testing

Sudden addition testing is done to simulate the sudden injection of water at a volume sufficient enough to cause phase separation. In order to do this test, it is imperative that all variables that have bearing on the location of the phase separation point be accounted for. The reason is that the volume of water suddenly added must induce phase separation by being at or extremely close to the phase separation point. By adding too much water, the proof of the phase separated material will be excessively low and the performance of the alcohol monitor will be falsely shown better than reality.

There are two versions of this test. The first version mixes the reservoir so that the alcohol monitor has to deal with emulsified phase separated alcohol-water. In the second version, the phase separated alcohol-water is allowed to settle to the bottom of the tank to simulate a pump on the bottom taking in a slug of phase separated alcohol-water before taking in fuel.

A plot of the data (figure 15) for this test shows the flow rate versus time. Measurement of the flow rate should be taken every 10 seconds until the flow rate is reduced below the test criteria or 5 minutes has elapsed, which ever comes first. Ideally, the alcohol monitor will reduce flow to less than 1 gpm in less than 1 minute on average under test conditions regardless if the phase separated fluid is a slug or emulsified.

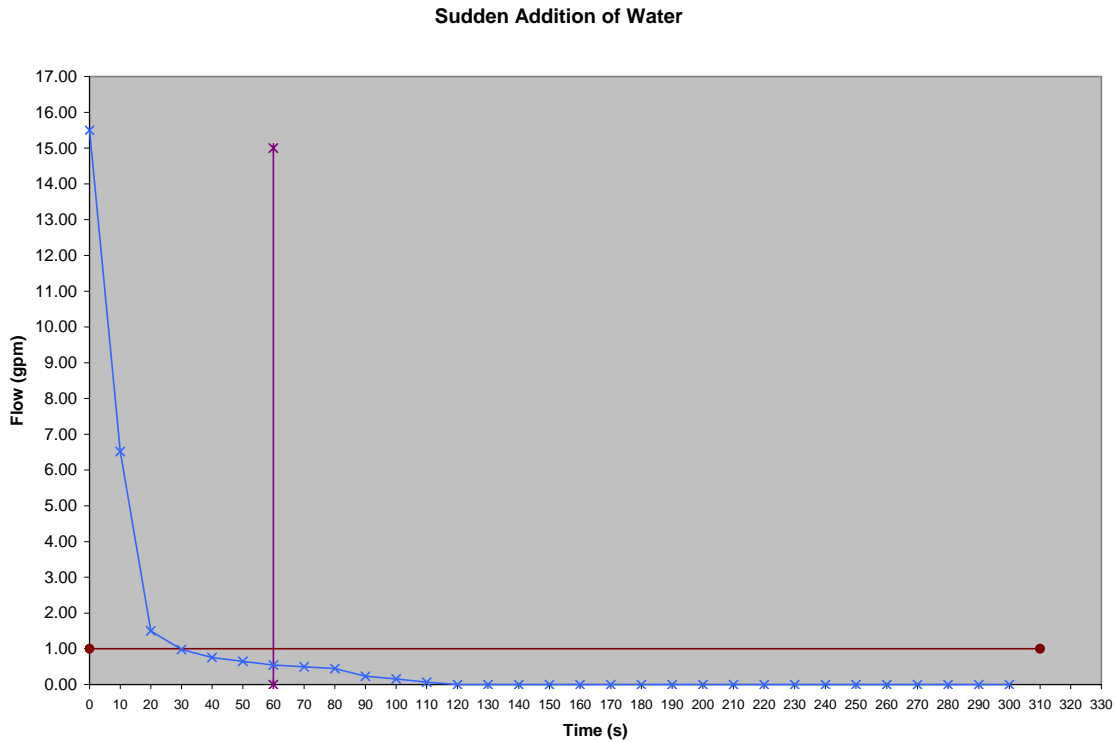


Figure 15: Sudden addition of water graph. The horizontal brown line represents 1 gpm flow rate and the vertical brown line represents 1 minute.

It should be noted that the test goal of reducing flow to less than one gpm in less than one minute is to ensure that the product meets performance criteria. Performance in the field is guaranteed to reduce flow to less than two gpm in less than 2 minutes. Please also note

that the test did not end immediately after reducing flow to zero. This is to ensure that the alcohol monitor will continue to impede flow with a sustained differential pressure.

Alcohol proof testing

Alcohol proof testing is designed to simulate the phase separated bottom layer and the alcohol monitor's response to only this layer. If E10 fuel needs 0.4% water by volume to cause phase separation, then the phase separated bottom layer will have 18% water in it⁵. This corresponds to a proof of 164. However, the items that can impact the phase separation point also impact the amount of water in the phase separated bottom layer. To be conservative and to ensure that the alcohol monitor can perform with the highest proof (least amount of water) phase separated layer, a higher proof alcohol should be used. Optimally, the test fluid should be 170 proof. If it can perform in 170 proof then it can perform in 160 proof or any lower proof alcohol. The test results for this test will plot up (figure 16) similar to the sudden addition of water test and the results should be similar.

170 proof ETOH Testing

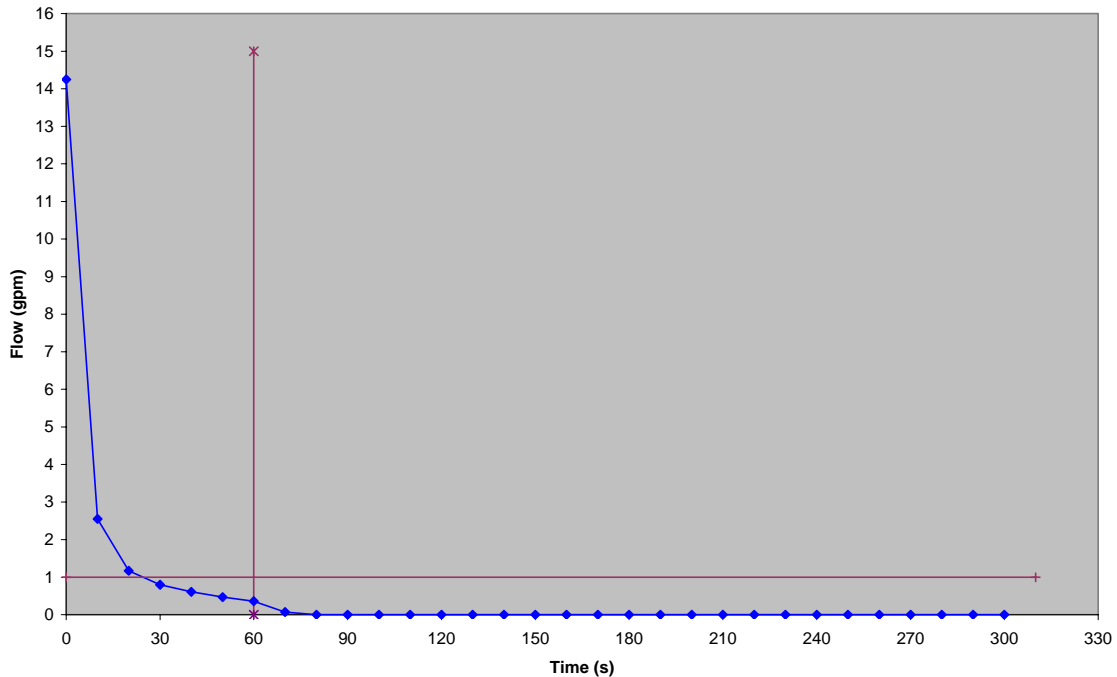


Figure 16: 170 proof ethanol graph. The horizontal brown line represents 1 gpm flow rate and the vertical brown line represents 1 minute.

Conclusion and Recommendations

Phase separation is controlled by many variables. The main variables are water content and temperature. However, alcohol concentration, alcohol type, cosolvents, and hydrocarbon composition of the gasoline also have bearing on phase separation. Since moisture content and temperature are also environmental variables, changing conditions

⁵ It is unknown if this data takes into account all the variables impacting the phase separation point of E10. This data comes from Lizzio, A. A. (2006) Performance of Bio-Tek® 70120 Alcohol Monitor. Lizzio reports that the data comes from other sources but fails to mention what those sources are.

can cause alcohol blended fuels to spontaneously phase separate in the storage tank, in the lines, or after it has been dispensed.

Recommendations

- It is recommended that an alcohol monitor be used when alcohol blended fuels are used.
- Do not use an alcohol monitor with alcohol-free gasoline. Instead, use a Cim-Tek Hydrosorb® filter to remove possible water contamination.
- If a car stalls due to phase separation, check to see if the fuel is phase separated in the storage tank or if environmental conditions are causing phase separation in the customer's vehicle. Remember, fuel can phase separate after it has passed the alcohol monitor.
- Use Cim-Tek's Hydroburn® at the maintenance dose to increase the fuel's water tolerance to help prevent post alcohol monitor phase separation.
- If phase separation has occurred in a customer's vehicle, use Cim-Tek's Hydroburn in the customer's tank to fix the problem.
- If phase separation has occurred in the storage tank, use Cim-Tek's Hydroburn at a ratio of 3 parts Hydroburn to 1 part phase separated fluid to reverse the phase separation and restore octane. Please note that agitation is necessary to reverse phase separation in a timely manner.
- Use Cim-Tek's desiccating vent breather to ensure that only dry air enters the storage tank.

Glossary

Angstrom	A unit of length that is equal to 10^{-10} of a meter.
Aromatic Hydrocarbon	A hydrocarbon that contains one or more benzene rings
Colloidal	Particles that are 10 to 10,000 angstroms in size and dispersed in a fluid.
Congeval	To become gelatinous or to become like jelly.
Commingling	This literally means to mix things together. Specifically, it refers to mixing two or more different species.
Cosolvents	Other solvents added to gasoline such as another alcohol.
Desiccate	To remove water from an object and dry it out.
Emulsion	A mixture between two immiscible liquid phases so that one phase is suspended as colloidal particles in the other phase.
Entrained	To be picked up and carried in the flow of a fluid.
Ethanol	Ethyl alcohol: an organic solvent of chemical formula $\text{CH}_3\text{CH}_2\text{OH}$.
Ethers	An organic compound composed of two hydrocarbons linked by an oxygen atom. Used as an oxygenator in motor fuel.
Homogeneous	Refers to a mixture or solution that is the same throughout.
Hydrocarbon	Organic molecules consisting of only carbon and hydrogen atoms.
Hygroscopic	The ability to draw moisture out of the surrounding air and retain that moisture.
Methanol	Methyl alcohol: an organic solvent of chemical formula CH_3OH .
Miscible	Refers to the ability of fluids to mix and form a homogeneous mixture.
Octane	This is a fuel's ability to minimize knocking in an engine. That is the antiknock characteristics of the fuel. The higher the rating the less knock.

Octane booster	A chemical additive designed to increase the octane rating of a motor fuel.
Oxygenator	A chemical additive designed to increase the amount of oxygen available for combustion with a motor fuel.
Phase Separation	A process in which two or more previously miscible phases dissociated and form distinct phases either as an emulsion and/or stratified layers.
Phreatic water	Water in the subsurface that is below the water table.
Proof	A measure of the amount of water in an alcohol. It is basically the percentage of alcohol multiplied by two.
Stratified	To be in distinct and separate layers.
Vadose water	Water in the subsurface that is above the water table.

References

- American Petroleum Institute (1988) Alcohols and ethers: A technical assessment of their application as fuels and fuel components. API publication N. 4261.
- Buchholz, F.L. (1998) Absorbency and superabsorbency, *in* Modern superabsorbent polymer technology, Buchholz, F.L. and Graham, A.T. *editors*, Wiley-VCH, New York, NY.
- Krause, K. (1995) Water phase separation in oxygenated gasoline: Corrected version of Kevin Karuse memo. Korotney, D. editor.
- Gramajo de Doz, M.B., Bonatti, C.M., and Solimo, H.N. (2004) Water tolerance and ethanol concentration in ethanol-gasoline fuels at three temperatures. *Energy and Fuels*, 18, 334-337.
- Lizzio, A.A. (2006) Performance of Bio-Tek 70120 alcohol monitor. Report to Central Illinois Mfg. Co.
- Muzikova, Z. Pospisil, M. Cerny, J., Sebor, G., and Zadrazil, I. (2008) Water tolerance of petrol-ethanol blends. *Goriva I Maziva*, 47, 1:34-53.
- Owen, K. and Coley, T. (1995) *Automotive Fuels Reference Book*, 2nd ed., SAE, Warrendale, PA.