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To: Geoff Cooper
Renewable Fuels Association

From: Robert L. McCormick
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Re: Water Uptake of Ethanol-Gasoline Blends in Humid Environments

Today a large majority of the gasoline used in the United States contains 10 vol% ethanol (E10), and in some areas 15 vol% blends (E15) are being offered for use in automobiles.[1] Recreational equipment (watercraft, ATVs, and snowmobiles, for example) and lawn/garden equipment (collectively non-road equipment) is designed to operate on E10. This equipment may be used seasonally, and then subject to storage for many months. Some organizations and owners of non-road equipment have expressed concerns about ethanol blends, and in particular about the potential for E10 blends to take up water from humid air leading to phase separation.

Phase separation occurs when an excessive amount of water is introduced into the fuel tank leading the ethanol and water to mix and and sink to the bottom of the tank. The engine cannot operate on the ethanol/water mixture, and the mixture may also cause corrosion of metals in the engine fuel system.

At the request of the Renewable Fuels Association, the National Renewable Energy Laboratory undertook an investigation of water uptake by ethanol blends in humid environments. A survey of available information on phase separation was conducted, and new experimental results were acquired on the rate of water uptake by ethanol-gasoline blends and on the potential for phase separation to occur in small non-road engine tanks in humid environments. Here we present a top level summary of the results. A detailed technical report is attached. In summary, the NREL investigation found the following:

1. Ethanol blends can hold more water without phase separation than hydrocarbon, and more ethanol improves their resistance to phase separation. This is an advantage that can help keep fuel systems "dry" by moving low levels of water out of the system.

2. In a small engine fuel tank in a constantly high-temperature, high-humidity environment, it takes three months or longer for E10 and other ethanol blends to take up enough water for phase separation. This confirms the statement by Mercury Marine that water uptake in E10 blends "…does not happen at a level or rate that is relevant."[2]

[1] In January 2011 USEPA announced approval of the use of E15 in 2001 and newer automobiles only.
[2] BoatUS Magazine. "Three Ethanol Myths Clarified." http://www.boatus.com/magazine/2011/december/ethanol.asp

3. Significant gasoline weathering (evaporation of the most volatile components) can occur over one month of storage in a high-temperature, high-humidity environment, with total mass losses as high as 30-70% for certain tanks. This means gasoline weathering, which can have a negative effect on fuel quality, generally occurs well in advance of any issues related to phase separation. The fuel vapor pressure may drop to levels where the fuel is not fit for purpose (engine will be difficult or impossible to start) and there may also be gum formation.

Water Tolerance of Ethanol-Gasoline Blends

Phase separation is a function of ethanol content, water content and temperature. Water is almost totally insoluble in hydrocarbon gasoline, so any water present will exist as a separate phase or layer in the tank. Unlike gasoline, ethanol is fully miscible with water – they can be combined in any proportion to make a homogeneous mixture (a solution). Gasoline-ethanol blends have a much higher water tolerance than pure hydrocarbon gasoline. This is shown in Figure 1, where as ethanol content is increased the amount of water that can be tolerated without phase separation increases significantly.

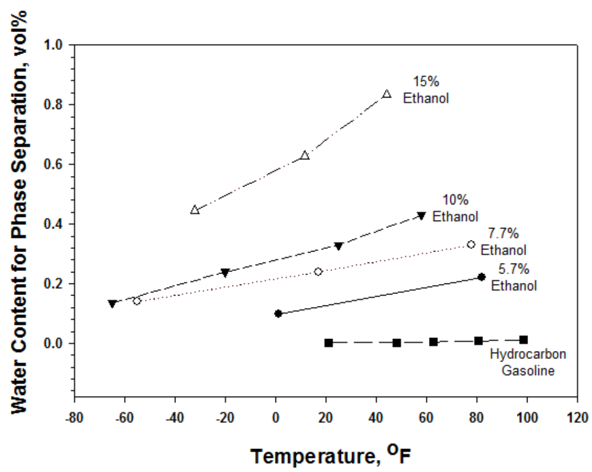

Figure 1: Water tolerance (phase separation temperature) of ethanol-gasoline blends.

This is an advantage because, as noted by Mercury Marine, the ethanol in E10 "…tends to keep low levels of water moving through the fuel system, keeping the system 'dry.'"[2] As also shown in Figure 1, water tolerance of a blend is dependent on temperature. At higher temperatures, the fuel can dissolve a greater concentration of water than can be tolerated at lower temperatures. For example an E10 blend can tolerate (exist as a single phase) over 0.4 vol% water at 60°F, but only 0.25 vol% water at -20°F. To put these numbers in perspective, 0.4% of a gallon is about 1 tablespoon – a relatively large amount of water to contaminate a small engine fuel tank. Fuel transporters and dispensers take measures to reduce water exposure of ethanol blends, and phase separation in the marketplace is rare.

Figure 2. Capped test tube.

Rate of Water Uptake by Ethanol-Gasoline Blends

To investigate the water uptake rate, hydrocarbon gasoline and ethanol-gasoline blends were placed in glass test tubes and held at constant temperature of 82°F and relative humidity of 92% in an environmental chamber. The samples tested were E0 (conventional gasoline blendstock for oxygenate blending), E10, E15, E25, and E83. Samples of 10 mL volume were placed in 15 mL graduated, glass test tubes. Tests were conducted with both a high headspace volume (HV) and a low headspace volume (LV), although differences between these were minor. The test tubes were closed with caps that had a small hole in the center. This was done to prevent rapid fuel evaporation (see Figure 2). About once per week samples were allowed to reach room temperature and inspected for haze and phase separation.

Samples were tested for water content during the first three weeks. At the fourth week, no haze or phase separation was observed and so humidity exposure was continued. At six weeks, the blends remained clear and bright but were tested for all properties. Results for water analysis by D6304 are shown in Figure 3. Overall rates of moisture uptake were estimated for the test tube samples. The rate of moisture uptake increases as ethanol content is increased from 10 to 25 vol%, however moisture uptake was lower for the E83 sample. The moisture uptake difference between E10 and E15 is small, but E10 blends took up water at a much greater rate than hydrocarbon gasoline. In conjunction with this increase in fuel water content upon humidity exposure, all of the blends with the exception of E83 exhibited a dramatic mass loss from fuel evaporation at the end of the experiment (known as "weathering"). Percent mass loss of the final aliquots is also provided in Figure 3. Over the test period weathering of the fuels was severe, with mass loss in the 20 to 40% range.

Water Uptake and Potential for Phase Separation in Small Non-Road Engine Tanks

Ethanol-gasoline blends were held in lawn mower fuel tanks in an environmental chamber with a 24-hour temperature cycle from 70°F, 100% humidity to 100°F, 60% humidity for three months. These conditions correspond to the most humid summertime conditions that can be found in the United States (for example, Houston or New Orleans), and the study period of three months is significantly longer than the maximum gasoline storage time recommended by most small engine manufacturers.[3] E0, E10, E15, E25, and E83 blends were prepared. One set of blends was held in tanks designed for 2015 model year Honda lawn mowers with 0.25 gallon capacity (Type A). A second set of blends was stored in tanks designed for 2008 model year and older Tecumseh small engines with 0.5 gallon capacity (Type B). The tanks were filled to one-third capacity and fitted with their appropriate fuel hoses and valves in the same configuration recommended in the OEM equipment manuals for storage.

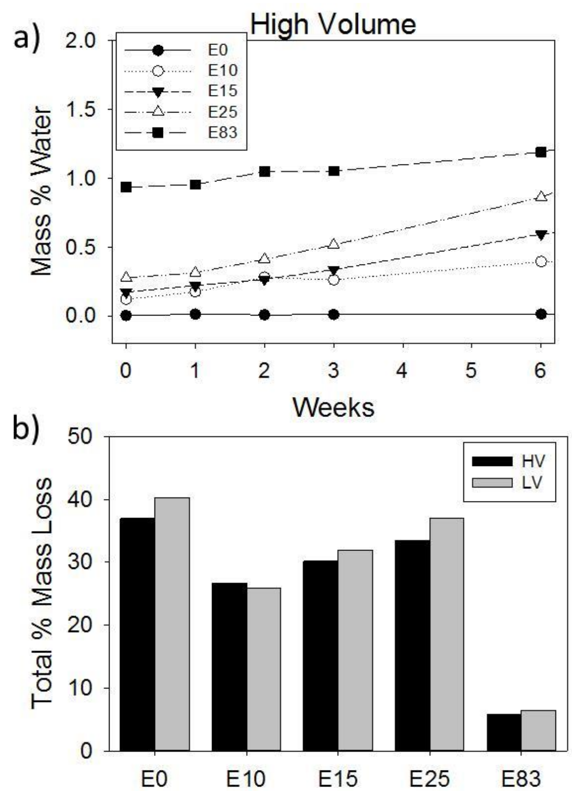

Figure 3. a) Water content of test tube samples over time. b) Weight loss from fuel weathering of test tube samples.

[3] See, for example, Briggs & Stratton fuel recommendations. ("Fuel will become stale when stored over 30 days. Stale fuel causes acid and gum deposits to form in fuel system or on essential carburetor parts.") www.briggsandstratton.com/eu/en/support/faqs/fuel-recommendations

Water concentrations in the tanks over time for each fuel are shown in Figure 4. Phase separation was eventually observed only for the E10 blend in Tank A at 12 weeks. The E10 in Tank A showed a significant amount of haze when sampled, which settled into a separate phase after several hours. The moisture uptake rates show water was absorbed more rapidly as fuel ethanol content increased – in agreement with observations for the test tubes.

Blends held in fuel tanks experienced considerable mass loss by the end of three months of storage in the environmental chamber. The percent mass loss of each blend is shown in Figure 5. Results for the tanks are slightly different because the 2015 tank (Tank A) and the 2008 tank (Tank B) met different federal evaporative emission requirements. With the exception of E83, blends held in Tank A experienced 10% to 20% mass loss, while the blends in Tank B lost between 30% and 70% of their initial mass. Fuels in both tanks weathered to have vapor pressure below 5.5 psi and likely also experienced increases in T10, T50, T90, and gum content making these fuels no longer fit for purpose. Blends held in Tank A had estimated vapor pressures below 5.5 psi at eight weeks, indicating these deleterious changes occurred prior to phase separation of the E10 at 12 weeks.

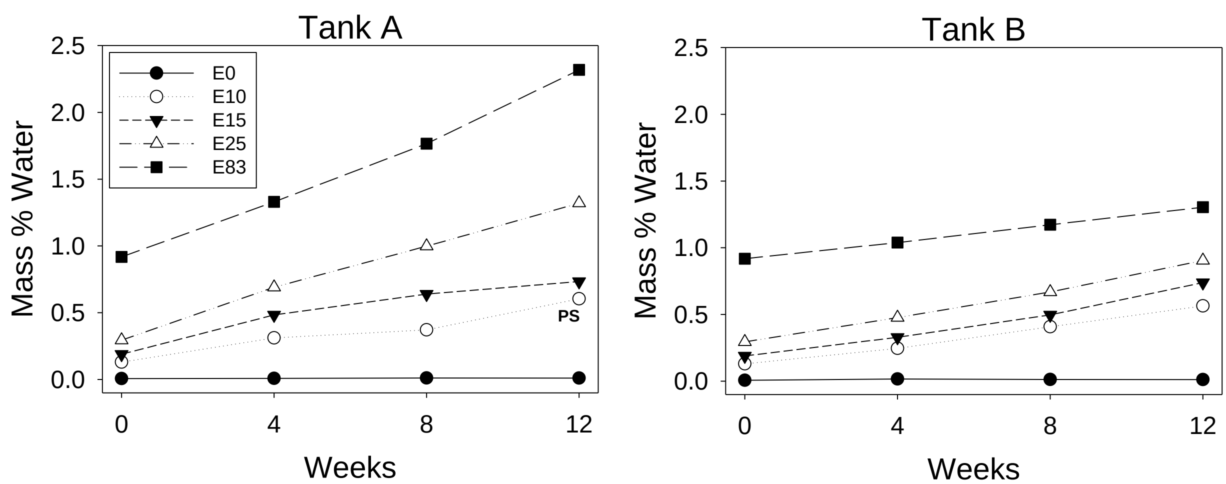

Figure 4. Water content of lawn mower fuel tanks over exposure time.

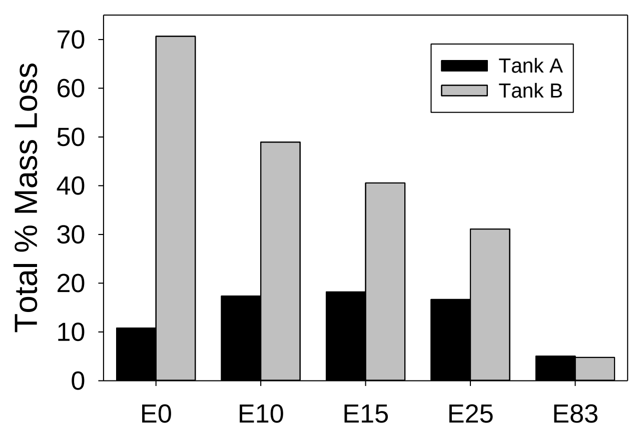

Figure 5. Total mass loss after 3 months of storage for blends held in small engine fuel tanks.