

Water Uptake and Weathering of Ethanol-Gasoline Blends in Humid Environments

NREL TSA 14-665 for the Renewable Fuels Association

Earl D. Christensen and Robert L. McCormick
National Renewable Energy Laboratory

September 2016

Summary

The rate of moisture uptake from humid air into gasoline-ethanol blends was measured in two experiments:

1. Glass test tubes held at constant temperature (82°F) and humidity (92%),
2. Small lawn mower fuel tanks undergoing diurnal cycling of temperature and humidity from 100% humidity and 70°F to 60% humidity and 100°F.

Gasoline is highly volatile and evaporation or permeation through the tank walls occurs during these experiments and this fuel weathering was also quantified. Experiments were conducted using a summertime conventional blendstock for oxygenated blending as the E0, as well as for blends with denatured fuel ethanol at 10, 15, 25, and 83 vol%.

Exposure of gasoline or gasoline-ethanol blends to ambient air in open test tubes results in very rapid evaporation of the most volatile fuel components. Under these conditions weathering of the fuel to be unfit for purpose because of low vapor pressure, and potentially high T50 and T90, high sulfur and gum, occurs more rapidly than moisture uptake from the environment.

Using test tubes capped with a 0.3 mm vent hole showed that the rate of moisture uptake increased with increasing ethanol content up to 25 vol%. While higher ethanol blends such as E15 or E25 can take up moisture faster, the much higher water tolerance of higher ethanol blends makes them less likely to phase separate. Phase separation occurred for E10 and E15 blends, however before phase separation was observed roughly 20 wt% of the gasoline had evaporated and the vapor pressure had dropped to less than approximately 5 psi. Ethanol-free gasoline (E0) did not phase separate, but was found to weather to the same degree during this timeframe. Given this loss of the most volatile components it is likely that T50, T90, sulfur content, gum content, and driveability index had increased to the point that the fuels were unfit for purpose even before phase separation because of these gasoline property changes.

Unlike open containers or capped test tubes, fuel tanks are closed tightly to limit gasoline evaporation, but for plastic tanks fuel can escape by permeation through the tank walls. As gasoline volume is reduced by combustion of the fuel or permeation ambient air can flow into the tank. Air inhalation vents of fuel tanks allow for tank breathing during diurnal cycling and thus contact with ambient air during storage.

For tank materials where ethanol permeation is more rapid than that of hydrocarbon, fuel ethanol content and water tolerance can decrease over time. In this situation, moisture uptake from humid air can result in phase separation. Similar to evaporation, the fuel quality degrades as the lightest components permeate the tank wall resulting in an unfit for purpose fuel well before the onset of phase separation.

Fuel tank manufacturers recommend emptying the tank if equipment is to be stored as long as 3 months. These experiments have shown that this practice is needed to prevent loss of fuel quality from hydrocarbon weathering as well as to safeguard against phase separation due to water uptake. Loss of

fuel quality by weathering occurs in conjunction with water uptake resulting in undesirable property changes prior to the onset of phase separation. Water uptake of an ethanol blend during storage in a humid environment can result in phase separation; however, if fuel is stored long enough for phase separation to occur the fuel was likely also unfit for purpose because of reduction in vapor pressure and other undesirable changes to fuel properties before phase separation was observed. An ethanol-free gasoline stored in the same conditions for the same period of time would likely be problematic despite a lack of phase separation.

Table of Contents

Summary	ii
List of Figures	v
List of Tables	vi
Acronyms and Abbreviations	vii
Introduction	1
Experimental Approach	2
Results	7
Moisture Uptake in Constant Temperature and Humidity Experiments.....	7
Moisture Uptake in Fuel Tanks during Diurnal Cycling Experiments.....	11
Discussion.....	17
Conclusions	19
Appendix: Weathering Rate and Chemical Compositional Changes in Constant Humidity Test Tube Experiments	20
References	23

List of Figures

Figure 1: Water tolerance (phase separation temperature) of ethanol-gasoline blends.	1
Figure 2. Test tubes, caps, and drilled hole vent.	4
Figure 3. Photograph of fuel tanks and environmental chamber. Type A tank = Honda EVOH/LDPE, Type B tank = Tecumseh HDPE.	5
Figure 4. Daily temperature/humidity cycle used for exposure of fuel in lawn mower tanks to a humid environment.	5
Figure 5. Water content of aliquots during exposure. PS indicates the point of phase separation.....	7
Figure 6. Photographs of phase separated HV samples from the test tube experiments.	8
Figure 7. Photographs of phase separated LV samples from the test tube experiments.	8
Figure 8. Mass loss of final aliquots of high volume (HV) and low volume (LV) blends.	9
Figure 9. Vapor pressures approximated from detailed hydrocarbon analysis and the Wilson equation. The line at 5.5 psi is the minimum vapor pressure required for flex-fuel blends under summer conditions.....	10
Figure 10. Octane numbers (AKI) approximated from detailed hydrocarbon analysis and ethanol concentration based on blending octane numbers.....	11
Figure 11. Fuel caps of each small engine fuel tank.	12
Figure 12. Water content blends during exposure. PS indicates the point of phase separation.	12
Figure 13. E10 blends from each tank type at the end of test.	13
Figure 14. Total mass loss after 3 months of storage for blends held in small engine fuel tanks.	14
Figure 15. Vapor pressures of blends before, during, and after the 3 month exposure. Initial and final vapor pressures were measured by ASTM D5191; the vapor pressure at 8 weeks was approximated from detailed hydrocarbon analysis and the Wilson equation.	14
Figure 16. Changes in hydrocarbon composition measured by detailed hydrocarbon analysis. Hydrocarbons are divided into carbon number groups, the lightest components having less than 7 carbon atoms (< C7) and the remaining composition having 7 or more (C7+).	15
Figure 17. Initial and final ethanol content of blends, E83 not shown.....	16
Figure 18. Octane numbers (AKI) approximated from detailed hydrocarbon analysis and ethanol concentration based on blending octane numbers.....	16
Figure A-1: Changes in hydrocarbon composition measured by detailed hydrocarbon analysis. Hydrocarbons are divided into carbon number groups, the lightest components having less than 7 carbon atoms (< C7) and the remaining composition having 7 or more (C7+).	20
Figure A-2. Initial and final ethanol content of blends, E83 not shown.	21
Figure A-3. Mass loss rates of aliquots during exposure expressed as g/L/day.	22
Figure A-4. Mass loss rate of final aliquot during exposure expressed as g/L/day.	22

List of Tables

Table 1. Properties of summertime conventional gasoline blendstocks for oxygenate blending (sCBOB) used for blend preparation.	2
Table 2. Properties of denatured fuel ethanol (DFE) used for blend preparation.	2
Table 3. Average July relative humidity of select locations in the U.S. compared to test conditions.	6
Table 4. Overall rates of moisture uptake. HV samples over six weeks, LV samples over entire experiment.	9
Table 5. Moisture uptake rates of blends over three months of exposure.	13
Table 6. Mass loss rates of the fuel tanks.	14

Acronyms and Abbreviations

AKI	Anti-knock index (the average of RON and MON)
DFE	Denatured fuel ethanol
DHA	Detailed hydrocarbon analysis (via ASTM D6729)
DVPE	Dry vapor pressure equivalent (modern measurement of RVP)
EVOH	Ethylene vinyl alcohol
Exx	Ethanol blend containing xx vol% ethanol
HDPE	High density polyethylene
HV	High volume (i.e. low head-space volume)
Hygroscopy	The ability of a substance to attract and hold water molecules from the surrounding environment. Hygroscopic substances include sugar, caramel, honey, glycerol, ethanol, sulfuric acid, many fertilizer chemicals, table salt, and a wide variety of other substances.
LDPE	Low density polyethylene
LV	Low volume (i.e. high head-space volume)
MON	Motor octane number
OEM	Original equipment manufacturer
RON	Research octane number
RVP	Reid vapor pressure (traditional term for gasoline vapor pressure, today measured as DVPE by ASTM D5191)
sCBOB	Summertime conventional blendstock for oxygenate blending

Introduction

Unlike gasoline, ethanol is fully miscible with water. Therefore, a gasoline-ethanol blend exhibits much greater water tolerance than pure hydrocarbon gasoline before separating into two phases. As shown in Figure 1, water tolerance of a blend is dependent on temperature and ethanol concentration. At high temperature, the fuel can dissolve a greater concentration of water than can be tolerated at lower temperatures. With higher concentrations of ethanol a greater amount of water can be tolerated at a given temperature and the temperature dependence is reduced – note the much lower slope of the E15 curve in Figure 1. When phase separation of an ethanol blend does occur, the alcohol will be partially extracted into the water phase producing a hydrocarbon rich upper layer and an alcohol rich, aqueous bottom layer. If phase separation occurs in a fuel tank the fuel pump will deliver primarily water and alcohol to the engine and a vehicle or piece of equipment will be unable to start. Phase separation in a dispenser tank can result in a water-alcohol mixture being delivered into a fuel tank rather than gasoline. The introduction of a water-alcohol phase into a vehicle or engine is highly problematic therefore, fuel transporters and dispensers take measures to reduce water exposure of ethanol blends, and phase separation in the marketplace up to the point of retail dispensing is rare.

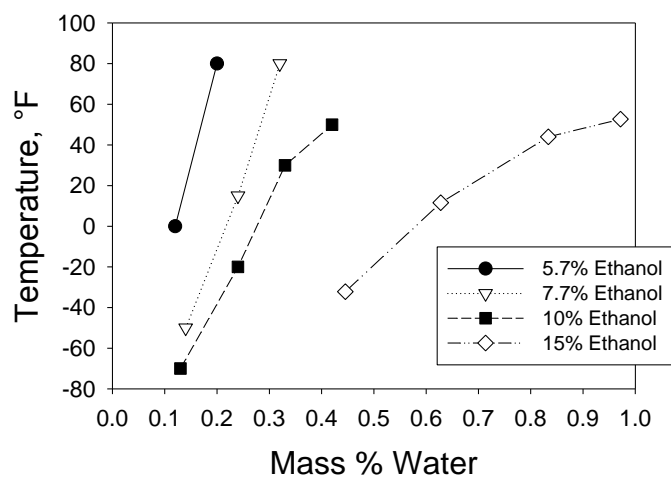


Figure 1: Water tolerance (phase separation temperature) of ethanol-gasoline blends.

Ethanol is hygroscopic – it attracts moisture from humid air. There has been concern that gasoline-ethanol blends stored in humid environments for extended periods of time may be able to attract sufficient moisture to result in phase separation. This is of particular concern with non-road equipment as these engines may be used for short periods of time followed by longer-term storage. In this project we measure the rate of moisture uptake into gasoline-ethanol blends in test tubes held at constant temperature and humidity, as well as in small lawn mower fuel tanks undergoing diurnal cycling of temperature and humidity. Gasoline is highly volatile and evaporation or permeation through the tank walls occurs during these experiments. This fuel weathering was also quantified.

Experimental Approach

Denatured fuel ethanol (DFE) and a summertime gasoline blendstock for oxygenate blending (sCBOB) were used to prepare blends containing 0, 10, 15, 25, and 83 volume percent ethanol: E0, E10, E15, E25, and E83, respectively. The properties of the sCBOBs and DFE are provided in Tables 1 and 2, respectively. The sCBOB-1 was used for the first task (test tubes) and sCBOB-2 was used for the second (small engine fuel tanks). Blends were prepared gravimetrically and the volume percent ethanol verified by ASTM method D5501 (a gas chromatography method). All blends were within 0.3% of target ethanol content.

Table 1. Properties of summertime conventional gasoline blendstocks for oxygenate blending (sCBOB) used for blend preparation.

Property	ASTM Method	sCBOB-1	sCBOB-2
Water, %wt	D6304	0.003	0.007
Vapor Pressure, psi	D5191	6.7	5.4
T10, °C		61	67
T50, °C		98	103
T90, °C	D86	154	159
Final Boiling Point, °C		198	197
RON	D2699	87.9	87.1
MON	D2700	81.9	81.6
AKI (RON +MON)/2	D4814	84.9	84.4
Paraffin, %vol		11.5	11.8
Isoparaffin, %vol		47.9	48.1
Aromatic, %vol	D6729	23.7	28.0
Naphthene, %vol		7.8	5.7
Olefins, %vol		8.4	5.6

Table 2. Properties of denatured fuel ethanol (DFE) used for blend preparation.

Property	ASTM Method	DFE
Water, %wt	D6304	1.03
Ethanol, %vol		97.6
Methanol %vol	D5501	0.1
Sulfur, ppm	D5453	2.7
Copper, ppm	D1688	<0.05
Inorganic Chloride, ppm		1.0
Existent Sulfate, ppm	D7319	1.9
Washed Gum, mg/100 mL	D381	3

During the first phase fuel was placed in glass test tubes held at constant temperature in an environmental chamber. The environmental chamber was held at $28 \pm 1^\circ\text{C}$ (82°F); the temperature used for verifying evaporative emissions of non-road fuel tanks according to CFR 1060.520.¹ A saturated solution of potassium sulfate was placed in the bottom of the chamber which produced a relative humidity of 92% at 28°C . The chamber was purged with nitrogen at a low flow rate to prevent the formation of a flammable air-fuel mixture in the head space. Samples were placed in 15 mL graduated, glass test tubes at fill volumes of 10 mL and 5 mL: referred to as high and low fill volumes (HV and LV, respectively). The LV samples have twice the headspace of the HV samples. Initially blends were placed in the chamber in uncapped fully open test tubes. After only one week the samples almost entirely evaporated indicating moisture uptake could not be monitored at this rate of sample weathering. To limit evaporation while allowing for exposure to the surrounding atmosphere the test tubes were closed with vented caps (a small hole in the center of the cap). Experimentation with several vent diameters led us to select a diameter 0.3 mm. With this vent diameter blends showed less than 5% mass loss in one week, which was deemed sufficient for weekly monitoring. An example test tube and cap are shown in Figure 2.

Four vented test tubes were prepared for each blend and placed in the chamber. Each week samples were allowed to reach room temperature and inspected for haze and phase separation. At weeks 1, 2, and 3 the test tube for each blend level was removed for measurement of sample weight, water content by ASTM method D6304, ethanol content by D5501, and detailed hydrocarbon analysis (DHA) by D6729. Samples which formed haze or phase separation were homogenized with a vortex mixer followed by centrifugation prior to sample removal for water, ethanol, and DHA testing. The final sample was inspected visually at weeks 4 and 5, and removed and analyzed if phase separation had occurred. All HV samples were analyzed at 6 weeks. The remaining 5 ml was returned to the environmental chamber until phase separation was observed or 11 weeks. Note that these samples now had a head space equivalent to that of the LV samples and thus experience a different moisture uptake rate. The final LV samples were not analyzed until visible phase separation occurred or 8 weeks. The E83 blend was not analyzed by DHA as this concentration of ethanol is beyond the scope for that method. Sample mass was recorded weekly to determine extent of evaporation.

During the second phase (small engine fuel tanks under diurnal cycling), blends were held in an environmental chamber with a 24 hour temperature cycle from 21°C to 38°C (70°F to 100°F) for 3 months (see Figure 3). The daily cycle is shown in Figure 4. The relative humidity of the chamber cycled from near 100% to 60% from the low to the high temperature. Two sets of E0, E10, E15, E25, and E83 blends prepared from the DFE and sCBOB-2 were stored in small equipment fuel tanks. One set of blends was held in tanks designed for current model year Honda lawn mowers with 0.25 gallon capacity, constructed of ethylene vinyl alcohol (EVOH) and low-density polyethylene (LDPE) with a high-density polyethylene (HDPE) exterior (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, constructed of HDPE (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). Measurements of water content by ASTM method D6304, ethanol content by D5501, and DHA by D6729

were conducted monthly. During sampling the tanks were shaken thoroughly to provide a homogenous sample and the blends were inspected visually for any signs of haze or phase separation.



Figure 2. Test tubes, caps, and drilled hole vent.



Figure 3. Photograph of fuel tanks and environmental chamber. Type A tank = Honda EVOH/LDPE, Type B tank = Tecumseh HDPE.

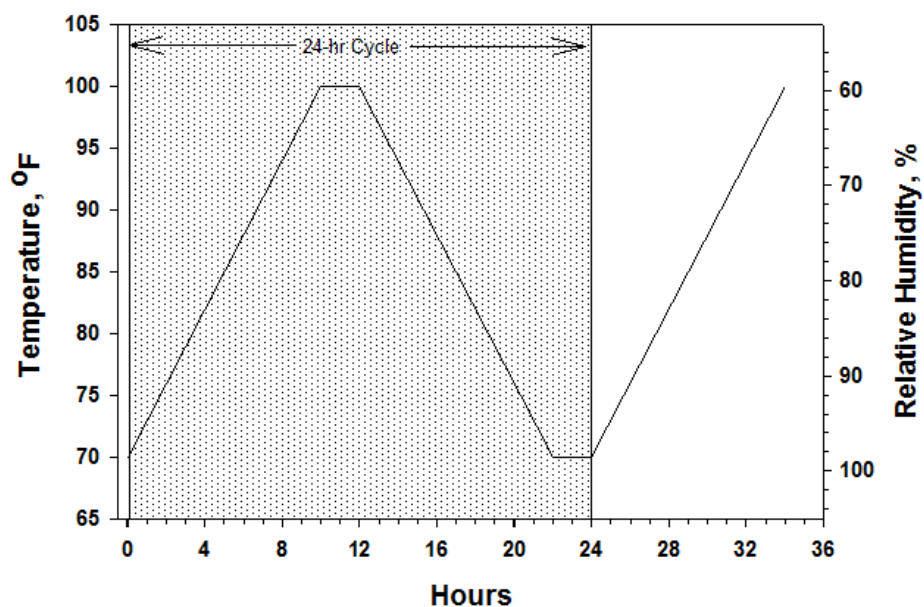


Figure 4. Daily temperature/humidity cycle used for exposure of fuel in lawn mower tanks to a humid environment.

To provide context for the test environments, the level of humidity utilized in these tests along with humidity data for several locations in the U.S. are provided in Table 3. The constant humidity test tube experiment simulates the most humid part of the day in a hot, humid climate continuously. The diurnal cycle simulates a more humid than average day in a hot, humid climate.

Table 3. Average July relative humidity of select locations in the U.S.² compared to test conditions.

	Average Morning Humidity	Average Afternoon Humidity
Test Condition - Constant	92%	92%
Test Condition - Diurnal	100% (70°F)	60% (100°F)
Houston, TX	93%	55%
New Orleans, LA	92%	66%
Orlando, FL	93%	66%
Richmond, VA	92%	58%

Results

Moisture Uptake in Constant Temperature and Humidity Experiments

High volume (HV, low headspace) samples were tested for all properties at weeks 1 through 3. At the fourth week no haze or phase separation was observed in the final test tube so it was returned to the chamber for continued exposure. At 6 weeks the blends remained clear and bright but were tested for all properties. To further explore the possibility of phase separation the remaining sample volume (approximately 5 mL) was returned to the chamber to continue monitoring for any visible changes. At 8 weeks the portion of the E10 blend that had been returned to the chamber showed visible haze and was removed for analysis. The E15 and E25 showed phase separation at 9 and 11 weeks, respectively. Water concentrations of blends taken from each test tube are provided in Figure 5 and photographs of the phase separated samples are shown in Figures 6 and 7. The point of phase separation or haze formation is noted with PS in Figure 5. *Note that for the HV samples phase separation only occurred after approximately 50% of the sample had been removed for analysis.* Low volume (LV, high headspace) E15 and E10 showed phase separation at 4 and 5 weeks, respectively (Figure 7). The observation that the LV E15 blend experienced phase separation earlier than the LV E10, which is the opposite of the case for the HV blends, deserves comment. This is also opposite of expectation given the higher water tolerance of E15 compared to E10. This irregularity is due to variability in seals or vent diameters of the test tube caps leading to inconsistent degrees of exposure with the surrounding atmosphere and rates of weathering. This issue is discussed in more detail in the Appendix.

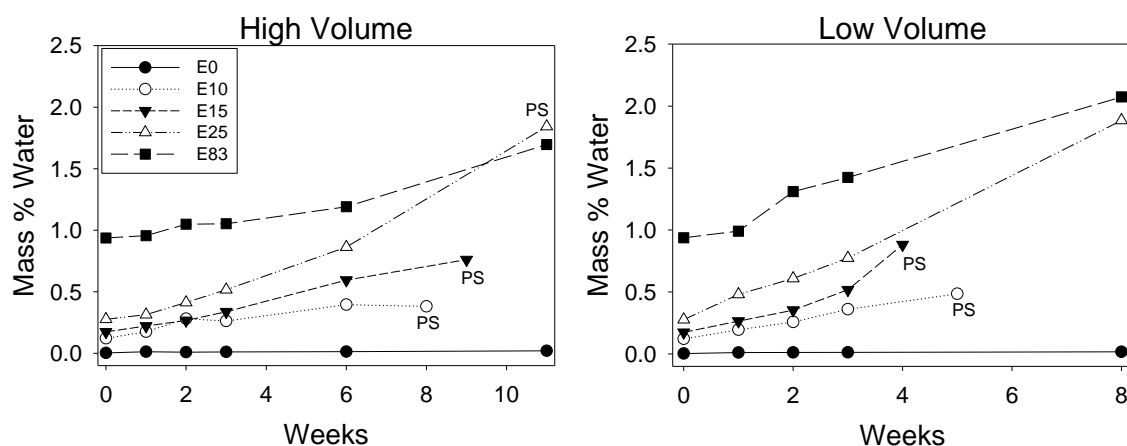


Figure 5. Water content of aliquots during exposure. PS indicates the point of phase separation.

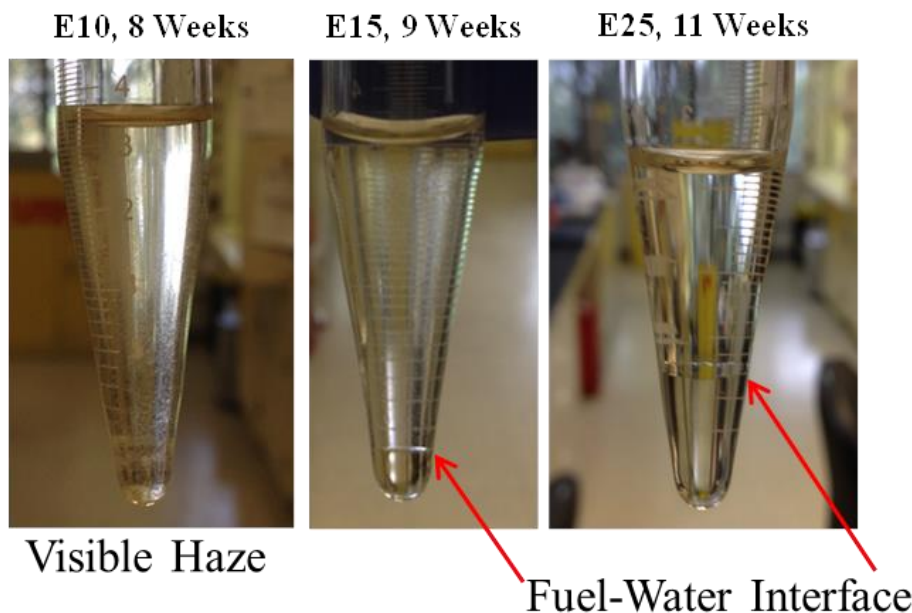


Figure 6. Photographs of phase separated HV samples from the test tube experiments.

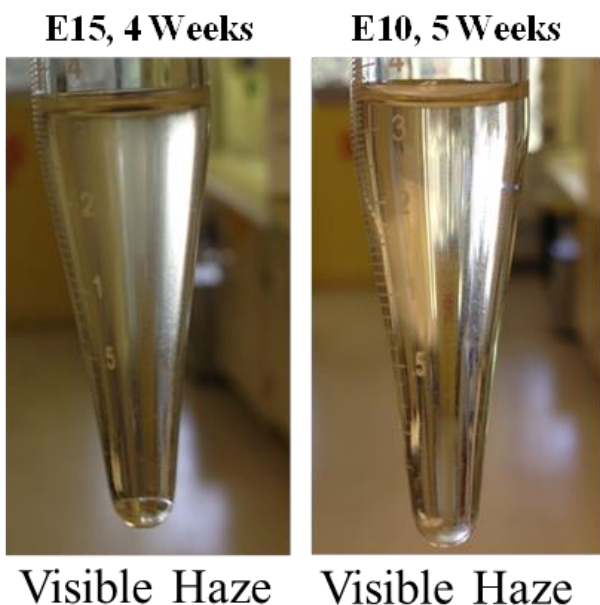


Figure 7. Photographs of phase separated LV samples from the test tube experiments.

Overall rates of moisture uptake were estimated for the test tube samples. For the HV samples this rate is calculated over the 6 weeks of humidity exposure before the sample volume was reduced. For the LV samples this rate was calculated over the entire time of humidity exposure shown in Figure 5 – to some extent averaging out the irregularity observed for the E15 sample at 4 weeks. These results are shown in Table 4. Overall, the rate of moisture uptake increases as ethanol content is increased from 10 to 25 vol%, however this was lower for the E83 samples. Increasing headspace volume had a significant impact on the overall rate of moisture uptake for ethanol blends.

Table 4. Overall rates of moisture uptake. HV samples over six weeks, LV samples over entire experiment.

	HV ppm/day	LV ppm/day
E0	6.0	6.3
E10	80.6	108.7
E15	78.0	207.9
E25	100.9	262.0
E83	55.6	217.1

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. Percent mass loss of the final aliquots is provided in Figure 8. For the HV samples the mass loss is corrected for the 5 ml of sample removed at 6 weeks humidity exposure. At the points at which phase separation or haze formation were observed in E10, E15, or E25 the samples had lost between 26 and 33% of the starting mass. The E0 experienced mass loss of nearly 40% by the end of the experiment.

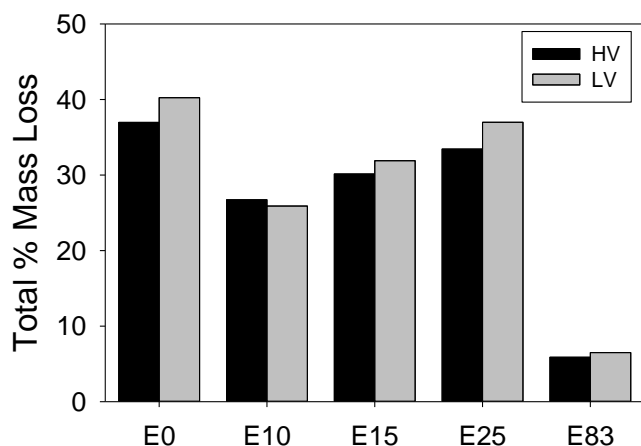


Figure 8. Mass loss of final aliquots of high volume (HV) and low volume (LV) blends.

This dramatic fuel weathering would be expected to have a negative impact on fuel quality, especially vapor pressure. Although the sample volumes at the end of the test were not sufficient to measure vapor pressures, this can be approximated from DHA. Using the individual component vapor pressures and their molar concentrations the total vapor pressure can be calculated.³ For example, sCBOB-1 had a measured vapor pressure of 6.7 psi at the beginning of the test and the approximation from DHA was 6.8 psi. From this approximation of the vapor pressure of the hydrocarbons the vapor pressure of an ethanol blend can also be estimated using the Wilson equation.⁴ Estimated vapor pressures of the humidity exposed blends are provided in Figure 9. The vapor pressures after weathering were reduced to less than 5.5 psi, the lower limit on summertime fuel in the ASTM specification for flex fuel blends, D5798. Although the range of ethanol concentration in Figure 6 is not applicable to the flex fuel specification, D5798 provides an indication that the vapor pressure of these blends was reduced to a

level that would likely be unacceptable for use. For example the E0 stored in these conditions would have a vapor pressure of 2 to 3 psi. Samples taken from the HV test tubes at 6 weeks had approximate vapor pressures below 5.5 psi, indicating the fuel had weathered weeks prior to phase separation. This degree of weathering may also have caused additional problematic changes in fuel properties such as increased T10, T50, T90, sulfur content, gum content, and driveability index. Additional detail on the rate of fuel weathering and chemical compositional changes is presented in the Appendix.

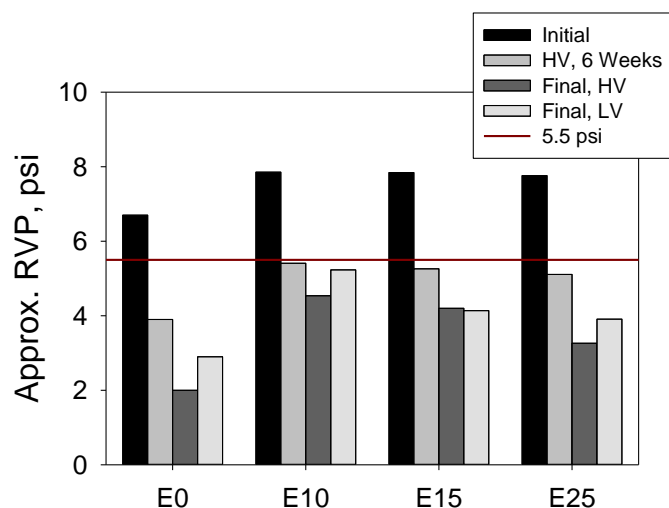


Figure 9. Vapor pressures approximated from detailed hydrocarbon analysis and the Wilson equation. The line at 5.5 psi is the minimum vapor pressure required for flex-fuel blends under summer conditions.

Fuel weathering and phase separation change the composition of the gasoline, which results in changes not only in the vapor pressure and distillation temperatures, but also affects the antiknock index (AKI or octane rating). Although sample volumes were too small to conduct AKI testing, these values can be approximated from DHA results. The AKIs of the samples were approximated from blending octane numbers of components identified by DHA and the blending octane of ethanol. These results are provided in Figure 10. As weathering progressed the concentration of light weight isoparaffins was reduced causing a loss of AKI, which is notable at 6 weeks for the blends as well as the HV and final LV E0 samples. At the final sampling of the HV E10 sample, after phase separation was observed, the AKI is estimated to have fallen below 87, making the hydrocarbon layer of low quality for combustion in a spark ignited engine. Ethanol is an octane improver, and having some of this content extracted into a water layer further lowered the AKI of the blend. In the case of E15, despite having phase separated the AKI remained above 87 indicating that ethanol remaining in the fuel maintained adequate AKI. It is notable that the final HV E0 sample shows an apparent increase in AKI. This is primarily due to a loss of normal paraffins and resultant concentration of substituted aromatics, which generated a high aromatic, high boiling point fuel. This is also observed in the final HV E25. Hydrocarbon weathering lowered AKI for E0, E10, and E15 prior to phase separation. Phase separation and partial removal of ethanol from the gasoline resulted in further loss of AKI in E10 and E15.

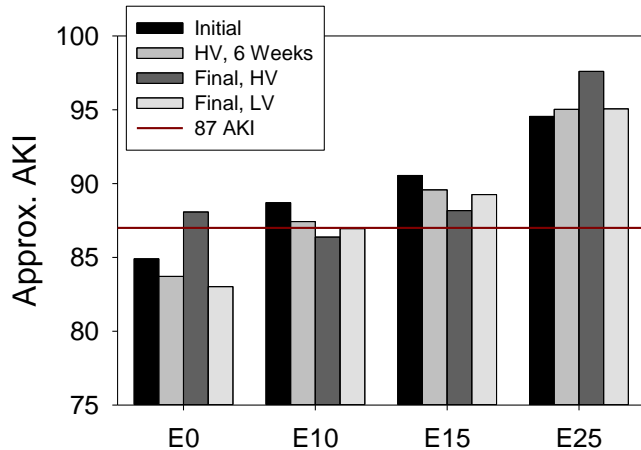


Figure 10. Octane numbers (AKI) approximated from detailed hydrocarbon analysis and ethanol concentration based on blending octane numbers.

Moisture Uptake in Fuel Tanks during Diurnal Cycling Experiments

An EPA study indicates that almost all volatile organic compound emissions from small non-road tanks occur during refueling, or via permeation of fuel through the tank walls rather than by evaporation and escape of volatiles through small openings.⁵ The tanks are tightly sealed specifically to prevent fuel evaporation. However, fuel tanks require a small amount of ventilation to allow air to be drawn in as fuel is consumed during operation as a fully sealed tank would create a vacuum as fuel volume is removed, eventually stopping fuel flow. Photographs of the fuel tank caps used in these experiments are provided in Figure 11 highlighting their air inhalation vents. These vents allow the fuel tanks to breath during operation as well as during temperature fluctuations. At high temperatures the pressure inside the fuel tank increases, accelerating permeation of volatile compounds through the tank walls as well as any vapor escape through the cap. When temperatures drop the tank pressure decreases, creating a vacuum which draws in the surrounding atmosphere through the inhalation vent.

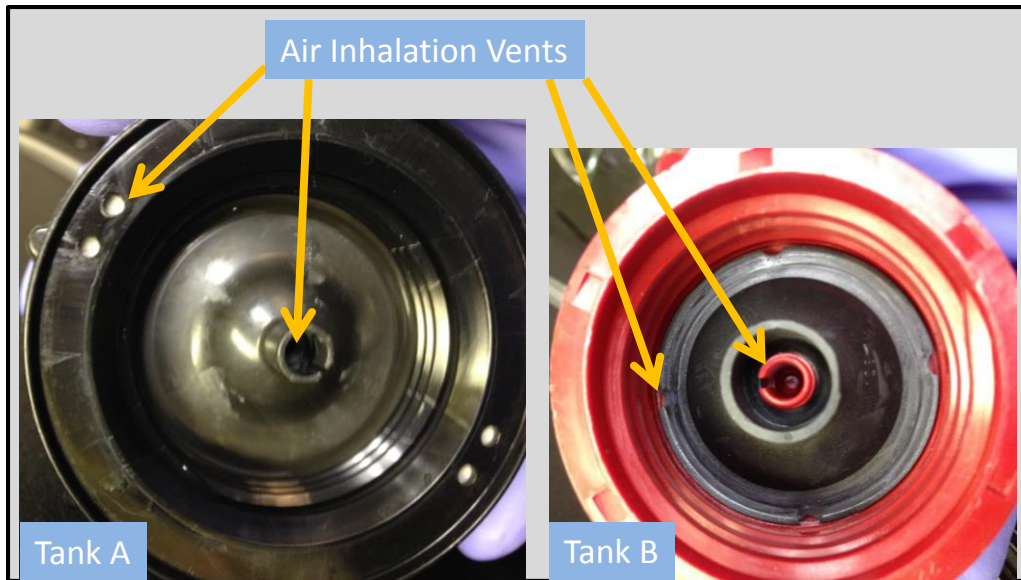


Figure 11. Fuel caps of each small engine fuel tank.

Water concentrations in the tanks over time for each fuel are shown in Figure 12. Phase separation was observed only for the E10 blend in Tank A. A picture comparing the Tank A and Tank B E10s at end of test is shown in Figure 13. The E10 in the Tank A showed a significant amount of haze when sampled which settled into a separate phase after several hours. The moisture uptake rates expressed as ppm/day, provided in Table 5, show water was absorbed more rapidly as fuel ethanol content increased – in agreement with observations for the test tubes. Moisture uptake rates were very similar for E0, E10, and E15 between Tanks A and B, which resulted in nearly the same water concentration at the end of three months. However, water uptake rates were considerably higher for Tank A when filled with E25 and E83.

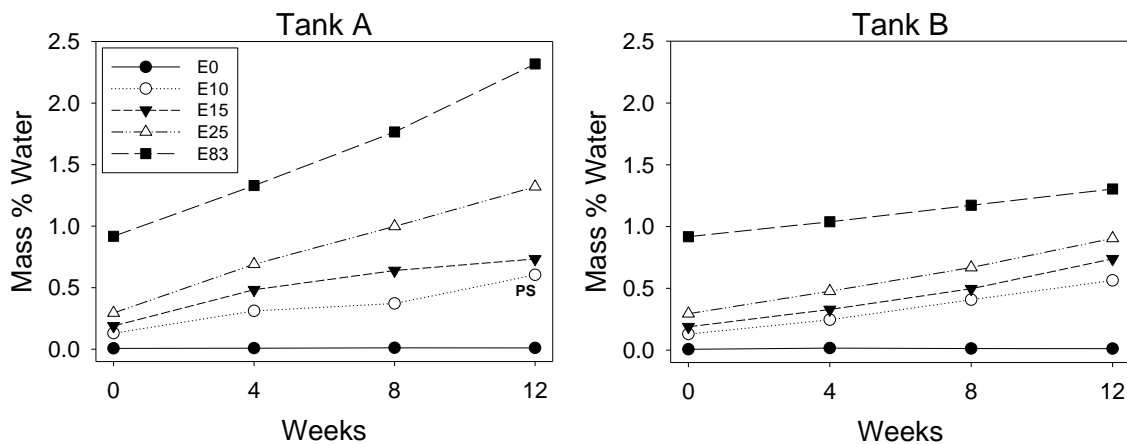


Figure 12. Water content blends during exposure. PS indicates the point of phase separation.

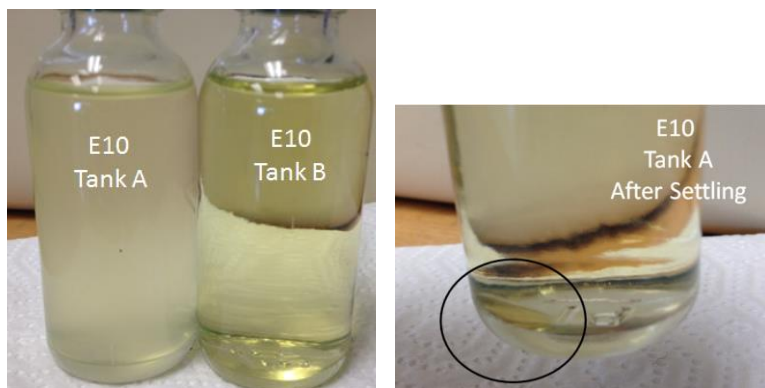


Figure 13. E10 blends from each tank type at the end of test.

Table 5. Moisture uptake rates of blends over three months of exposure.

	Tank A ppm/day	Tank B ppm/day
E0	0.4	0.6
E10	56.5	51.7
E15	64.8	65.4
E25	122.3	72.6
E83	166.8	46.0

Blends held in fuel tanks experienced considerable mass loss by the end of 3 months of storage in the environmental chamber. The percent mass loss of each blend is shown in Figure 14. 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. The rates of mass loss per tank volume, expressed as g/L/day, are provided in Table 6. For Tank A E83 had the lowest mass loss rate, followed by E0, with slightly higher mass loss rates for the E10 to E25 blends which are very similar to each other. For Tank B mass loss rates are inversely proportional to ethanol content, with the highest rate for E0. These results suggest that the material of construction for Tank A is slightly more permeable for ethanol in mid-level blends than for hydrocarbon. The opposite appears true for Tank B where decreasing mass loss rate with increasing ethanol content suggests the tank wall is more permeable to hydrocarbon than to ethanol.

Figure 15 shows the vapor pressures of the blends measured by ASTM D5191 at the beginning and end of the test as well as an approximation of their vapor pressures from DHA at 8 weeks. Fuels in both tanks weathered to have vapor pressure below 5.5 psi and likely also experienced increases in T10, T50, T90, gum content and driveability index making these fuels no longer fit for purpose. Blends held in Tank A had approximated vapor pressures below 5.5 psi at 8 weeks, indicating these deleterious changes occurred prior to phase separation of the E10.

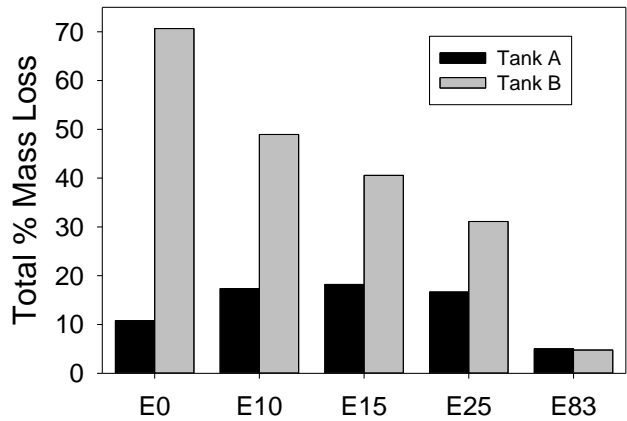


Figure 14. Total mass loss after 3 months of storage for blends held in small engine fuel tanks.

Table 6. Mass loss rates of the fuel tanks.

	Tank A g/L/day	Tank B g/L/day
E0	0.3	2.0
E10	0.5	1.3
E15	0.6	1.1
E25	0.5	0.8
E83	0.2	0.1

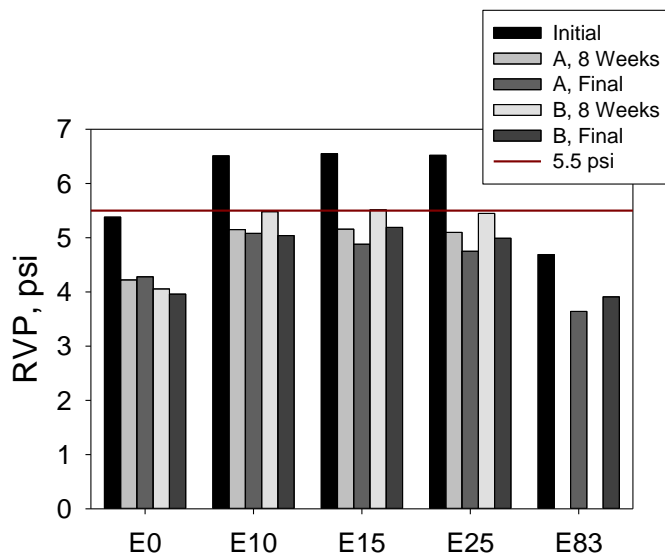


Figure 15. Vapor pressures of blends before, during, and after the 3 month exposure. Initial and final vapor pressures were measured by ASTM D5191; the vapor pressure at 8 weeks was approximated from detailed hydrocarbon analysis and the Wilson equation.

Considering the results from blends held in vented test tubes, one might expect a significant difference in the vapor pressures of blends from Tank A versus Tank B at the end of test due to the much more extreme weathering of blends in Tank B. However, that was not the case. The final vapor pressures of the E10s, for example, are nearly identical despite the fact that the blend held in the Tank A lost 17% of its mass compared to the 44% lost in Tank B. Vapor pressures of the E15, E25, and E83 are somewhat higher from Tank B even though percent mass loss from this tank design was substantially greater. This is likely because mass loss from the fuel tanks is almost entirely from permeation. Lighter components will permeate faster, hence the reduction in RVP, but the entire gasoline is permeating through the tank wall.

Figure 16 provides a comparison of the concentrations of light and heavy components of the blends before and after the test. Blends in both tanks show a loss of light compounds and corresponding concentration of heavier components as a result of weathering. However, the heavier components have a lower concentration in Tank B when compared to Tank A for all blends except E0. Figure 17 shows the ethanol concentrations before and after the test. For each blend held in Tank A the concentration of ethanol was significantly reduced, consistent with ethanol permeating the tank wall more readily than hydrocarbon. Ethanol concentration was increased in blends held Tank B, consistent with hydrocarbon permeating more readily than ethanol. The ethanol concentration of the E10 from Tank A had decreased to 5.7% while the E10 from Tank B had increased to 10.7%. The decrease in ethanol from Tank A lowered the water tolerance of this blend leading to phase separation, which did not occur in Tank B at similar water concentration.

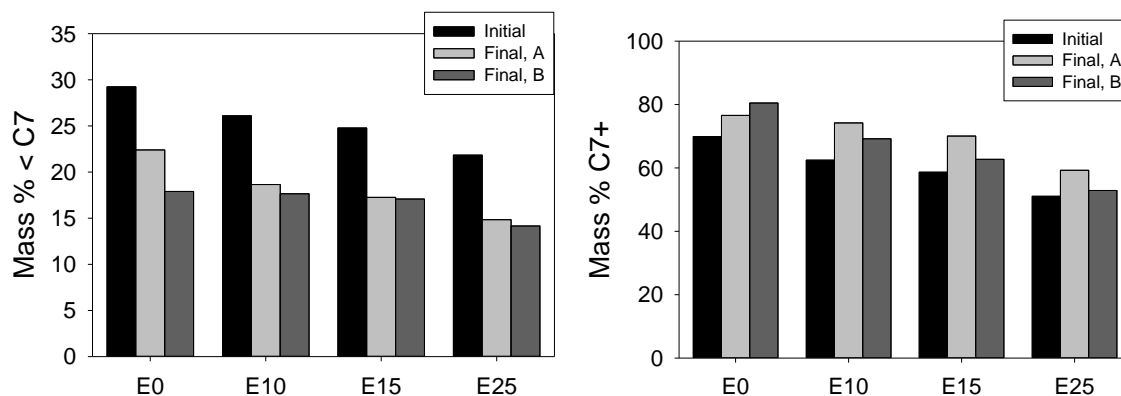


Figure 16. Changes in hydrocarbon composition measured by detailed hydrocarbon analysis. Hydrocarbons are divided into carbon number groups, the lightest components having less than 7 carbon atoms (< C7) and the remaining composition having 7 or more (C7+).

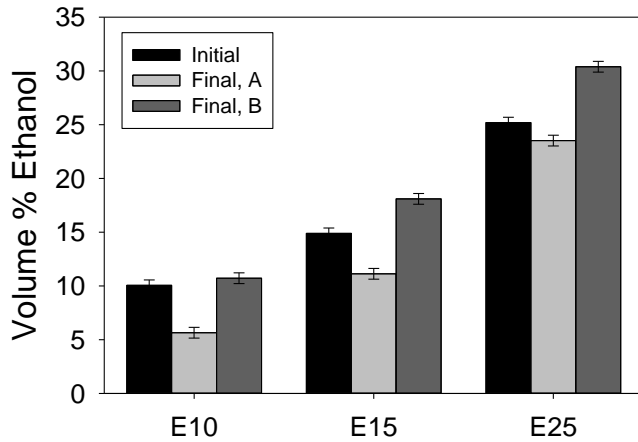


Figure 17. Initial and final ethanol content of blends, E83 not shown.

Similar to the vented test tube experiments, the AKI of these blends was impacted by weathering. Figure 18 shows the approximated AKI values for the blends at 8 and 12 weeks compared to the initial values for each tank. The E0 shows a drop in AKI by 8 weeks in both fuel tanks, which is also observed with ethanol blends. The E10 held in Tank A showed a considerable loss of AKI after phase separation at the end of test due to loss of ethanol (Fig 17). Notably the E15 and E25 held in Tank B show increases in AKI, which is due to an increase in ethanol concentration relative to the hydrocarbon blendstock (Fig 17). As observed with the vented test tubes a loss of light isoparaffinic hydrocarbons results in a loss of AKI during weathering. This loss of AKI was observed in the E0 and ethanol blends, and AKI loss was exacerbated by phase separation for the E10 held in Tank A.

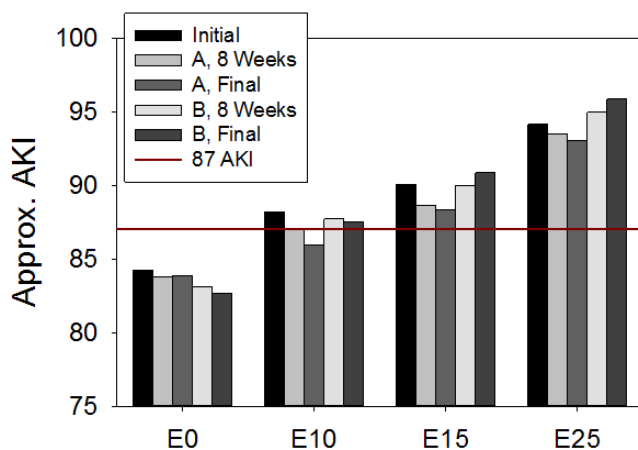


Figure 18. Octane numbers (AKI) approximated from detailed hydrocarbon analysis and ethanol concentration based on blending octane numbers.

Discussion

Results from constant temperature/humidity tests in glass test tubes represent a situation where fuel weathers by evaporation. In uncapped tubes this evaporation occurs rapidly at 28°C (82°F) such that all of the fuel evaporates in less than one week. Internet videos and other anecdotal presentations of moisture uptake by ethanol-gasoline blends held in open containers (mason jars, beakers, etc.) fail to take into account the extreme fuel weathering that occurs in this situation – which has a much more rapid and significant impact of fuel quality than moisture uptake. A more realistic scenario is a fuel container with a small opening such as the test tubes with caps that have a 0.3 mm opening as used here. This dramatically reduces the evaporation rate and reveals that ethanol-gasoline blends can absorb moisture from humid air at a faster rate than hydrocarbon gasoline – an expected result given the hygroscopic nature of dry ethanol. When held for a sufficient amount of time in a humid environment the blend can absorb enough moisture to result in phase separation. Nevertheless, even in this situation fuel evaporation causes a dramatic reduction in fuel quality such that the weathered fuel is no longer fit for purpose well before it has taken up enough moisture from the environment to phase separate. Pure hydrocarbon gasoline stored in the same environment for the same period of time would be unfit for use due to weathering, despite much lower water uptake and lack of phase separation.

In evaporation at constant temperature fuel components evaporate at a rate proportional to their vapor pressure. The lightest most volatile components evaporate at a much higher rate than moderate to low volatility components, hence the large reduction in vapor pressure and the concentration of heavier components. For example, in the HV tubes the E25 blend saw a reduction in the lightest components with less than seven carbon atoms from about 23 wt% to below 5 wt% while the components with seven or more carbon atoms increased in concentration from 50 wt% to over 60 wt% (see Appendix).

Small engine fuel tanks have for many years been designed to have a very low leakage rate of fuel vapor to the outside environment. Obviously this design feature is for improved consumer satisfaction by preventing gasoline from rapidly evaporating out of the tank in hot weather. Thus, the capped test tubes are not an adequate model for what happens in an actual fuel tank. Fuel tank caps do have small inhalation vents which are designed to allow for air to be drawn in during use while limiting fuel loss during storage; however, evaporation is not the primary mode of fuel loss in a plastic fuel tank as is the case with a glass test tube. Gasoline can escape from plastic tanks by permeation through the tank wall. While lower molecular weight, high volatility components can permeate tank walls at a higher rate than heavier components, the effect is much smaller than for direct fuel evaporation. For example, in our tests of Tank B, a HDPE tank with high permeation rate, the E25 blend saw a reduction in the lightest components with less than seven carbon atoms from about 23 wt% to 15 wt% while the components with seven or more carbon atoms increased only slightly (Figure 16). As noted above, changes in carbon distribution for E25 in the HV test tubes were much larger. These observations, as well as the fact that final vapor pressures were very similar for the two tank types even though mass loss rate was as much as a factor of 6 higher in Tank B, show that all components of the gasoline are permeating at a significant rate.

The fuel tank results can be explained by examination of what is known about evaporative emissions from small non-road engine fuel tanks. Differences in the tanks arise because Tank B is intended for 2008 and earlier model year engines which were not subject to evaporation/permeation emission regulations (which did not come into effect for this class of engines until 2012).⁶ Tank A's much lower rate of fuel mass loss is driven by this tank's materials of construction which are intended to meet the 1.5 g/m²/day permeation limit in the U.S. Environmental Protection Agency regulations.¹ While all gasoline components can permeate through tank walls, lighter, lower molecular weight gasoline components will permeate more rapidly than heavier components, which accounts for the reduction in RVP observed for these samples. Note that the HDPE used to construct Tank B is highly permeable to hydrocarbon relative to ethanol (higher rate of mass loss for E0 compared to Exx blends in Figure 14) resulting in an increase in ethanol content for fuels stored in Tank B (Figure 17). The materials used for Tank A allow a much lower overall permeation rate, and appear to be slightly more permeable to ethanol at moderate levels than to hydrocarbon (higher rate of mass loss for E10 to E25 blends relative to E0 in Figure 14), resulting in the observed reduction in ethanol content.

While it is tempting to compare the tank mass loss results from this study to results of small engine evaporative emission tests, this work did not follow evaporative emission testing protocols making such comparisons invalid. Nevertheless, it is notable that there are examples in the literature of plastic fuel systems with very low steady state and diurnal permeation emissions that show higher permeation for ethanol (similar to Tank A), as well as examples of systems with higher overall permeation that show a preference for emission of hydrocarbon.⁷

Despite vastly different mass loss rates, fuels stored in these two tanks had similar water uptake rates for E0, E10, and E15 resulting in nearly identical water concentrations at the end of 3 months. At nearly the same concentration of water the E10 stored in Tank A phase separated while the one stored in Tank B did not. As shown in Figure 1 higher concentrations of ethanol impart higher water tolerance on blends. The E10 in Tank A phase separated due to water uptake in conjunction with a reduced water tolerance from loss of ethanol to permeation.

Similar to experiments with vented test tubes the vapor pressures of fuels stored in fuel tanks were significantly reduced after storage due to loss of light hydrocarbons. Analysis of the gasoline composition prior to phase separation indicated the vapor pressure of the blends was most likely unacceptable after two months of storage. In the case of the E10 stored in Tank A this fuel may have been unfit for use approximately one month prior to the onset of phase separation. Blends which did not experience phase separation were unfit for use by the end of 3 months of storage.

The OEMs of the fuel tanks utilized in these experiments recommend emptying the tank if equipment is to be stored as long as 3 months. These experiments have shown that this practice is needed to prevent loss of fuel quality as well as to safeguard against phase separation. If fuel is stored long enough for phase separation to occur the fuel is likely also unfit for purpose because of reduction in vapor pressure and other undesirable changes to fuel properties.

Conclusions

- Exposure of gasoline or gasoline-ethanol blends to ambient air in open containers results in very rapid evaporation of the most volatile fuel components. Under these conditions weathering of the fuel to be unfit for purpose because of low vapor pressure, and potentially high T50 and T90, high sulfur and gum, and high driveability index are larger issues than moisture uptake from the environment.
- Use of containers with a very small open area or leak significantly reduces the evaporation rate. Under these conditions ethanol blends will absorb moisture faster from a humid environment than E0. While higher ethanol blends such as E15 or E25 can take up moisture faster, the much higher water tolerance of higher ethanol blends makes them less likely to phase separate.
- Under conditions where fuel evaporation through a leak occurs, fuel quality degrades rapidly as volatile components are removed. The fuel experiences a decrease in RVP, and increases in the amount of heavier components. This is likely to result in increased sulfur, gum, T10, T50, T90, and driveability index as well as reduction in octane numbers – all of which are considered a degradation of fuel quality.
- Any liquid water that enters a container of hydrocarbon gasoline forms a separate phase. In this sense hydrocarbon gasoline is more prone to phase separation. However, the rate of moisture uptake from humid air for hydrocarbon gasoline is roughly one tenth that of ethanol blends – hydrocarbon gasoline does not attract moisture the same way that ethanol blends do.
- Unlike open containers or capped test tubes, fuel tanks are closed tightly to limit gasoline evaporation, but for plastic tanks fuel can escape by permeation through the tank walls. As gasoline volume is reduced by combustion of the fuel or permeation ambient air can flow into the tank. Air inhalation vents of fuel tanks allow for tank breathing during diurnal cycling and thus contact with ambient air during storage.
- For tank materials where ethanol permeation is more rapid than that of hydrocarbon, fuel ethanol content and water tolerance can decrease over time. In this situation, moisture uptake from humid air can result in phase separation. Similar to evaporation, the fuel quality degrades as the lightest components permeate the tank wall resulting in an unfit for purpose fuel well before the onset of phase separation.
- Fuel tank manufacturers recommend emptying the tank if equipment is to be stored as long as 3 months. These experiments have shown that this practice is needed to prevent loss of fuel quality as well as to safeguard against phase separation. If fuel is stored long enough for phase separation to occur the fuel is likely also unfit for purpose because of reduction in vapor pressure and other undesirable changes to fuel properties.

Appendix: Weathering Rate and Chemical Compositional Changes in Constant Humidity Test Tube Experiments

The hydrocarbon composition of these blends changed significantly by the end of the test regardless of whether phase separation was observed. This change was quantified by DHA and is shown in Figure A-1. The lightest hydrocarbons, having 6 or less carbon atoms are denoted as < C7 and the somewhat heavier and less volatile components having 7 or more carbon atoms are denoted as C7+. The amount of the lightest compounds decreased to less than half their initial concentrations in most of the blends and the heavier compounds increased. This change in composition, referred to as weathering, is the result of the more volatile components of the gasoline evaporating at a faster rate than the less volatile ones, concentrating the heavier components.

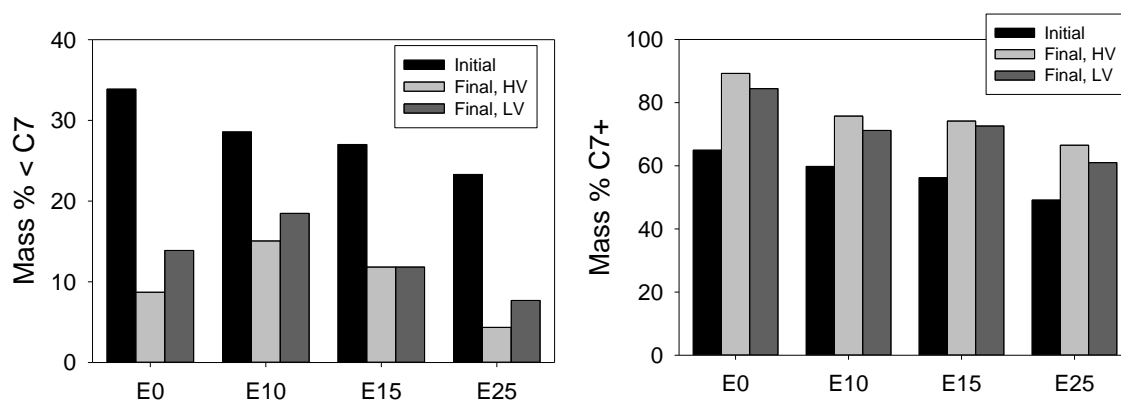


Figure A-1: Changes in hydrocarbon composition measured by detailed hydrocarbon analysis. Hydrocarbons are divided into carbon number groups, the lightest components having less than 7 carbon atoms (< C7) and the remaining composition having 7 or more (C7+).

Evaporation of the light ends of the hydrocarbons also resulted in loss of ethanol from the E10 and E15 blends. Figure A-2 shows the ethanol concentration at the beginning and end of the test. For both HV and LV, ethanol was reduced in the E10 and 15. As shown in Figure 1, lower concentration ethanol blends have lower water tolerance. Weathering of E10 and E15 blends not only reduced vapor pressure, but also reduced water tolerance due to loss of ethanol. In the case of E25 the ethanol concentration was increased by weathering. It is notable that the ethanol concentration of the E25 LV was higher than that of the E25 HV at the end of the test. Both E25 samples had nearly the same water content at the end of test (1.8 mass % in HV and 1.9% in LV) yet the LV experiment did not show phase separation. This is due to increased water tolerance of the LV sample relative to the HV. Both E83 samples (not shown in Figure A-2) had an increase in ethanol concentration from 83 to 87 volume %.

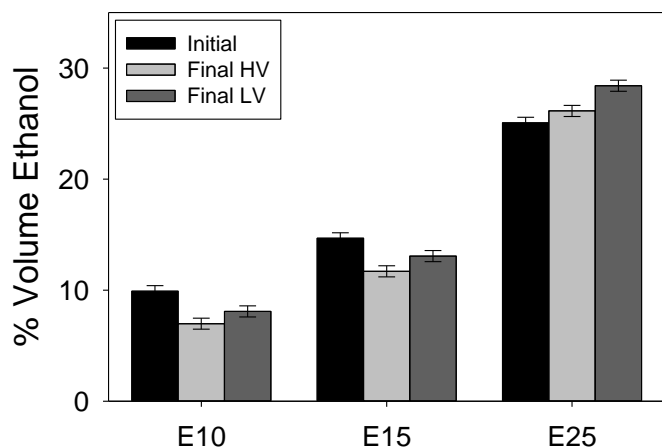


Figure A-2. Initial and final ethanol content of blends, E83 not shown.

The test tubes used in these experiments were unfortunately inconsistent in their cap seals and/or vent diameters, which impacts both weathering and water absorption rates. For example, there is a notable irregularity in the data shown in Figure 5. The LV E15 blend experienced phase separation earlier than the LV E10, which is the opposite of the case for the HV blends. This is also opposite of expectation given the higher water tolerance of E15 compared to E10. This irregularity is due to variability in seals or vent diameters of the test tube caps leading to inconsistent degrees of exposure with the surrounding atmosphere and rates of weathering. These inconsistencies are notable when comparing weathering expressed as mass change per test tube volume (g/L/day) shown in Figure A-3. These values are from each individual test tube removed at each time point and there is considerable scatter in the data. The mass loss of the final aliquot was recorded throughout the experiment, shown in Figure A-4, and provides a comparison of mass loss rate of a single test tube to the variability from one test tube to the next. Mass loss rates of single tubes were considerably more consistent when compared to the variation observed with multiple test tubes. The final aliquot of the LV E15 lost mass at a greater rate than any other LV sample, which explains why this E15 formed haze prior to the E10. The HV E10 and E15 final aliquots lost mass at similar rates (had more consistent vents/seals) resulting in phase separation occurring in the E10 prior to the E15; consistent with the higher water tolerance of E15. Thus, the more rapid mass loss and water uptake observed for the final E15 LV aliquot is a consequence of inconsistent tube venting. This result highlights the sensitivity of water uptake rate to weathering rate.

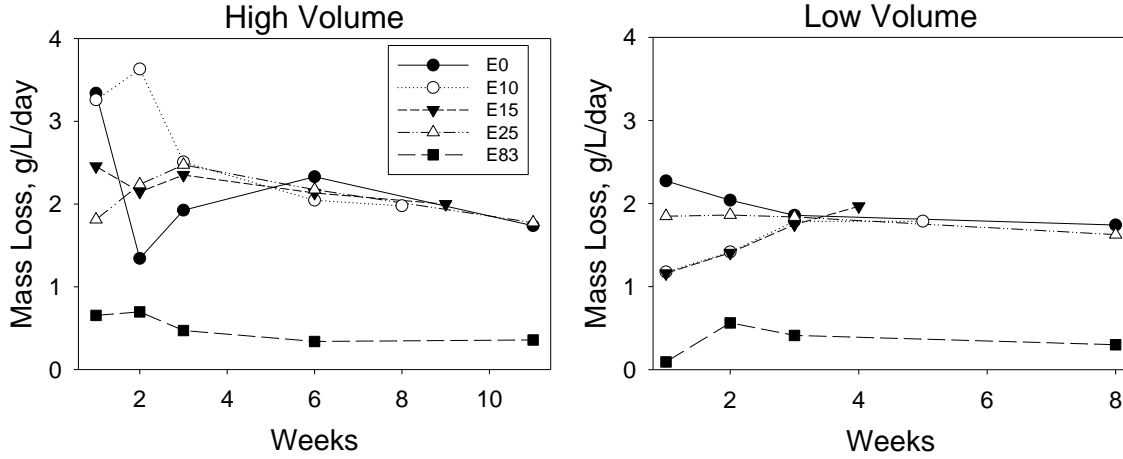


Figure A-3. Mass loss rates of aliquots during exposure expressed as g/L/day.

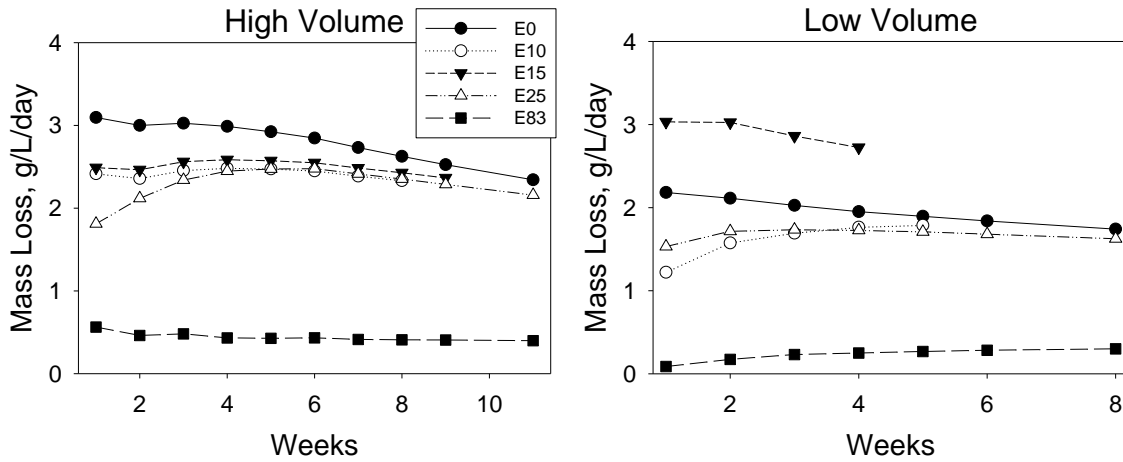


Figure A-4. Mass loss rate of final aliquot during exposure expressed as g/L/day.

Variability in weathering rates of the test tubes complicates predictions of water uptake rate from this experiment. Under these test conditions an E10 blend filled to one third the container capacity phase separated in 5 weeks of exposure. The ethanol concentration of this blend had been reduced to 8% by that time. Given that fuel tanks are designed to prevent gasoline evaporation we cannot directly compare this scenario with vented containers to real-world storage. This experiment has shown that absorption of moisture from the surrounding atmosphere may result in phase separation; however, this occurs in conjunction with gasoline and ethanol evaporation. During storage the vapor pressure and water tolerance of a blend will change along with water uptake and the rates of these changes are dependent on container headspace and vapor leakage rate.

References

- ¹ *United States Code of Federal Regulations* 1060.103, April 30, 2010.
- ² <http://www.currentresults.com/Weather/US/humidity-city-august.php>, accessed November 14, 2015.
- ³ Maynard, J. B.; Sanders, W. N., Determination of the Detailed Hydrocarbon Composition and Potential Atmospheric Reactivity of Full-Range Motor Gasolines. *Journal of the Air Pollution Control Association* 1969, 19 (7), 505–510.
- ⁴ Christensen, E.; Yanowitz, J.; Ratcliff, M.; McCormick, R. L. Renewable Oxygenate Blending Effects on Gasoline Properties. *Energy& Fuels* 2011, 25 (10), 4723–4733.
- ⁵ U.S. Environmental Protection Agency, *2007 Progress Report: Vehicle and Engine Compliance Activities*. EPA-420-R-08-011, October 2008.
- ⁶ Manufacturers of Emission Controls Association, *Emission Control of Small Spark-Ignited Off-Road Engines and Equipment*, January 2009.
- ⁷ Kimura, K., Wolf, L., Baustian, J., Haskew, H. Hydrocarbon Permeation in Gasoline Vehicle Fuel Systems Using Isobutanol Blends. *SAE Int. J. Fuels Lubr.* 5(3):2012, doi:10.4271/2012-01-1582.