NRT Quick Reference Guide: Fuel Grade Ethanol Spills (including E85)

Report spills to the National Response Center 1-800-424-8802

Chemical Properties

Blend labels and names: Fuel Grade Ethanol (FGE) is ethanol that has been denatured (rendered undrinkable) and produced for blending with gasoline at low proportions or to create alternative fuels such as E85. Nearly all gasoline sold as a motor fuel today is E10 (a fuel blend containing up to 10% fuel grade ethanol in regular, unleaded gasoline). **E10** is generally labeled as regular unleaded gasoline or labeled "may contain up to 10% ethanol." **E85** is a fuel restricted for use in "flex-fuel" vehicles and primarily marketed in the Midwestern states near the main source of ethanol feedstock grains. FGE and E85 are the fuels primarily discussed in this guide. The percent ethanol in E85 is nominally 85%, but varies by geographic area and season, and may have a minimum of 70% for cold weather blends to a minimum of 79% for use in warmer temperatures.
Comparison of ethanol and ethanol-gasoline blends to regular gasoline: Responders are familiar with the characteristics of regular gasoline spills into water. Therefore, this guide compares the characteristics and behavior of FGE and ethanol-gasoline blends ("blends" in this guide) to regular gasoline.
Similarities between ethanol and gasoline: Both are organic solvents, are highly volatile, flammable liquids, and are less dense than water.
Differences between ethanol and gasoline: Ethanol is completely miscible (soluble) in water at any ratio, while gasoline has a low solubility in water. Fighting fires of fuel blends containing 10% or more ethanol by volume requires the use of an Alcohol Resistant-Aqueous Film Forming Foam (AR-AFFF).
Properties generally proportional to blend ratio: The characteristics of an ethanol-gasoline fuel blend generally are continuously proportional to the relative ratio of ethanol and gasoline. That is, the higher the % ethanol, the more like ethanol (as a polar solvent) the mixture behaves, and vice versa.
Fuel blend solubility and separation: Introduction of water to ethanol-gasoline blends will promote separation of the ethanol and gasoline. This is likely to occur during spills into high water volumes. Lab tests indicate that a water-to-fuel blend ratio greater than 1 to 7 causes separation. During separation, the ethanol and water combine, while the gasoline portion floats toward the water surface.
The following section shows the properties of pure ethanol, Fuel Grade Ethanol/E85, and pure gasoline in a side-by-side comparison.

Ethanol (un-denatured), ethyl alcohol, or grain alcohol

DOT Placard: UN 3065, UN 1170
Application: Organic Solvent & Fuel Additive
CAS: 64-17-5
Ethanol is a volatile, flammable, colorless clear liquid with a characteristic vinous or wine-like odor and pungent taste. Ethyl alcohol is commonly known as grain alcohol and can be consumed. It is a polar liquid, and therefore hydrophilic and completely soluble in water. It is produced by fermenting simple or complex sugars, cellulose, or starch. The most common feedstock for ethanol in the United States (US) is corn, but switchgrass, bagasse, sugarcane, sorghum, barley and sugar beets are also used. The production involves fermenting the mash (crushed grain) or chemically converting cellulose-hemicellulose to sugar and then fermenting it. The product is then distilled and dehydrated for use as a fuel. The molecular formula of ethanol is C_2H_6O.

Note: The values below will change slightly for denatured ethanol (when 2-5% gasoline is added).

Molecular Weight: 46.07 g/mol
Volatility: vapor pressure is 42-44 mm Hg at 68°F (20°C)
Freezing point: -173°F (-114°C)
Vapor Density: 1.59 (air = 1); heavier than air
Boiling Point: 173.1°F (78.4°C)
Flashpoint: 55.4°F (13°C)
Flammability Class: 3
Specific Gravity (liquid): 0.79 g/ml at 68.0°F (20°C)
Solubility: Fully soluble (miscible) in both fresh and salt water or other polar liquid, and non-polar liquids such as gasoline or other organic solvents.
Electrical Conductivity: Ethanol is a good electrical conductor (as are all polar liquids).
Flame Visibility: Under certain conditions flames of burning pure ethanol may be less visible than for blends with gasoline.

Fuel Grade Ethanol (95-98% ethanol in gasoline) and E85 (70-79% ethanol in regular gasoline)

DOT Placard: UN 1987 for denatured ethanol, and UN 3475 for blends with more than 10% ethanol
Application: Motor Fuel, and Fuel Additive
CAS: No CAS # for blends
FGE is produced in the US to be used both as a gasoline blending component and as the primary fuel component in fuels like E85. FGE is commonly transported via tank truck, tank car and barge, but currently in only a few pipelines modified to accept it. Ethanol is typically added to gasoline at distribution terminals. In the US, ethanol must be denatured before shipping (to render it non-potable for tax purposes) by adding gasoline or gasoline-range hydrocarbons at a concentration of 2-5%.

The values of blends for **Molecular Weight, Volatility, Freezing Point, Vapor Density, Boiling Point, Flashpoint, and Specific Gravity (liquid)** will typically be **intermediate between ethanol and gasoline.** They are generally proportional to the percentages of ethanol and gasoline in the blend.
Flammability Class: 3
Solubility: soluble (miscible) in water, but the gasoline and ethanol may separate in the presence of water.
Electrical Conductivity: Good electrical conductor due to the ethanol content.

Motor Gasoline (regular unleaded)

DOT Placard: UN 1203
Application: Motor Fuel
CAS: 8006-61-9 or 86290-81-5
Gasoline is typically a hydrocarbon distillation product of crude oil, commonly used as a motor fuel. It is a complex mixture of mostly lighter hydrocarbons (low molecular weight) that may include both straight chain alkanes ranging from C_6 to C_{10} and ring shaped (cyclical, aliphatic or aromatic) components such as benzene, toluene, ethylbenzene, and xylene isomers (BTEX) plus others. Gasoline is a clear, colorless to amber-colored, volatile, non-polar liquid with a typical petroleum odor. It is less dense than water with low solubility in water. Hence, it floats on water. Vapors are heavier than air. Leaked vapors may travel to a source of ignition and then flash back to the gasoline source.

Note: The values below are approximate and will change only slightly for E10, commonly marketed simply as gasoline. They will also vary depending on seasonal blends.

Molecular Weight: 72 g/mol (approx.)
Volatility: highly volatile (greater than ethanol); vapor pressure is 300-500 mm Hg at 68°F (20°C)
Freezing point: -40°F (-6.2°C)
Vapor Density: 3 to 4 (air = 1); heavier than air
Boiling Point: 140 to 390°F (60 to 199°C), various components of gasoline boil off in this range.
Flashpoint: -36°F (-38°C)
Flammability Class: 3
Specific Gravity (liquid): 0.73 g/ml at 68.0°F (20°C)
Solubility: Poorly soluble (miscible) in water, although the light components such as BTEX are slightly soluble. Gasoline is very soluble in non-polar liquids, such as acetone and other organic solvents.
Electrical Conductivity: Pure gasoline is a poor electrical conductor.

Fuel Grade Ethanol & E85 Blend Response Options

Department of Transportation (DOT) Emergency Response Guide 127 (ID#3475) for Flammable Liquids (Polar/Water-miscible), ***with some additions:***
Eliminate all ignition sources (no smoking, flares, sparks or flames in immediate area).
Area must be well ventilated.
All equipment used when handling the product must be grounded.
Do not touch or walk through spilled material.
Stop leaks if you can do it without risk.
Prevent entry into waterways, sewers, basements or confined areas.
A vapor suppressing **alcohol resistant** foam may be used to reduce vapors.
Alcohol breaks down the film of regular foams.
Absorb or cover with dry earth, sand or other noncombustible material and transfer to containers.
Use clean non-sparking tools to collect absorbed material.
Dike far ahead of liquid spill for later disposal.
Water spray may reduce vapor, but may not prevent ignition in closed spaces.
Minimize the potential for groundwater contamination by removing fuel soaked soils.

Containment on Water: Depending on the potential receptors, gasoline spills on the water may be allowed to spread unrestricted to promote evaporation. Some exclusion booming may be effective on any gasoline sheen that forms. Absorbent boom may be less effective on blend spills. The greater the proportion of ethanol in the blend, the more it will dissolve into the water column, resulting in less effectiveness of all booms. If the decision is made to deploy boom, it should still be effective for floating product, such as any gasoline fraction that has phase separated from the blend and refloated.
Aerial Spraying: May not be effective in enhancing ethanol evaporation.
Air Monitoring:
- **Ethanol** – CGI and FID, or photo ionizing detector (PID) and confined space gas detector (such as a MultiRAE Plus Five-Gas air monitor or similar device).
- **Gasoline** - photo ionizing detector (PID) and confined space gas detector (such as a MultiRAE Plus Five-Gas air monitor or similar device).

Water Intakes: Quickly determine if sensitive water intakes (such as for drinking, process, aquaculture, or cooling water) are threatened by the spill since **blend spills may rapidly affect the entire water column** of the receiving water body. Contact potentially affected facility operators and discuss the threat with them.
Water Monitoring: See "**Detection, Sampling, and Analysis**" below.

Health & Safety

Ethanol vapors	**IDLH = 3300ppm**	**LEL = 3.3%**	**UEL = 19.0%**	**TEEL3 = 3300ppm**	**Flammability class = 3 (Ignites at normal temperatures)**
Gasoline vapors	**IDLH = (Benzene) 500ppm**	**LEL = 1.4%**	**UEL = 7.4%**	**TEEL3 = 1500ppm**	**Flammability class = 3 (Ignites at normal temperatures)**

Protective Clothing: Wear positive pressure self-contained breathing apparatus (SCBA). Structural firefighters' protective clothing will provide limited protection.
Evacuation: For large spills, consider initial downwind evacuation for at least 300 meters (1000 feet) and consider initial evacuation for 800 meters (1/2 mile) in all directions since such fires spread rapidly. For fire, if tank, rail car, or tank truck is involved in a fire, isolate for 800 meters (1/2 mile) in all directions.
Electrical Conductivity: **Warning - Fuel blends with significant amounts of ethanol are good electrical conductors!**
Vapors near engine air intakes: There is a risk of "runaway engines" if vapors create a rich fuel mixture, resulting in engine over-rev and inability to stop the engine.
Ethanol entering firefighting (FF) water intake hoses: Firefighters should avoid drawing raw water with potentially high levels of spilled product into fire monitors due to its potential to feed the flames, rather than extinguish them.

Fuel Grade Ethanol Spills (including E85) (side 2)

Effect of Receiving Water Types

Groundwater: Spills to groundwater or threatening groundwater pose unique problems and are not covered by this NRT Quick Reference Guide.

Expected Behavior of Ethanol Blend Spills into Surface Waters:

General considerations – The behavior of FGE/E85 when spilled into different types of surface waters, and thus the response needed, is not well documented at this time. However, based on limited experiences, physical chemistry, and some lab trials, the following guidance is provided. It is expected that the spill behavior will be related to the mixing energy (still vs. flowing water) and size/depth (dilution volume) of the receiving body. Behavior is probably less dependent on salinity. Also, because the gasoline fraction is carried down into the water column and dispersed by the ethanol, more of the volatile and toxic compounds of gasoline (such as benzene, toluene, ethylbenzene and xylenes, BTEX), may tend to partition into the water as a result.

To still or slow water (ponds, lakes, bayous, etc.) – The blend should spread out and may phase separate as it mixes into the water column allowing a fraction of the gasoline to evaporate before the blend mixes into the water column. The spill will likely affect the deep layers and bottom, even though blends are lighter than water. In this case the mixing is driven by the natural affinity of ethanol for water, resulting in a gradual diffusion into it. The remaining gasoline fraction more readily disperses into the water column as a result of its bond with ethanol, but the gasoline-ethanol bonding is weak relative to water-ethanol bonding, so the gasoline will separate out and float toward the surface.

To flowing or fast water (rivers, streams, rapids, breaking surf, etc.) – The mixing energy of the receiving water will likely result in rapid to near immediate mixing of the blend into the whole water column. Blend separation with resulting floating of the gasoline may also occur in larger water volumes.

To large, deep water bodies – Such spills allow the blend an unrestricted ability to flow out and dilute down into the water column. This is likely to result in blend separation, with the gasoline then tending to refloat. A gasoline slick or sheen may form at the surface, but its location and size will depend on how dispersed or diluted the spill has become.

To small, shallow water bodies – Such spills restrict dilution, so concentrations of the spilled blend may remain elevated for an extended period. The gasoline may also be carried into the entire water column, but may subsequently separate and refloat.

Salinity effect – Salinity of the receiving water is expected to have only minor direct effects on the behavior of a blend spill. Environmental degradation in saltwater may be slower than in fresh water. Higher salinity will also reduce the already low solubility of gasoline components, resulting in lower bioavailability to organisms. The presence of a higher salinity (denser) layer (a "salt wedge") at the bottom of parts of an estuary generally retards water layer mixing, and could result in slower mixing of the blend into the bottom layer.

Thermoclines – The presence of a cold, dense (heavier) layer of water below warmer (lighter) surface water retards the mixing of these water layers (similar to the salt wedge discussed above). Therefore, a thermocline may also slow the mixing of a blend into the lower cold layer.

Biological Effects

An ethanol or ethanol-gasoline blend spill into a surface water environment is expected to result in an acute exposure. As a result, the areas affected by high ethanol concentrations may quickly show biological injury such as fish kills. Some effects on reptiles and mammals exposed to high blend concentrations can be expected, especially on delicate tissues such as eyes. Ethanol concentrations of 1 part per thousand for 24 hours will injure most crustaceans, and sensitive crustaceans may be affected when exposed for 72 hours to 0.5 ppm ethanol. Once the ethanol fraction becomes diluted below about 1%, it should begin to be degraded by microbes, with an expected half-life of 3 to 5 days in the environment. The gasoline that separates from the ethanol should tend to re-float, although it is difficult to predict to what extent this will occur and has not been confirmed by experimental data. Once at the water surface, gasoline will generally evaporate in a few hours. The more soluble fractions of the gasoline, such as the BTEX, may remain in the water column at higher concentrations than for a regular gasoline spill due to the dispersant effect of the ethanol. The extent of this mechanism and the resulting biological injury is not yet well documented. The high biological oxygen demand/chemical oxygen demand (BOD/COD) of E85 may lower dissolved oxygen (DO) enough to cause fish kills. In flowing streams, such kills have occurred 30 to 40 miles downstream. Water DO levels should be monitored and aeration/sparging methods used if practical.

Regulatory Status

OPA – Any discharge of oil, including gasoline, is subject to the Oil Pollution Act of 1990 (OPA). Fuel Grade Ethanol generally contains 2-5% gasoline, and ethanol-gasoline fuel blends have higher amounts of gasoline, so they are subject to OPA.

CERCLA – Ethanol is not a Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) hazardous substance. Petroleum, including but not limited to gasoline, is subject to OPA.

CWA – The Federal Water Pollution Control Act of 1972 (aka CWA) covers pollution discharges into the waters of the US. A discharge of ethanol denatured with oil (e.g., gasoline) is subject to Section 311 of the CWA.

Shipping Regulations (for samples) – Ethanol and gasoline are highly flammable and hazardous materials. The packaging and shipping of pure or high concentrations ethanol samples are subject to strict regulations established by DOT and the Occupational Safety and Health Administration (OSHA). Consult the analytical laboratory receiving the samples to determine if they have additional packaging or shipping requirements. Multiple small volume (1 oz.) samples may be shipped in special packaging.

Detection, Sampling, and Analysis

General Considerations – Detection of blend spills into water should focus on each part of the blend (the ethanol and the gasoline) separately, since they: 1) often separate in large water volumes; 2) take differing pathways in the water column; 3) may require different response methods; 4) require different detection methods; and 5) may affect different natural resources, and in different ways.

ETHANOL DETECTION

Field (rapid) Detection:

- **Visual** – Unlike the surface slick of oil and gasoline, undenatured **ethanol cannot be visually tracked** since it is clear and mixes down into the water column.
- **Odor** – Ethanol gives off a vapor with a characteristic vinous or wine-like odor. The odor detection threshold is approximately 6 ppm (mg/L) ethanol in water.
- **Field meters** – Field ethanol meters are not currently available. However, some potentially field-adaptable laboratory meters that use near infrared (NIR) detection produce usable readings (+/- 0.1% by volume or better) within minutes and are being evaluated by the National Response Team (NRT) Science & Technology Committee. Devices that measure sample density (specific gravity), such as hydrometers, cannot be adapted for environmental ethanol measurement. The availability of titration or colorimetric methods is also being investigated.
- **pH or DO measurements** – A spill of E85 may lower the pH and/or DO (due to the high BOD/COD). These are easily measured parameters using commonly available field meters. However, the usefulness of this method for tracking a spill plume is not well established.
- **Fluorometry (such as SMART methods)** – Fluorometry cannot detect ethanol since it does not fluoresce. For low detection levels, lab analysis must use gas chromatography (GC)/FID with or without purge and trap, as for hydrocarbons like gasoline. However, if a field flow through sampling system is deployed, such as the earlier Special Monitoring of Applied Response Technology (SMART) protocol, it could potentially be modified to allow periodic sub-sampling of the flow for ethanol detection.

Laboratory Analysis (results in hours to days) – Responders generally require rapid detection (field meters or tests) of ethanol levels in affected waters due to the short response time window. Sampling, transport and lab analysis can rarely meet this requirement. However, confirmatory sampling for injury assessment studies or modeling validation may benefit from such sampling and analysis. At least one laboratory analyzer (Anton Paar Alcolyzer) uses NIR detection. Gas chromatography is also used in the laboratory.

GASOLINE DETECTION

- **Visual** – The subsurface gasoline from a blend spill may not be detected visually. However, any gasoline that separates and reaches the surface may form a slick or sheen that is observable. Gasoline slicks and sheens often disappear quickly.
- **Odor** – Gasoline floating on the surface gives off a vapor with a characteristic petroleum odor.

Field meters and fluorometry (such as SMART methods) – Fluorometry is a common method to detect hydrocarbons, including gasoline, in the water column. Refer to NRT SMART protocols.

Aquatic Detection Sampling Plans

Purpose - Since the subsurface (water column) part of a blend spill cannot be visually detected, the purpose of field sampling is to track the movement of the unobservable plumes to prevent or mitigate the potential impacts on water intakes and biological resources, as well as to calibrate, verify, and re-initiate plume trajectory modeling forecasts. Additionally, actual detection (vs. modeling only) should be used to confirm that concentrations are below damaging concentration prior to reopening water intakes.

Time window and location - To be useful, detection plans must be prepared rapidly and implemented within hours if practical. Sampling should attempt to locate the leading and lateral edges of the ethanol plume, areas of maximum concentrations, as well as the extent of actionable (response significant) concentrations.

Waste Disposal

Because wastes generated from the spill cleanup may be flammable, the wastes may exhibit the hazardous waste characteristic of ignitability and should be disposed of accordingly. Do not store spill-saturated wastes near sources of heat or ignition, and use a well ventilated area to avoid vapor buildup. If it can be done safely—and without contaminating the soil or groundwater—allow excavated contaminated soils to ventilate to encourage evaporation. Disperse vapors to avoid creating explosive conditions.