

Instructor Manual

Module

3

Chemical and Physical Characteristics of Ethanol and Hydrocarbon Fuels

Module Objective

Upon the completion of this module, participants should be able to describe the chemical and physical differences between gasoline, ethanol and ethanol-blended fuels.

Enabling Objectives

1. Compare the chemistry of gasoline, ethanol, and ethanol-blended fuels.
2. Describe the characteristics of ethanol-blended fuels.

Instructor Note:

Module Time: 40 minutes/ 55 minutes

Materials:

- Activity 3.1 and 3.2
 - Worksheets 3.1 and 3.2
- Emergency Response Considerations video – (Show the video segment from 4:32 to 6:47)

Instructor Note:

Show the video Emergency Response Considerations (4:32 to 6:47).

Introduction

In order to understand the nature of ethanol-blended fuels, emergency responders will need to understand the characteristics of polar solvents and hydrocarbons, their differences, and how these types of products interact. Ethanol is classified as a polar solvent. A polar solvent is a compound such as alcohol, most acids, or ammonia with a separation of charge in the chemical bonds. These have an affinity for water and will readily go into solution. Under some conditions, ethanol-blended fuels will retain certain characteristics as a gasoline-type fuel, and under others it will exhibit polar solvent-type characteristics. Understanding these conditions will help emergency responders mitigate the various incidents according to the conditions found.

Characteristics of Gasoline

Hydrocarbon fuels (gasoline, diesel fuel, kerosene, jet fuel, etc.) generally have similar characteristics whether they are flammable liquids or combustible liquids. In this program we will specifically identify the characteristics of gasoline as they relate to ethanol and gasoline blends. Gasoline is a hydrocarbon produced from crude oil. It is immiscible with water and will not mix with water at any concentration. It has a flash point of approximately -45°F , varying with octane rating. Gasoline changes seasonally and is blended specifically for each region of the country. An important point to note is that even in winter weather, it will ignite. Gasoline has a vapor density between 3 and 4. Therefore, as with all products with a vapor density greater than 1.0, gasoline vapors will seek low levels or remain close to ground level. Gasoline has a specific gravity of 0.72-0.76 which indicates it will float on top of water since it is immiscible or insoluble. Its auto-ignition temperature is greater than 530°F . Gasoline varies in composition. It is a mixture of many hydrocarbons typically with a boiling point between 100°F and 400°F but some portions, will boil at less than room temperature. Gasoline is not considered a poison but does have harmful effects after long-term and high-level exposure that can lead to respiratory failure. Smoke from burning gasoline is black and has toxic components. The toxic components found in gasoline include benzene, toluene, xylene, heptane, hexane, etc. Gasoline's greatest hazard is its flammability even though it has a fairly narrow flammability range (LEL is 1.4% and UEL is 7.6%).

Gasoline Production

Gasoline is produced from crude oil. Crude oil varies greatly in color and viscosity from oil well to oil well; largely dependent on the geographic region where the crude oil originated. Crude oil is transported via pipeline, freighter ship/ barge, rail tank car and cargo tank truck to an oil refinery where it is processed into refined products like gasoline. An oil refinery uses engineering techniques such as fractional distillation and alkylation to produce gasoline. Similar to crude oil, gasoline is also transported via pipeline, freighter ship/ barge, rail tank car and cargo tank truck until it ultimately reaches retail fueling stations and consumers.

Characteristics of Ethanol

Ethanol is a renewable fuel source that is produced by a fermentation and distillation process of starch containing products like corn and sorghum in the U.S. In Brazil, the primary feedstock for ethanol production is sugar cane. New feedstocks are being developed for ethanol products such as corn cobs, corn stover, switchgrass and other natural products that will be conducive to the fermentation/ distillation process. An ethanol biorefinery uses engineering techniques, similar to gasoline production, such as distillation and dehydration to produce fuel grade ethanol. Ethanol for use in motor fuel blends will generally be denatured with 2-5% gasoline or a similar hydrocarbon. Denaturant has minimal effects on the overall characteristics of ethanol except for flash point; the addition of denaturant further depresses the flash point. This training program focuses on denatured fuel ethanol.

Ethanol Production

In dry milling, the entire corn kernel or other starchy grain is first ground into flour, which is referred to in the industry as "meal", and processed without separating out the various component parts of the grain. The meal is slurried with water to form a "mash." Enzymes are added to the mash to convert the starch to dextrose, a simple sugar. Ammonia is added for pH control and as a nutrient to the yeast. The mash is processed in a high-temperature cooker to reduce bacteria levels ahead of fermentation. The mash is cooled and transferred to fermenters where yeast is added and the conversion of sugar to ethanol and carbon dioxide (CO₂) begins. The fermentation process generally takes about 40 to 50 hours. During this part of the process, the mash is agitated and kept cool to facilitate the activity of the yeast. After fermentation, the resulting "beer" is transferred to distillation columns where the ethanol is separated from the remaining "stillage." The ethanol is concentrated to 190 proof (95% ethanol) using conventional distillation and then is dehydrated to approximately 200 proof (100% ethanol) in a molecular sieve system. The anhydrous ethanol is then blended with about 2-5% denaturant (such as natural gasoline) to render it undrinkable and thus not subject to beverage alcohol tax. It is then ready for shipment to gasoline terminals or retailers. The stillage is sent through a centrifuge that separates the coarse grain from the solubles. The solubles are then concentrated to about 30% solids by evaporation, resulting in Condensed Distillers Solubles (CDS) or "syrup." The coarse grain and the syrup are then dried together to produce dried distillers grains with solubles (DDGS), a high quality, nutritious livestock feed. The CO₂ released during fermentation is captured and sold for use in carbonating soft drinks and beverages and the manufacture of dry ice.

Characteristics of Denatured Fuel Ethanol

Denatured fuel ethanol is a polar solvent that is water-soluble. A polar solvent is a compound such as alcohol, most acids, or ammonia with a separation of charge in the chemical bonds. These have an affinity for water and will readily go into solution. Denatured fuel ethanol has a flash point of -5°F and a vapor density of 1.5, which indicates that it is heavier than air. Consequently, ethanol vapors do not rise, similar to vapors from gasoline which seek lower altitudes. Denatured fuel ethanol's specific gravity is 0.79, which indicates it is lighter than water and it has an auto-ignition temperature of 709°F and a boiling point of 165-175°F. Like gasoline, denatured fuel ethanol's greatest hazard as a motor fuel component is its flammability. It has a wider flammable range than gasoline (LEL is 3% and UEL is 19%).

Chemical Properties Comparison

Property	Gasoline	Denatured Fuel Ethanol
Flash Point	⁰ - 45 F	⁰ - 5 F
Auto Ignition Temp	⁰ 530 - 853 F	⁰ 709 F
Specific Gravity	0.72 – 0.76	0.79
Vapor Density	3 - 4	1.5
Vapor Pressure	8 - 15psi	~3psi
Boiling Point	⁰ 100 - 400 F	⁰ 165 - 175 F
Flammable Range	1.4% - 7.6%	3% - 19%
Smoke Characteristics	Black	Slight
Solubility	Trace	High

From the chart, there are some very similar properties of gasoline vs. denatured fuel ethanol. Importantly, there are also very different inherent properties. It's important to note that gasoline is a complex mixture of over 500 compounds that may have between five and 12 carbon atoms. Denatured fuel ethanol is a two carbon alcohol, also referred to as ethyl alcohol, that has 2-5% of a denaturant added to render the product undrinkable. Both gasoline and ethanol are very flammable products; gasoline has a lower flash point of -45°F compared to -5°F for ethanol. The densities of gasoline and denatured fuel ethanol are similar; both fuels are lighter than water which has a density of 1.0. Gasoline has a very broad boiling point range which indicates components will boil off over a broad temperature range. Ethanol on the other hand has a very narrow boiling point range. Ethanol has a lower vapor pressure than gasoline: 3psi vs. 8-15psi for gasoline. Note the differences in the flammability ranges for these two products. It is also important to understand the great difference between the water solubility of ethanol vs. gasoline.

Considerations for Ethanol Fires

The flame and smoke from undenatured/ neat ethanol fires is not easily visible. Undenatured/ neat ethanol does not produce visible smoke and has a hard-to-see blue flame. In a denatured form there is little smoke with a slight orange visible flame. The most striking difference between ethanol and gasoline, ethanol mixes easily with water. While it is possible to dilute ethanol to a condition where it no longer supports combustion, this is not practical in the field as it requires copious amounts of water. Even at five parts water to one part ethanol (5:1 ratio/ 500% dilution), it will still burn.

Invisible Flames – Ethanol

Because fires involving a high percentage of ethanol can burn with little to no smoke generation and visible flame, the use of a thermal imaging camera is highly recommended.

This picture is of an ethanol fire as seen through a thermal imaging camera. Use caution when approaching an ethanol fire as the actual fire may be much larger than the visible flame.



Activity 3.1: Comparison of Gasoline and Ethanol

Purpose:

To allow participants time to discuss the differences and similarities in the chemical and physical properties of ethanol and gasoline.

Instructor Note:

Time: 15 minutes

Materials: Worksheet 3.1

Instructor Directions:

1. Have participants take a few minutes to review the prior information and fill in Worksheet 3.1.
2. In the participant guide the chart is left blank. The answers are only in your instructor's guide.
3. Based on this information, lead into a discussion in which you have the participants predict how the differences in the fuels, particularly when combined, might lead to different outcomes during emergencies by asking the following questions:
 - When comparing gasoline and ethanol, which product is flammable?
 - **Answer:** Both gasoline and ethanol are flammable.
 - Even though gasoline and ethanol have similar specific gravities how would you expect the mixed blend to react if released into a water source such as a creek or pond?
 - **Answer:** The specific gravity indicates ethanol may float on top of water, however ethanol is miscible with water so it will readily mix with any body of water and travel with the current. The gasoline portion will float on top and will not mix with the water.

Participant Directions

1. Review the information in Module 3.
2. Fill in Worksheet 3.1.

Worksheet 3.1: Gasoline — Denatured Fuel Ethanol

Property	Gasoline	Denatured Fuel Ethanol
Flash Point	- 45°F	- 5°F
Ignition Temp	530 – 853°F	709°F
Specific Gravity	0.72 – 0.76	0.79
Vapor Density	3 - 4	1.5
Vapor Pressure	8 - 15psi	~3psi
Boiling Point	100 – 400°F	165 – 175°F
Flammable Range	1.4% - 7.6%	3% - 19%
Smoke Characteristics	Black	Slight
Solubility	Trace	High

Characteristics of Ethanol-Blended Fuels

Blending ethanol with gasoline has multiple effects. The higher the concentration of ethanol, the more the fuel has polar solvent-type characteristics with corresponding effects on conducting fire suppression operations. Water introduction to ethanol and gasoline fuel blends has a dramatic effect. Without water, ethanol and gasoline blends are homogeneous. Ethanol has an affinity for water. For instance, it is not necessary to add any gas line antifreeze to a gasoline/ ethanol blend since the ethanol will absorb trace amounts of water and pull it through the fuel system of the vehicle. In the case of using water to extinguish a fire during emergency response efforts, the water can pull the ethanol out of the blend resulting in a separate layer comprised of water, ethanol, and some hydrocarbon content. The gasoline will remain in top layer. This is the result of the ethanol having more polar character than non-polar character.

Phase separation can occur in fuel storage systems where water is present or get into the system which is a rare occurrence.

Blending ethanol and gasoline produces a mixture with its own unique physical characteristics. One of the noticeable differences in the blended fuel versus unblended gasoline is the visual difference of the smoke and flame characteristics. The higher the content of ethanol, the less visible the black smoke content and orange flame production there will be. These characteristics may be masked by other substrates that may also be burning such as vehicle tires.

Consideration for Ethanol-Blended Fuel Fires

The video *Responding to Ethanol Related Incidents*, shows that the most effective route for keeping an ethanol fire under control is the use of alcohol resistant foam, more commonly known as AR-AFFF. As ethanol is a polar solvent, this foam contains a special polymer which creates a barrier between the foam and fuel which forms a cohesive blanket to extinguish the fire. This foam blanket not only helps manage the fire, it will also keep other spills from catching, prevents any re-ignition and can provide post fire security. ***Because the AR foam is universally suitable for use on both ethanol and non-ethanol blended fires, the best practice is for emergency responders to keep an AR foam readily available for these incidents.*** Another noticeable difference of ethanol-blended fuels under fire conditions is that when foam or water has been flowed on the burning product, the gasoline will tend to burn off first, eventually leaving the less volatile ethanol/ water solution which may have reduced visible flame or smoke. (Source: EERC, 2007)

Activity 3.2: Definitions

Purpose

To allow participants to identify the definitions related to ethanol and ethanol-blended fuels.

Instructor Note:

Time: 15 minutes

Materials: Worksheet 3.2

Instructor Directions:

1. *Tell participants that the definition for ethanol has been given. Ask them to take five minutes and see if they can fill in the terms for each of the definitions provided in Worksheet 3.2.*
2. *Give participants 5-10 minutes to write in the terms for each of the definitions below. Point out that #1 has been completed for them.*
3. *After you call time, call on participants to provide an answer for each definition. Make sure everyone understands each definition before moving to the next.*

Participant Directions

1. A list of definitions is provided.
2. Write in the appropriate definition for each in the space provided.
3. You will have approximately 5-10 minutes to complete the activity.

Worksheet 3.2: Definitions

Polar solvent	Auto-ignition temperature
Ethanol	Flash point
Toxicity	Vapor density
Specific gravity	Flammable liquid
Hydrocarbon	Boiling point
Flammable range (Upper Explosive Limit [UEL]–Lower Explosive Limit [LEL])	Vapor pressure

1. Ethanol: It is a clear, colorless, flammable solvent; also known as ethyl alcohol, grain spirits, or neat alcohol (anhydrous). Unlike other alcohols of similar molecular weight, ethanol is considered a drinking alcohol. Ethanol found in transportation fuels has been denatured, generally by the addition of 2-5% gasoline (denatured fuel ethanol), rendering it unfit for drinking and thereby avoiding the Federal liquor tax.
2. Polar Solvent: A compound such as alcohol, most acids, or ammonia with a separation of charge in the chemical bonds. These have an affinity for water and will readily go into solution.
3. Hydrocarbon: A compound composed of carbon and hydrogen and commonly obtained through the refining of crude oil.
4. Flash point (The flash point of gasoline is -45°F; the flash point of ethanol is -5°F): The minimum temperature at which a liquid gives off vapor in sufficient concentrations to allow the substance to ignite. The lowest temperature at which a flammable liquid can form an ignitable mixture in air near the surface of the liquid.
5. Auto-ignition temperature: The minimum temperature required to ignite a gas or vapor to spontaneously combust in air without a spark or flame being present.
6. Specific gravity: The ratio of the density of a substance to the density of water.
7. Vapor pressure: The pressure exerted by a vapor that is in equilibrium with its solid or liquid form.
8. Vapor density: Relative weight of a gas or vapor in comparison to air.
9. Boiling point: The temperature at which the vapor pressure of a liquid equals the environmental pressure surrounding the liquid.
10. Flammable range (Upper Explosive Limit [UEL] – Lower Explosive Limit [LEL]): Concentration range for a gas or vapor within which a fire may result if an ignition source is introduced; includes an upper and a lower limit between which the fire danger lies.
11. Toxicity: The degree to which a substance can harm humans or animals if absorbed, inhaled, injected or ingested.
12. Flammable liquid: Any liquid with a flash point under 100°F; referred to as Class I liquids; examples are gasoline and ethanol.

Summary

Instructor Note:

Ask participants:

- *Are you surprised by any of the differences between gasoline and ethanol?*
- *Which differences are going to be of most concern to emergency responders?*
- *Mixed blends of fuel present interesting situations for emergency responders. Water is a readily available firefighting agent, and we have discussed how the fuel mixtures react with water. What other hazards are associated with ethanol and ethanol blends, and what can be done to minimize these hazards?*
 - **Answers:** *Flammability, respiratory, and contact hazards. Also the issue of conductivity which demands that grounding and bonding be part of the tactical plan for transfers. The proper use of protective equipment such as eye protection, self-contained breathing apparatus (SCBA), flame resistant clothing, and appropriate gloves.*

Ethanol is a polar solvent that is miscible with water and is flammable. Knowing ethanol will be the last fuel to burn and that it may burn with little visible smoke or flame is important in determining an approach to take in dealing with ethanol-involved incidents. The most effective route for keeping an ethanol fire under control is the use alcohol resistant foam, more commonly known as AR-AFFF. Because the AR foam is universally suitable for use on both ethanol and non-ethanol blended fires, the best practice is for emergency responders to keep an AR foam readily available for these incidents. (Source: EERC, 2007)