## Ethanol and E85 Properties, Specifications, and Information

Also known as ethyl alcohol or grain alcohol, ethanol ( $C_2H_5OH$ ) is an oxygenated hydrocarbon compound. It is produced primarily from grain, such as corn or wheat. The starch contained in the grain is converted into sugar and fermented to produce ethanol. Ethanol can also be produced by hydrolysis of cellulose contained in plant-based materials, including corn stalks, wheat stalks, other agricultural or forestry waste, and municipal waste. Several processes currently being developed for cellulose-derived ethanol include enzymatic and acid hydrolysis and thermal processes. Cellulose-derived ethanol and E85 are expected to be a necessary component to meeting various state and national renewable fuel standards.

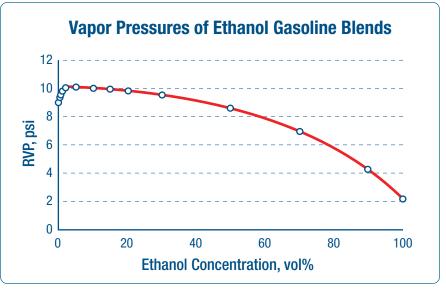
While ethanol for beverages and fuel are produced by a similar process, fuel ethanol is "denatured" by adding 2% hydrocarbons, such as natural gasoline to make it unfit for human consumption. Natural gasoline, a low-octane gasoline boiling-range hydrocarbon that is a by-product of natural gas production, can be used as a denaturant. Descriptive properties of fuel ethanol and E85 are listed in Table 1. Ethanol is a flammable, colorless liquid with a faint alcohol odor. The color of ethanol/ gasoline blends depends on the color of the gasoline in the blend. Blends may also have a gasoline-like odor.

Ethanol is a motor fuel that can be blended with gasoline. However, the unique chemical properties of ethanol must be accommodated in order to maintain engine performance, emissions, fuel economy, and driveability under all operating conditions. Since the heat of vaporization of ethanol is more

than twice the value of gasoline, it does not vaporize as readily under cold temperature conditions and until the engine reaches operating temperature. To ensure proper cold temperature engine start and warm-up operation in all regions of the United States, ethanol is blended with at least 15% hydrocarbons, which is more volatile than ethanol. In other countries, such as Brazil, where northern U.S. cold temperatures are not often encountered, it may be more practical to use neat (100%) ethanol. However, even in Brazil, most FFVs are equipped with small gasoline reservoirs that can be used for cold-temperature

# Ethanol Production, Blending, and Distribution

- Ethanol is produced at an ethanol plant. Prior to transporting, the fuel must be denatured by adding approximately 2% hydrocarbons, such as natural gasoline, to render it unfit for human consumption. A corrosion inhibitor is also added.
- The denatured ethanol is transported to the fuel supplier.
- Denatured ethanol is dispensed into the fuel supplier's ethanol storage tank in the same manner as gasoline and diesel fuel.
- A fuel carrier orders a tanker of E85.
- The fuel supplier dispenses 8.5 parts denatured ethanol to 1.5 parts hydrocarbons into the tanker truck.
- The fuel carrier delivers E85 to the retail fuel marketer for sale to the public.





engine starting. Unlike gasoline, ethanol vaporizes within a narrow temperature range. The combination of higher heat of vaporization and narrow vaporization temperature range requires careful attention to the hydrocarbon blending components and creates challenges for managing cold-start emissions.

With sufficient heat energy, ethanol vaporizes at a lower temperature than many of the hydrocarbons in gasoline and requires adjustment of the gasoline blending components to prevent high temperature vapor lock. Low-level ethanol/gasoline blends, up to about 20% ethanol, exhibit an increase in vapor pressure of about 1 psi, which should be compensated by adjusting the base gasoline properties. The opposite is true with high-level ethanol blends, such as E85, where a high vapor pressure gasoline blending component is needed to increase the vapor pressure of the blend to meet ASTM International specifications, which are discussed later in this section. Also unique to low-level ethanol blends, permeation of fuel system elastomer materials is substantially increased. Testing has confirmed that this is not the case with E85.<sup>2</sup>

Due to the reduced energy content of ethanol per gallon compared to gasoline, vehicle fuel economy on E85 is typically about 25% less compared to gasoline (measured in miles per gallon). Table 2 offers a comparison of the properties of E85 to those of methanol, ethanol, and gasoline.

Table 1. Properties of Fuel Ethanol and E85				
Property	Comment			
Vapor Density	Ethanol vapor, like gasoline vapor, is denser than air and tends to settle in low areas. Ethanol/gasoline blends, including E85, should be treated like gasoline blends with respect to handling and safety.			
Solubility in Water	Ethanol is extremely hydroscopic (i.e., attracts water). Water should be removed to the extent possible from fuel ethanol handling, storage, and distribution equipment. A small amount of water is soluble in E85, but at higher concentrations, the gasoline portion will separate from the ethanol/water mixture.			
Energy Content	For identical volumes, ethanol contains approximately 30% less energy than gasoline depending on the gasoline formulation. As a result, vehicle fuel economy of E85 can be expected to be reduced by about 25% depending on the gasoline formulation and the individual vehicle.			
Flame Visibility	A fuel ethanol flame is less bright than a gasoline flame but is easily visible in daylight.			
Specific Gravity	Pure ethanol and ethanol/gasoline blends are slightly more dense than gasoline.			
Conductivity	Ethanol and ethanol blends have increased electrical conductivity compared to gaso- line. This can affect materials compatibility due to increased corrosion of certain metal junctions and exposed electrical connections.			
Air-Fuel Ratio	Due to the oxygen content in ethanol, the ideal or "stoichiometric" air-fuel ratio for E85 is a lower value than it is for gasoline (i.e., fewer pounds of air per pound of fuel). FFVs are designed to detect ethanol and properly adjust the air-fuel ratio.			
Toxicity	Pure ethanol in small amounts is not toxic and is not considered carcinogenic; however, fuel ethanol and ethanol/gasoline blends must be treated as toxic and carcinogenic due to the addition of hydrocarbons and gasoline.			
Flammability	Depending on the hydrocarbon blending component, the vapor concentration in the storage tank head space of many E85 blends can fall into the flammable range. This is a concern primarily at low ambient temperatures.			

Table 2. Fuel Properties of Ethanol, Gasoline, and E85						
Property	Ethanol	Gasoline	E85			
Chemical Formula	C₂H₅OH	C <sub>4</sub> to C <sub>12</sub> Hydrocarbons	C <sub>4</sub> to C <sub>12</sub> Hydrocarbons and Oxygenated Hydrocarbons			
Main Constituents (% by weight)	52 C, 13 H, 35 O	85-88 C, 12-15 H	57 C, 13 H, 30 O			
Octane (R+M)/2	98-100	86-94	95-97			
Lower Heating Value (British thermal unit (BTU) per gallon)	76,300	116,900	83,600- 89,400			
Gasoline Gallon Equivalence (v/v gasoline)	1.5	1	1.3-1.4			
Miles per Gallon Compared to Gasoline	67%	_	73%			
Reid Vapor Pressure (psi)	2.3	7-16	7-12			
Ignition Point—Fuel in Air (%)	3-19	1-8	*			
Temperature (approx.) (°F)	850	495	*			
Specific Gravity (60/65°F)	0.794	0.72-0.78	0.78			
Cold Weather Starting	Poor	Good	Fair**			
Air-Fuel Ratio (by weight)	9	14.7	10			
Hydrogen-Carbon Ratio	3.0	1.85	2.75-2.95			

\*Depends on hydrocarbon blending component properties.

\*\*Depends on the fuel being blended to specifications.

Most transportation fuel sold in the United States is manufactured to ASTM specifications. ASTM International is a voluntary consensus standards organization that creates and maintains fuel quality specifications established by committees composed of vehicle and engine manufacturers, fuel system equipment manufacturers, fuel producers, fuel users, and other interested parties, such as state fuelquality regulators. Although ASTM standards are recognized by federal and most state governments as the primary means of ensuring fuel quality. EPA and most states have passed regulations and laws, which require gasoline to meet all or a portion of the ASTM gasoline guidelines. Various specifications for ethanol, E85, and denaturant are included in Appendix B. Also included are California specifications for denatured ethanol and denaturant.

#### **Seasonally Adjusted Blends**

The properties of ethanol for E85 blending should meet ASTM D4806. The ethanol content of E85 is seasonally adjusted to improve vehicle cold-start and warm-up performance. Denatured ethanol content can range from 68% to 85% by volume. The ASTM specification for E85 is ASTM D5798 "Specification for Fuel Ethanol (Ed75-Ed85) for Automotive Spark Ignition Engines" (see Table 3). Much like gasoline, the volatility of E85 is also adjusted seasonally and geographically by volatility class for vehicle cold-start and warm-up performance by increasing the proportion of light hydrocarbons during colder months. The seasonal and geographical volatility classes are determined by ASTM and contained in ASTM D5798. (A complete breakdown of geographical and seasonal volatility classes can be found in Appendix A.)

The octane of E85 is much higher than gasoline, ranging from 96 to 97 (R+M)/2 depending on hydrocarbon content. The energy content of E85 is lower than gasoline and ranges from approximately 83,600 BTU/

Table 3. ASTM D5798-10   Standard Specification for Fuel Ethanol (Ed75-Ed85) for Automotive Spark-Ignition Engines						
Property	Value for Class					
ASTM Volatility Class	1	2	3			
Ethanol Plus Higher Alcohols (minimum volume %)	79	74	68			
Hydrocarbons (including denaturant) (volume %)	17-21	17-26	17-30			
Vapor Pressure at 37.8°C	38-59	48-65	66-83			
kPa psi	5.5-8.5	7.0-9.5	9.5-12.0			
Lead (maximum, mg/L)	2.6	2.6	3.9			
Phosphorus (maximum, mg/L)	0.2	0.3	0.4			
Sulfur (maximum, mg/kg)	210	260	300			
	All Classes					
Methanol (maximum, volume %)	0.5					
Higher Aliphatic Alcohols, C3-C8 (maximum volume %)	2					
Water (maximum, mass %)	1.0					
Acidity as Acetic Acid (maximum, mg/kg)	50					
Inorganic Chloride (maximum, mg/kg)	1					
Total Chlorine as Chlorides (maximum, mg/kg)	2					
Gum, Unwashed (maximum, mg/100 mL)	20					
Gum, Solvent-Washed (maximum, mg/100 mL)	5.0					
Copper (maximum, mg/100 mL)	0.07					
Appearance	Product shall be visibly free of suspended or precipi- tated contaminants (shall be clear and bright).					

gallon to 89,400 BTU per gallon (depending on the hydrocarbon content) compared to the typical gasoline energy content of approximately 116,100 BTU per gallon. Thus a gallon of E85 contains approximately 72% to 77% as much energy as a gallon of gasoline.

#### **Hydrocarbons**

Although unleaded gasoline has been used to blend E85, a higher volatility component, such as natural gasoline (a high-volatility, low-octane byproduct of natural gas production), can be used to meet ASTM volatility requirements due to the low vapor pressure of ethanol. It is important to meet ASTM volatility requirements to reduce the occurrence of flammable vapor regimes in vehicle fuel tanks. Due to the different types of hydrocarbon components that have been used in E85, the range of vapor flammability in tanks is wider than gasoline. The National Renewable Energy Laboratory compared the fuel tank head-space flammability of seven E85 fuel blends, two gasoline samples, and denatured ethanol.<sup>3</sup> Headspace vapors for the two gasoline samples became flammable when the temperature dropped to approximately -19°C (-2°F) and -25°C (-13°F) or lower. The E85 blends, on the other hand, produced flammable vapors at temperatures below values ranging from -2°C (28°F) to -22°C (-8°F). Denatured ethanol was found to be flammable at room temperature and all temperatures down to approximately -6°C (22°F). Therefore, stations should not store denatured ethanol for blending E85 or other ethanol blends due to risk of explosion.

Table 4. Flammability Limits of Gasoline and Ethanol					
Fuel Gas	Lower Explosive or Flammable Limit (LEL/LFL) (% in air)	Upper Explosive or Flammable Limit (UEL/UFL) (% in air)			
Gasoline	1.4	7.6			
Ethanol	3.3	19			

### **Fuel Additives**

According to EPA regulations, all commercial grades of gasoline must contain specified levels of additives, detergents, and corrosion inhibitors. A corrosion inhibitor should be added to the ethanol portion of the E85 blend according to Renewable Fuels Association (RFA) recommendations.<sup>4</sup> The hydrocarbon component of E85 should contain the EPA-specified levels of detergent additives and corrosion inhibitors; however the RFA and vehicle manufacturers do not recommend the use of detergent additives in the ethanol portion of the E85 blend. Overuse of additives with E85 may result in poor vehicle operation. RFA has also made certain recommendations about appropriate detergent treatment of E85. Some detergents, such as polyisobutylene amine, have performed poorly in FFV operation. At some blend levels, these additives may precipitate out of the blend resulting in excessive fuel system deposition. Consequently, to minimize the occurrence of additive-related problems, RFA has issued a recommendation to contact them directly concerning additives.<sup>4</sup>

NREL and the Coordinating Research Council (CRC) collaborated to survey U.S. summer and winter E85 against ASTM D5798 standards. A summary of the results of 123 samples each season is contained in CRC Report No. E-85. Additional E85 CRC fuel quality survey data can be obtained from Report Nos. E-79 and E-79-2.<sup>5</sup>

#### **Materials Recommendations**

As with all liquid motor fuels, it is important to maintain proper fuel handling and housekeeping practices to minimize contamination. Certain materials commonly used with gasoline may be incompatible with high-level alcohol blends. Some materials may degrade over time, potentially leading to equipment problems. It may also contaminate the fuel, which may adversely affect vehicle fuel system operation or cause component malfunction and lead to degraded driveability and performance. The materials and components presented in this handbook have performed satisfactory in the field with E85.

In general, E85 can cause corrosion of some soft metals and reduce the tensile strength of some nonmetallic materials. It may also cause swelling and loss of function on certain nonmetallic materials. E85 acts like a "cleaning agent" and will initially mobilize sludge in storage tanks. Only E85-compatible materials should be used in the storage and dispensing systems. Zinc, brass, lead, and aluminum have shown sensitivity to degradation. Terne-plated steel (lead/tin/alloy coating), which has been commonly used for vehicle fuel tanks, and lead-based solder are also incompatible with E85. Use of these metals should be avoided due to the possibility of fuel contamination and potential impacts on vehicle operation. Unplated steel, stainless steel, black iron, and bronze have shown acceptable resistance to E85 corrosion.

Nonmetallic materials that degrade when in contact with fuel ethanol include natural rubber, polyurethane, cork gasket material, leather, polyvinyl chloride, nylon 6/6, methyl-methacrylate plastics, and certain thermoplastic and thermoset polymers. Nonmetallic materials successfully used for transferring and storing ethanol include thermoset-reinforced fiberglass, thermoplastic piping, and thermoset-reinforced fiberglass tanks (as listed for this application by UL). Contact with E85 causes some elastomers to swell.