



# Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel<sup>1</sup>

This standard is issued under the fixed designation D 4806; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope\*

1.1 This specification covers nominally anhydrous denatured fuel ethanol intended to be blended with unleaded or leaded gasolines at 1 to 10 volume % for use as a spark-ignition automotive engine fuel. The significance of this specification is shown in **Appendix X1**.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

- D 86 Test Method for Distillation of Petroleum Products at Atmospheric Pressure
- D 381 Test Method for Gum Content in Fuels by Jet Evaporation
- D 512 Test Methods for Chloride Ion in Water
- D 891 Test Methods for Specific Gravity, Apparent, of Liquid Industrial Chemicals
- D 1152 Specification for Methanol (Methyl Alcohol)
- D 1193 Specification for Reagent Water
- D 1613 Test Method for Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products
- D 1688 Test Methods for Copper in Water
- D 2622 Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry
- D 3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry
- D 3505 Test Method for Density or Relative Density of Pure Liquid Chemicals
- D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter

- D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products
  - D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
  - D 4306 Practice for Aviation Fuel Sample Containers for Tests Affected by Trace Contamination
  - D 4814 Specification for Automotive Spark-Ignition Engine Fuel
  - D 5453 Test Method for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence
  - D 5501 Test Method for Determination of Ethanol Content of Denatured Fuel Ethanol by Gas Chromatography
  - D 5580 Test Method for Determination of Benzene, Toluene, Ethylbenzene, *p/m*-Xylene, *o*-Xylene, C<sub>9</sub> and Heavier Aromatics, and Total Aromatics in Finished Gasoline by Gas Chromatography
  - D 5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products
  - D 6423 Test Method for Determination of pH<sub>E</sub> of Ethanol, Denatured Fuel Ethanol, and Fuel Ethanol (Ed75-Ed85)
  - D 6428 Test Method for Total Sulfur in Liquid Aromatic Hydrocarbons and Their Derivatives by Oxidative Combustion and Electrochemical Detection<sup>3</sup>
  - D 6550 Test Method for Determination of Olefin Content of Gasolines by Supercritical-Fluid Chromatography
  - E 203 Test Method for Water Using Volumetric Karl Fischer Titration
  - E 300 Practice for Sampling Industrial Chemicals
  - E 1064 Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration
- ### 2.2 Other Standards:
- United States Code of Federal Regulations, Title 27, Parts 20 and 21<sup>4</sup>
  - United States Federal Specification O-E-760b Ethyl Alcohol (Ethanol): Denatured Alcohol: and Proprietary Solvent<sup>5</sup>

<sup>1</sup> This specification is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.A0 on Gasoline and Oxygenated Fuels.

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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>3</sup> Withdrawn.

<sup>4</sup> Order as Code of Federal Regulations Title 27 Parts 200-End: from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401.

<sup>5</sup> Order from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401.

\*A Summary of Changes section appears at the end of this standard.

### 3. Terminology

#### 3.1 Definitions:

3.1.1 *ethanol, n*—ethyl alcohol, the chemical compound C<sub>2</sub>H<sub>5</sub>OH.

3.1.2 *gasoline, n*—a volatile mixture of liquid hydrocarbons, generally containing small amounts of additives, suitable for use as a fuel in spark-ignition, internal combustion engines.

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3.1.3 *gasoline-ethanol blend, n*—a fuel consisting primarily of gasoline along with a substantial amount (more than 0.35 mass % oxygen) of denatured fuel ethanol.

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3.1.4 *oxygenate, n*—an oxygen-containing, ashless, organic compound, such as an alcohol or ether, which may be used as a fuel or fuel supplement.

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#### 3.2 Definitions of Terms Specific to This Standard:

3.2.1 *denaturants*—natural gasoline, gasoline components, unleaded gasoline, or toxic or noxious materials added to fuel ethanol to make it unsuitable for beverage use but not unsuitable for automotive use.

3.2.2 *denatured fuel ethanol*—fuel ethanol made unfit for beverage use by the addition of denaturants.

3.2.3 *fuel ethanol*—ethanol with impurities common to its production (including water but excluding denaturants).

3.2.4 *impurities*—in commercially produced fuel ethanol, compounds other than ethanol or denaturants present, such as methanol and fusel oil (for example, amyl and isoamyl alcohols).

3.2.5 *pHe*—a measure of the acid strength of alcohol fuels.

### 4. Performance Requirements

4.1 *Denatured Fuel Ethanol*—When fuel ethanol is denatured as specified in Section 5, it shall conform to the following requirements at the time of blending with a gasoline.

|  |   |
|--|---|
| Ethanol, volume %, min   | 92.1  |
| Methanol, volume %, max  | 0.5   |
| Solvent-washed gum,<br>mg/100 mL, max                                | 5.0   |
| Water content, volume %, max   | 1.0 (Note 1)  |
| Denaturant content, volume %, max                                    | 1.96  |
| volume %, max  | 5.0   |
| Inorganic Chloride content, mass<br>ppm (mg/L), max                  | 40 (32)   |
| Copper content, mg/kg, max   | 0.1   |
| Acidity (as acetic acid CH <sub>3</sub> COOH),<br>mass % (mg/L), max | 0.007 (56) (Note 3)   |
| pHe  | 6.5 to 9.0  |
| Sulfur, mass ppm, max  | 30  |
| Appearance   | Visibly free of suspended or precipitated contaminants (clear and bright) |

NOTE 1—In some cases, a lower water content may be necessary to avoid phase separation of a gasoline-ethanol blend at very low temperatures. This reduced water content, measured at the time of delivery, shall be agreed upon between the supplier and purchaser.

NOTE 2—If denatured fuel ethanol is prepared by the addition of denaturants to undenatured fuel ethanol after it has been produced rather than during the dehydration process, the 15.56/15.56°C (60/60°F) specific gravity in air of the undenatured fuel ethanol shall be in the range from 0.7937–0.7977.

NOTE 3—Denatured fuel ethanol may contain additives, such as corrosion inhibitors and detergents, that may affect the titratable acidity (acidity as acetic acid) of the finished fuel ethanol. Although the base fuel ethanol may meet the acidity specification, the effect of these additives may produce an apparent high titratable acidity of the finished product. Contact the ethanol supplier if there is a question regarding the titratable acidity of

your denatured fuel ethanol to verify that the base ethanol meets the acidity requirements of 4.1.

4.2 *Other Properties*—Limits more restrictive than those specified above, or the specification of additional properties such as color, may be agreed upon between the supplier and the purchaser.

### 5. Denaturants

5.1 The only denaturants used for fuel ethanol shall be natural gasoline, gasoline components, or unleaded gasoline at a minimum concentration of two parts by volume per 100 parts by volume of fuel ethanol. One denatured formula specifically designed for fuel use by the Alcohol and Tobacco Tax and Trade Bureau (TTB) of the U.S. Treasury Department is Formula C.D.A. 20. It requires that for every 100 gal of ethanol of not less than 195 proof, a total of 2.0 gal of denaturant be added. Another fuel alcohol rendered unfit for beverage use and manufactured at an alcohol fuel plant (AFP) requires the addition of 2 gal or more of materials listed by the director to each 100 gal of ethanol. The fuel ethanol formulas approved by the U.S. Treasury Department include materials, which are not allowed by this ASTM specification. This specification prohibits the use of hydrocarbons with an end boiling point higher than 225°C (437°F) as determined by Test Method D 86, although they may be permitted by TTB regulations. Some kerosines, for instance, promote piston scuff in automotive engines. The denaturants permitted by this specification may be included as part of the 10 volume % denatured fuel ethanol blended with a gasoline if they do not exceed five volume % of fuel ethanol. Any part of these denaturants that are present at concentrations higher than five volume % of fuel ethanol are considered as part of the base gasoline. The maximum denaturant limits are specified by United States Internal Revenue Service (IRS) regulations.

NOTE 4—TTB regulations concerning the preparation, use, and handling of denatured ethanols are published in the *United States Code of Federal Regulations, Title 27*, Parts 19, 20, and 21. 27 CFR 19.1005 contains regulations for rendering fuel alcohol unfit for beverage use by an AFP. 27 CFR 21.24 contains the formula for manufacturing completely denatured alcohol, C.D.A. 20.

5.2 *Prohibited Denaturants*—Although this specification permits only hydrocarbons in the gasoline boiling range to be used as denaturants, specific mention must be made of some materials that have extremely adverse effects on fuel stability, automotive engines, and fuel systems. These materials shall not be used as denaturants for fuel ethanol under any circumstances. They are as follows: methanol which does not meet Specification D 1152, pyrroles, turpentine, ketones, and tars (high-molecular weight pyrolysis products of fossil or nonfossil vegetable matter). While any significant amount of methanol will lower the water tolerance and increase the vapor pressure of a gasoline-ethanol blend, these effects become more serious when methanol is present at more than 2.5 parts by volume per 100 parts by volume of fuel ethanol. Also, methanol, which does not meet Specification D 1152, frequently contains impurities, such as turpentine and tars. Similarly, ketone denaturants tend to degrade fuel stability or increase the tendency of a gasoline-ethanol blend to corrode metals and attack elastomers. These effects become more

serious if the concentration of a ketone such as 4-methyl pentanone (methyl isobutyl ketone) exceeds one part by volume per 100 parts by volume of fuel ethanol. There is no information available on the effects of denaturants other than those mentioned above; but unless a denaturant, such as a higher aliphatic alcohol or ether, is known to have no adverse effect on a gasoline-ethanol blend or on automotive engines or fuel systems, it shall not be used.

## 6. Workmanship

6.1 The fuel ethanol shall be visually free of sediment and suspended matter. It shall be clear and bright at the ambient temperature or 21°C (70°F), whichever is higher.

6.2 The specification defines only a basic purity for this product. The product shall be free of any adulterant or contaminant that may render the material unacceptable for its commonly used applications.

## 7. Sampling, Containers, and Sample Handling

7.1 The reader is strongly advised to review all intended test methods prior to sampling to understand the importance and effects of sampling technique, proper containers, and special handling required for each test method.

7.2 Correct sampling procedures are critical to obtain a sample representative of the lot intended to be tested. Use appropriate procedures in Practice **D 4057** or Practice **E 300** for manual method sampling and in Practice **D 4177** for automatic method sampling, as applicable.

7.3 The correct sample volume and appropriate container selection are important decisions that can impact test results. Refer to Practice **D 4306** for aviation fuel container selection for tests sensitive to trace contamination. Refer to Practice **D 5854** for procedures on container selection and sample mixing and handling. Where practical, fuel ethanol should be sampled in glass containers. If samples must be collected in metal containers, do not use soldered metal containers. This is because the soldering flux in the containers and the lead in the solder can contaminate the sample. Plastic containers should be avoided.

7.4 *Sample Size*—A minimum of about 1 L or 1 U.S. qt is recommended. If specific gravity is to be determined by a hydrometer method, additional volume may be required. This depends on the size of the hydrometer.

7.5 *Lot Size*—A lot shall normally consist of the amount contained in a tanker compartment or other bulk container in which it is delivered. If this definition does not apply, the definition of a lot must be agreed upon between the supplier and purchaser.

NOTE 5—See Sections 5, 6, and 7 on Significance, Safety, and Statistical Considerations, respectively, of Practice **E 300** for a detailed discussion of the statistics of sampling.

## 8. Test Methods

8.1 The scope of some of the test methods specified in **8.2–8.10** do not include denatured fuel ethanol. The precisions of those test methods may differ from the reported precisions when testing denatured fuel ethanol.

8.2 *Water Content*—Test Methods **E 203** or **E 1064**.

8.3 *Solvent-Washed Gum Content*—Test Method **D 381**, air jet apparatus.

8.4 *Acidity*—Test Method **D 1613**.

8.5 *pHe*—Test Method **D 6423**.

8.6 *Appearance*—The product shall be visibly free of suspended or precipitated contaminants (clear and bright). This shall be determined at indoor ambient temperature unless otherwise agreed upon between the supplier and the purchaser.

8.7 *Specific Gravity*—Test Methods **D 891**, Procedure B or Test Method **D 4052**. For Test Methods **D 891**, Procedure B (hydrometer), no formal precision statement is available, but practical experience indicates that precision is no better than 0.0005. Test Methods **D 891** Procedure C (pycnometer), with an interlaboratory precision (reproducibility) of 0.0002, should be used as a referee method.

8.8 *Inorganic Chloride Content*—Modification of Test Methods **D 512–81(1985)**<sup>e1</sup>, Method C.

8.8.1 The modification of Test Methods **D 512–81(1985)**<sup>e1</sup>, Method C consists of using 5 mL of sample diluted with 20 mL of water in place of the 25-mL sample specified in the standard procedure. The water shall meet Specification **D 1193**, Type II. The volume of the sample prepared by this modification will be slightly larger than 25 mL. To allow for the dilution factor, report the chloride ion present in the fuel ethanol sample as the chloride ion present in the diluted sample multiplied by five.

8.8.2 The precision of this modified method has not been determined, but for the actual amount of chloride ion found in the diluted sample, it is expected to be similar to the precision of Test Methods **D 512–81(1985)**<sup>e1</sup>, Method C.

8.9 *Copper Content*—Modification of Test Methods **D 1688**, Test Method A.

8.9.1 The modifications of Test Methods **D 1688**, Test Method A (atomic absorption, direct) consists of mixing reagent-grade ethanol (which may be denatured according to BATF of the U.S. Treasury Department Formula 3A or 30) in place of water as the solvent or diluent for the preparation of reagents and standard solutions. However, this must not be done to prepare the stock copper solution described in the section on Copper Solution, Stock in Test Method **D 1688**. Because a violent reaction may occur between the acid and the ethanol, use water, as specified, in the acid solution part of the procedure to prepare the stock copper solution. Use ethanol for the rinse and final dilution only.

8.9.2 The precision of this modified method has not been determined, but it is expected to be similar to the precision of Test Method **D 1688**, Test Method A.

8.10 *Ethanol Content*—Test Method **D 5501**.

8.11 *Sulfur Content*—Test Methods **D 2622**, **D 3120**, **D 5453**, or **D 6428**. California specifies that compliance with the California sulfur standard for denatured ethanol shall be determined using Test Method **D 5453–93**. EPA allows Test Methods **D 3120**, **D 5453**, or **D 6428** for measuring sulfur in gasoline as long as these alternative test method results are correlated to the EPA designated Test Method **D 2622** when determining compliance with Federal EPA sulfur standards.