Alcohols, Ethers, and Gasoline-Alcohol and -Ether Blends

A Report on Fire-Safety Considerations at Petroleum Marketing Facilities

API PUBLICATION 1642
FIRST EDITION, FEBRUARY 1996

American
Petroleum
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Suggested revisions are invited and should be submitted to the director of the Manufacturing, Distribution and Marketing Department, American Petroleum Institute, 1220 L Street, N.W. Washington, D.C. 20005.

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0 Introduction

Gasoline blended with alcohols and ethers (oxygenates) has become a standard product since the implementation of reformulated gasoline regulations. When oxygenates are blended with gasoline, the properties of the resulting blend can differ from those of base gasoline. The objective of this report is to educate gasoline marketing personnel about how gasolines blended with oxygenates might impact fire-safety during transport, storage and dispensing. This publication also addresses storage and handling of oxygenates at terminals and bulk plants, and storage and handling of M85 (a blend of 85 volume percent methanol and 15 volume percent gasoline). Examination of fire safety characteristics of neat oxygenates and oxygenate blends suggests that current industry fuel handling practices are adequate for these fuels.

The term "oxygenated gasoline" will be used throughout this report to denote gasoline blended with alcohols and ethers. Thus, all reformulated gasolines are included in the definition of oxygenated gasolines. In this report "base gasoline" will refer to gasoline that has not had any oxygenates added to it, i.e., gasoline that is all hydrocarbons. Reformulated blendstock for oxygenate blending is an example of base gasoline. "Neat alcohols" and "ethers" refer to these oxygenate constituents before being blended with gasoline. "Ethanol" for blending in base gasoline will be assumed to have five volume percent hydrocarbons as denaturant.

Section 4 is devoted to a general discussion of the impact of fuel fire-safety characteristics. Section 5 addresses specific fire-safety issues for handling and storing oxygenates in terminals and bulk plants. Section 6 addresses the same issues at service stations. Neat oxygenates are covered only in Section 5 because these blending components are not present at service stations.

1 Scope

This publication examines the fire safety considerations for fuels at petroleum marketing facilities. It focuses on gasoline blended with oxygenates, and M85, but also includes neat alcohols and ethers since they may be present at terminals and bulk plants for blending purposes. Diesel fuels and "clean" or reformulated diesel fuels are not addressed. Current reformulated gasolines are included within the scope of this report.

This publication is not an API recommended practice for handling these fuels, nor is it intended to be a primer on fuel marketing operations fire-safety. Readers not already familiar with recommended practices for gasoline handling and storage fire-safety should obtain and review the appropriate API and NFPA publications cited in Section 2 before reading this report. This publication does not address health considerations associated with use or exposure to these fuels.

Figure 1 illustrates the portion of the gasoline marketing system covered in this report.

2 References

2.1 STANDARDS

Unless otherwise specified, the most recent editions or revisions of the following standards, codes, and specifications shall, to the extent specified herein, form a part of this publication.

API

Manual of Petroleum Measurement Standards (MPMS), Chapter 1, "Vocabulary"

Pub 2026 *Safe Descent Onto Floating Roofs of Tanks in Petroleum Service*

Pub 2219 *Safe Operation of Vacuum Trucks in Petroleum Service*

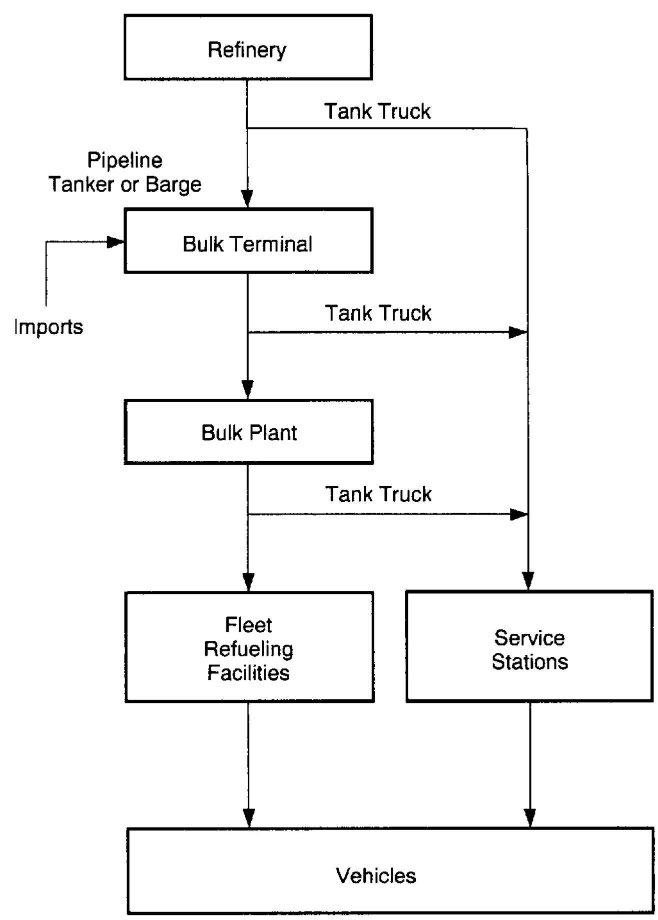

Figure 1—Typical Gasoline Distribution System Flowpath

Pub 4498 *An Engineering Analysis of the Effects of Oxygenated Fuels on Marketing Vapor Recovery Equipment*
RP 1604 *Removal and Disposal of Used Underground Petroleum Storage Tanks*
RP 1626 *Storing and Handling Ethanol and Gasoline-Ethanol Blends at Distribution Terminals and Service Stations*
RP 1627 *Storing and Handling of Gasoline-Methanol/Cosolvent Blends at Distribution Terminals and Service Stations*
RP 1631 *Interior Lining of Underground Storage Tanks*
RP 2003 *Protection Against Ignitions Arising Out of Static, Lightning, and Stray Currents*
RP 2015 *Safe Entry and Cleaning of Petroleum Storage Tanks*
RP 2027 *Ignition Hazards Involved in Abrasive Blasting of Atmospheric Storage in Hydrocarbon Service*

ASTM[1]
D86 *Standard Method for Distillation of Petroleum Products*
D4806 *Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark Ignition Fuel*
D4814 *Standard Specification for Automotive Spark-Ignition Engine Fuel*

NFPA[2]
Fire Protection Handbook, 17th Edition
National Electrical Code—1993 Handbook
30 *Flammable and Combustible Liquids Code*
325M *Fire Hazard Properties of Flammable Liquids, Gases, and Volatile Solids*

2.2 OTHER REFERENCES

In addition, this publication draws upon the work presented in the following publications:

Dictionary of Scientific and Technical Terms, Third Edition, McGraw-Hill Book Company, New York City, New York, 1984.

Alexander, J.E., E.P. Ferber, and W.M. Stahl, "Avoid Leaks from Reformulated Fuels," *Fuel Reformulation,* Vol. 4, No. 2, March/April 1994.

Douthit, Walt, et al, "Performance Features of 15 vol% MTBE/Gasoline Blends," SAE Paper 881667, 1988.

Henry Jr., Cyrus P., "Electrostatic Hazards and Conductivity Additives," *Fuel Reformulation,* Vol. 3, No.1, January/February 1993.

Machiele, Paul A., "Flammability and Toxicity Tradeoffs with Methanol Fuels," SAE Paper 872064, presented at International Fuels and Lubricants Meeting and Exposition, Toronto, Ontario, November 2-5, 1987.

3 Definitions

For the purposes of this publication, the following definitions apply:

3.1 *Autoignition temperature* is the minimum temperature to which a substance in air must be heated in order to initiate or cause self-sustained combustion independently of the heating or heated element.

3.2 The *boiling point* is the temperature at which a liquid exerts a vapor pressure of 14.7 pounds per square inch gauge (760 millimeters mercury). When an accurate boiling point is unavailable for the material in question, or for mixtures that do not have a constant boiling point, the 10 percent point of a distillation performed in accordance with ASTM D86 may be used as the boiling point of the liquid.

Note: This information will be reflected in the 1996 edition of NFPA 30.

3.3 *Bonding* is the permanent joining of metallic parts to form an electrically conductive path which will assure electrical continuity and the capacity to conduct safely any current likely to be imposed.

3.4 *Denatured fuel ethanol* is ethanol which has had five volume percent of hydrocarbons added to it to make it unfit for human consumption. Hydrocarbons suitable for use as denaturants are detailed in ASTM D-4806.

3.5 A *flammable liquid* is a liquid having a closed cup flash point below 100°F (37.8°C), having a vapor pressure not exceeding 40 pounds per square inch gauge (2068 millimeters mercury) at 100°F (37.8°C), and is known as a Class I liquid.

3.6 *Flammability limits* are the minimum and maximum concentrations of vapor in air that are flammable and will support combustion. A vapor-air concentration below the lower flammable limit (LFL) is too lean to ignite while a concentration above the upper flammable limit (UFL) is too rich to ignite.

3.7 *Flameout* is the extinguishing of a flame in a combustion device. Flameout occurs in vapor incineration units at refineries, terminals, and bulk plants when the vapor-air mixture goes outside of the flammability limits.

3.8 The *flash point* is the minimum temperature of a liquid at which sufficient vapor is produced to form a flammable mixture with air.

3.9 The *heat of vaporization* is the quantity of heat absorbed or given off by a substance in passing between liquid and gaseous phases. For petroleum products, heat of

[1]American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.
[2]National Fire Protection Association, 1 Batterymarch Park, P.O. Box 9101, Quincy, Massachucetts 02269-9101.

vaporization is expressed in British thermal units per pound (Kcal per kilogram), the temperature is the boiling point, or boiling range, and the pressure is 14.7 pounds per square inch (101.4 kilopascals). Heat of vaporization is also known as latent heat of vaporization.

3.10 The *initial boiling point* is the recorded temperature when the first drop of distilled liquid is liquefied and falls from the end of the condenser, as specified in ASTM D86.

3.11 *Grounded* means connected to earth or to some conducting body that serves in place of the earth.

3.12 *Miscibility* is the tendency or capacity of two or more liquids to form a uniform blend (that is, to dissolve in each other). Degrees of miscibility are total miscibility, partial miscibility, and immiscibility.

3.13 *M85* is a blend of 85 volume percent methanol and 15 volume percent gasoline. This blend is used in methanol vehicles, or flexible fuel vehicles that can use M85, gasoline, or any blend in between.

3.14 An *oxygenate* is an oxygen-containing, ashless, organic compound such as an alcohol or ether which can be used as a fuel or fuel supplement.

3.15 *Reid vapor pressure (RVP)* is the vapor pressure of gasoline or gasoline blending components measured at 100°F, according to ASTM Test Method D323.

Note: ASTM Test Method D323 is valid for base gasolines and blends of gasoline and ethers. Gasolines containing alcohols must use an appropriate "dry" procedure as specified in ASTM D4814.

3.16 *True vapor pressure* is the pressure of vapor in equilibrium with liquid. True vapor pressure is used to distinguish vapor pressure at ambient temperature, as opposed to 100°F as used in the Reid vapor pressure test.

3.17 *T20 or 20 volume percent distillation temperature* is the temperature at which 20 volume percent of a wide boiling range fluid has vaporized. The T20 value is used as the boiling point for determining the flammability classification under NFPA guidelines.

3.18 *Ullage* is the available space in a container unoccupied by contents.

3.19 *Vapor pressure* is the equilibrium pressure exerted by vapors produced from a liquid at a given temperature.

3.20 *Vapor density* is the weight of a volume of pure vapor (that is, vapor with no air present) compared to the weight of an equal volume of dry air at the same temperature and pressure.

3.21 *Water solubility* is the degree to which a liquid or solid is soluble in water.

4 Fuel Characteristics

The fuels that are assessed in this report and where they would be found in the downstream product distribution system are noted in Table 1.

All fuels considered in this publication can be designated as Class I flammable liquids according to NFPA criteria, as specified in NFPA 30. Class I fuels can be divided further into Class IA or Class IB, depending on the fuel's boiling point. By definition, Class IA fuels boil below 100°F, and Class IB fuels boil above 100°F. All oxygenates considered in this publication can be classified as Class IB fluids based on their physical properties. The NFPA convention for broad boiling range liquids is to use the T20 temperature for flammability classification. Using the T20 convention, all oxygenated blends can be classified as Class IB flammable fuels.

Fuel properties and characteristics provide relative indications of the fire-safety potential of each fuel under various ambient storage and handling conditions. Boiling point, flash point, and vapor pressure values indicate the readiness of the fuel to form vapors under ambient conditions. Fuels with lower boiling points, lower flash points, and higher vapor pressures relative to gasoline would generally be considered more volatile than gasoline (that is, produce greater quantities of fuel vapor at the same temperature and pressure as gasoline). Fuels with vapor densities greater than one, which applies to all fuels considered in this publication, indicate fuel vapors that are heavier than air. These vapors will tend to lie close to the ground and potentially travel long distances, increasing the probability of encountering ignition sources.

Fuel flammability limits are important to indicate the relative potential for a flammable vapor-air mixture to develop once vapors are produced. In general, fuels with wide

Table 1—Typical Fuel Distribution Points

Fuels	Fuels Distribution Point
Gasoline	w/r/f
Neat methanol	w
Denatured ethanol	w
M85 (85 vol% methanol/15 vol% gasoline)	w/r/f
Methyl tertiary butyl ether (MTBE)	w
Ethyl tertiary butyl ether (ETBE)	w
Tertiary amyl methyl ether (TAME)	w
Tertiary amyl ethyl ether (TAEE)	w
Di-isopropyl ether (DIPE)	w
Tertiary butyl alcohol	w
Isopropyl alcohol	w
Gasoline with 15 vol% MTBE, 17 vol% ETBE, 17 vol% TAME, 10 vol% ethanol, or 5 vol% methanol with isopropyl alcohol	w/r/f

Note: w = wholesale distribution terminals, r = retail stations; f = fleet fueling facilities.

flammability limits are ones with higher potential to form flammable vapor-air mixtures. For example, neat methanol has greater potential to form flammable mixtures under typical ambient conditions than gasoline because its flammability limits are wider than those of gasoline. Gasolines stored at typical ambient temperatures are sufficiently volatile and produce vapors which exceed the upper flammability limit under most conditions. However, for the fuels considered in this publication, the possibility exists for vapor-air mixtures in enclosed spaces at low ambient temperatures to drop below their upper flammability limits and become flammable with potential for ignition.

Autoignition temperature indicates a fuel's ignition potential from exposure to hot surfaces. A fuel with a higher autoignition temperature compared with base gasoline would indicate a higher resistance to hot surface ignition.

The electrical conductivity of a fuel indicates the ease with which it will conduct electric charges. Fuels with sufficient electrical conductivity such as methanol allow electrostatic charges formed during fuel transfers to be quickly dissipated through proper grounding of fuel marketing equipment, such as tanks and dispensers. Diesel fuel has a low electrical conductivity, which means that it is very slow to dissipate accumulated electrostatic charges from fuel transfers. Very high voltages can be created from transfer of fuels having low electrical conductivity, as noted in Henry, *Fuel Reformulation,* Vol. 3, No. 1. API Recommended Practice 2003 provides detailed information about safeguarding against static electricity build-up in petroleum products during transfer operations.

Flame visibility indicates the degree to which a fuel fire can be seen in bright sunlight. Flame visibility is not a problem for hydrocarbon fuels because they have a highly luminous flame and produce soot. However, neat methanol flames are virtually invisible in bright sunlight, since neat methanol flames have no color and produce no soot. The appropriate hydrocarbon addition to methanol (15 volume percent in the case of M85) will produce a visible flame. Neat ethanol burns with a dimly visible flame in bright sunlight, but it too does not produce soot except for the gasoline denaturant. Ethers in general burn with visible flames, though the flame visibility of ethers has not been extensively measured or documented.

Note: The low luminosity of methanol and ethanol flames results in lower radiant heat transfer compared to base gasoline flames. This has some fire-safety advantages relative to base gasoline.

Gasoline properties vary according to the season of the year. In winter conditions, a more volatile fuel is generally desired so that the fuel evaporates readily at cold temperatures and allows easier starting and better cold driveability. In summer conditions, however, a less volatile fuel is desired to lower vapor generation at the higher ambient temperatures and prevent possible vapor lock in the fuel system, and to minimize evaporative emissions from vehicles. Gasoline blend volatility is typically controlled by regulating the amount of butane or other low molecular weight hydrocarbons in the fuel. All gasoline properties are affected to some degree by these seasonal changes in composition, but the two properties most affected are initial boiling point or T20, and vapor pressure. In winter conditions, gasoline blends contain high butane content, which lowers the T20 boiling point and raises the RVP. In summer, the reverse is true, with a lower butane content resulting in higher T20 boiling points and lower RVP values.

Fuel RVP is the most widely controlled fuel volatility parameter. However, in specific situations, the volatility of a fuel and its resultant impact on fire-safety is more closely related to the "true vapor pressure" which is the vapor pressure that exists at a given temperature. For example, a 13 psi RVP fuel at 30°F may be less volatile than a 9 psi RVP fuel at 70°F. Seasonally varying RVP keeps fuel volatility somewhat uniform as ambient temperature varies over the year. However, the process is not completely successful, and those handling fuels should consider necessary precautions. For instance, warm temperatures in spring before the changeover to summer grade gasoline represents a situation when the relative volatility of the gasoline being handled could be the highest measured all year.

5 Terminals and Bulk Plants

This section discusses the fire-safety concerns of several typical fuel storage and transfer operations at terminals and bulk plants using oxygenated gasoline, M85 and neat oxygenates. The section assesses the impacts of oxygenated gasolines on tank truck loading, bulk storage tank maintenance and cleaning, and vapor control system operation and maintenance. The storage and handling of oxygenated gasolines containing methanol, ethanol and cosolvents at terminals and bulk plants is addressed in API Recommended Practices 1626 and 1627.

5.1 TANK TRUCK LOADING

5.1.1 General

The analysis of tank truck loading determined four primary areas of concern when using oxygenated gasolines relative to base gasoline:

a. in-tank flammability.
b. vapor releases.
c. electrostatic charge accumulation.
d. accidental fuel spills.

5.1.2 In-Tank Flammability

A prerequisite for the initiation of any fuel fire is a vapor-air mixture in the flammable range. Flammable vapor-air mixtures can develop in tank trucks during the loading process. Vapor formation during tank truck loading is dependent on in-tank turbulence created from fuel entering the tank as well as the overall volatility of the fuel. Top loading without the use of submerged fill pipes generally results in the greatest in-tank turbulence, whereas submerged or bottom loading creates the least. With base gasoline, flammable vapor-air mixtures can be achieved relatively quickly once vapor is generated in the tank, as evidenced by gasoline's relatively high volatility and low lower flammability limit. However, even at low ambient temperatures the volatile characteristics of gasoline are such that vapor formation during the loading process typically results in exceeding the upper flammability limit in a very short time. Oxygenated gasoline and M85 have similar volatilities to base gasoline and the same fire-safety practices should be followed. Neat alcohols and ethers are less volatile and may allow formation of flammable mixtures during times when gasoline would not.

The same concerns about switch loading following base gasoline apply to oxygenated gasolines, M85, alcohols and ethers. If there is a flammable vapor-air mixture in the tank from a previous load of product a fire or explosion could occur if an ignition source is present. Oxygenated gasolines, M85, alcohols and ethers will all leave vapors in the tank which may create flammable vapor-air mixtures. Therefore, switch loading safety procedures, such as those described in API Recommended Practice 2003, are appropriate when loading static accumulating fuels (that is, diesel fuels) into tank trucks which have previously contained base gasoline, oxygenated gasoline, M85, alcohols, or ethers.

Note: Switch loading here refers specifically to loading diesel fuel into a tank that previously carried gasoline. The ullage space of tanks containing diesel fuel is not generally flammable unless a flammable mixture was already there from carrying a previous product or a mist of diesel fuel exists due to high velocity loading.

Alcohols and ethers are more likely to form flammable mixtures in the vapor spaces of tanks, but when gasoline is added, the hazards revert primarily to those presented by base gasoline. For these reasons, when splash-blending or sequentially blending oxygenates in a tank, it is safer to load the gasoline first because it will cause the vapor space to exceed the upper flammability limit. This is not a concern when loading finished oxygenated gasolines or when using in-line blending.

5.1.3 Vapor Releases

The vapor density of oxygenates is less than gasoline vapor, which suggests that oxygenate vapors might dissipate more quickly than gasoline vapors. However, the flammability range of alcohol and ether vapors is wider than that of gasoline vapors, which will cause these mixtures with air to remain within the flammable range longer (it takes longer to dilute these vapors below the lower flammability limit). These offsetting fire safety impacts of oxygenates are not sufficient to warrant changes to the current fire safety practices for handling vapor releases relative to base gasoline.

5.1.4 Electrostatic Charge Accumulation

Electrostatic charge accumulation is a major consideration when transferring large quantities of diesel fuel and other electrostatic accumulating fuels at high rates, such as in tank filling. If charge accumulation is high enough in the fuel inside the tank, an electrostatic discharge may occur. If there is a flammable vapor-air mixture in the tank from a previous load of flammable liquid fuel, an electrostatic discharge could cause a fire or explosion. Oxygenated gasoline, M85, alcohols, and ethers will leave vapors in tanks which may create flammable vapor-air mixtures. Therefore, switch loading safety practices, such as those described in API Recommended Practice 2003, are appropriate when loading static accumulating fuels into tank trucks which have previously contained gasoline or oxygenated gasolines. All of the oxygenated gasolines, whether splash-blended, in-line blended, or finished product loaded into tank trucks, are generally expected to have less potential for electrostatic charge accumulation compared with base gasoline. Charge build-up is not generally expected to be a concern if recommended fuel handling practices are followed, and the hazards presented by oxygenated gasolines, M85, alcohols, and ethers relative to base gasoline should not be significantly different.

5.1.5 Fuel Spills

Neat oxygenates generally have higher autoignition temperatures than base gasoline, indicating less potential for hot surface ignition. Thus, spilled neat oxygenates are generally expected to have less potential for hot surface ignition than base gasoline. Spills of M85, with its high content of methanol, again, is generally expected to have less potential for autoignition.

Spilled fuel will constitute a fire hazard if it evaporates and forms flammable vapor-air mixtures in open air. Spills of alcohol and ether fuels during splash-blend loading have somewhat less potential than base gasoline for forming flammable vapor-air mixtures since these fuels generally have lower volatilities, higher lower flammability limits, and lower vapor densities than base gasoline. However, these differences are small and spills of oxygenates may be treated as being flammable, just as for base gasoline.

5.2 BULK STORAGE TANK MAINTENANCE AND CLEANING

5.2.1 General

Four primary areas of bulk storage tank maintenance and cleaning procedures could be impacted by the use of alcohols, ethers, and gasoline blends containing these fuels:

a. tank bottoms removal.
b. vapor-freeing.
c. interior tank surface cleaning and repair.
d. exterior tank cleaning.

5.2.2 Tank Bottoms Removal

An integral part of most bulk storage tank maintenance procedures is the removal of tank bottoms. Tank bottoms can include liquid fuel, solids, and water in widely varying proportions. One area of concern with oxygenated gasolines related to the tank bottoms removal process from bulk tanks would be higher potential for flammable vapor-air mixtures inside bulk tanks. At the typical bulk storage temperatures experienced at facilities in the United States, neat oxygenates to be used as blending components have higher potential for forming flammable vapor-air mixtures inside bulk tanks than base gasoline. (Alcohols cannot have water bottoms because water and alcohols are completely miscible; however, bottoms consisting of solids may form.) Based mainly on their lower volatilities and higher flash points, the alcohols in particular, and the ethers to a lesser extent, have greater potential to develop and maintain flammable vapor-air mixtures than base gasoline at the storage temperatures typical of bulk facilities. Oxygenated gasolines have the same fire-safety characteristics as base gasoline. Likewise, M85 is generally expected to have the same fire-safety characteristics as gasoline, though M85 may allow formation of flammable vapor-air mixtures in tank vapor spaces before base gasoline in low ambient temperatures.

The potential for the development of flammable tank bottoms with oxygenated gasolines containing low levels of alcohols is higher than that for base gasoline. The alcohols present in oxygenated gasolines can be drawn out of solution into any water present in the tank bottoms. For instance, only 21 volume percent methanol in water is required to make water/methanol blends flammable, as noted in Machiele, SAE Paper 872064. This is not a problem for ethers since their solubility with water is much lower than the alcohols.

Note: For a complete discussion of alcohol and ether miscibility with tank bottoms, see Douthit, et al, SAE Paper 881667.

The fire hazard potential of liquid spills during tank bottoms removal is generally expected to be the same for oxygenated gasolines and M85 as for base gasoline. Care should be taken to prevent tank bottoms containing oxygenates from getting into the ground water.

Vacuum trucks are typically used to remove tank bottoms. The vacuum truck itself is a source of ignition and should be located upwind from the tank, preferably on top of the dike or on the other side of the dike, to avoid igniting any vapors being vented from the tank or from a spill. The vacuum truck tank vent should similarly be directed downwind to a hazard-free area away from people and ignition sources, as specified in API Publication 2219.

5.2.3 Vapor-Freeing

The vapor-freeing process is important when performing any interior work in storage tanks. Even after all tank bottoms are removed, flammable vapor-air mixtures may exist in the tank before the start of the vapor-freeing process. Vapors remain in the tank from the liquid fuel product and tank bottoms as well as those generated from fuel residues and deposits on the walls of the tank. When storing base gasoline, the vapor spaces of cone roof gasoline storage tanks without interior floating roofs or decks are normally above the upper flammability limit of the fuel for most bulk facilities during most of the year. However, most gasoline and gasoline blends are usually stored in tanks with internal or external floating roofs. Many different kinds of exterior work, including tank inspection, gauging, cleaning, and sampling, can be safely performed on tanks in service, when appropriate industry procedures are followed.

The vapor space in bulk storage tanks containing base gasoline, oxygenated gasoline, or M85 is not generally expected to be flammable under almost all ambient conditions. Bulk storage tanks containing neat oxygenates could have flammable vapor spaces under ambient conditions, and proper precautions are essential.

By its nature, the vapor-freeing process releases vapors to the atmosphere (except in air pollution control areas where regulations require vapors to be captured) by purging vapors from tanks. Care should be taken to prevent ignition sources of any type in the area of the tanks and downwind of the tanks when performing vapor-freeing, since the released vapors may form flammable vapor-air mixtures. As with fuel vapor releases during tank bottoms removal, the potential for forming flammable vapor-mixtures from fuel vapors released during the vapor-freeing process is governed by the vapor's density and flammability limits. The same precautions taken with vapors from base gasoline during vapor-freeing should be taken with vapors from oxygenated gasoline, M85, and neat oxygenates.

5.2.4 Interior Tank Maintenance

Normal maintenance of bulk storage tanks at bulk terminals and plants includes periodic repair or cleaning to remove liquid fuel, solids and water that tend to build-up in the tanks. This section applies to all types of aboveground bulk storage at wholesale distribution facilities, including external and internal floating roof tanks, and fixed roof tanks. Typical industry practice includes a safety regimen for performing bulk tank maintenance, regardless of the type of tank, as specified in API Recommended Practice 2015.

For all these processes, oxygenated gasoline, M85, and neat oxygenates present fire-safety hazards similar to those presented by base gasoline, and, therefore, procedures followed for base gasoline are generally considered appropriate. Some additional precautions may be warranted for neat oxygenates, since these products can have flammable vapor spaces in bulk tanks at typical ambient temperatures.

A potential fire-safety hazard exists when cutting access holes in metal tanks, or welding inside or outside metal tanks as the surface of the tank is heated up and fuel vapors are released. The same practices and procedures for performing hot work on tanks that contained base gasoline are generally considered appropriate for tanks that contained oxygenated gasoline.

5.2.5 Exterior Cleaning

The main concern with exterior tank cleaning and repair work is the release of fuel vapors from the tank and the formation of flammable vapor-air mixtures in the work vicinity. Exterior tank surfaces are typically cleaned using hand scraping, steam or abrasive blasting. The abrasive materials are jetted onto the tank surface using compressed air, and as a result tank surfaces can become hot. Electrostatic discharge is also a concern when surface blasting tanks since an electrical potential may be developed between the blasting nozzle and the tank surface. Sparks from the blasting material hitting the tank surface may also occur, but energy releases from such sparks are generally not high enough to ignite fuel vapors. Safety procedures that should be followed are outlined in API Recommended Practice 2015, API Publication 2026, and API Recommended Practice 2027.

Vapor releases from bulk tanks storing oxygenated gasoline, neat alcohols, ethers, or M85 should be treated as flammable. The same fire-safety procedures used for base gasoline during exterior tank cleaning should be followed during cleaning of tanks containing these fuels.

5.3 VAPOR CONTROL SYSTEM OPERATION AND MAINTENANCE

5.3.1 General

A safety concern with vapor control system operation is the release of fuel vapors or liquid fuel from failed or malfunctioning equipment.

5.3.2 Fuel Leaks

Fuel leaks from the liquid product return side of vapor control systems can constitute a fire hazard if exposed to hot surfaces or if allowed to evaporate and form flammable vapor-air mixtures in the presence of ignition sources. Oxygenated gasolines, alcohols, ethers, and M85 can adversely affect certain types of materials used to make gaskets and seals found in vapor control systems, as noted in API Publication 4498 and Alexander, Ferber, and Stahl, *Fuel Reformulation,* Vol. 4, No. 2. Thus, vapor control systems may become more susceptible to leaks when handling oxygenated gasolines, alcohols, ethers, and M85 if incompatible materials are present. All leaks from vapor control systems should generally be treated as though they were base gasoline with regard to fire-safety. As with any fuel, care should be taken to prevent released fuel containing oxygenates from getting into the ground water or a stormwater drainage system.

5.3.3 Vapor Control System Efficiency

While a loss in vapor control system efficiency is a major concern from an environmental point of view, such occurrences can also have important fire-safety consequences, since such decreases in efficiency can allow greater amounts of vapors to be released to the open air. Adsorption and thermal oxidation systems have the most potential to be negatively impacted by the use of oxygenated gasolines. Adsorption systems may experience a decrease in vapor control efficiency when processing oxygenated gasolines and M85, since the alcohols in these fuels may degrade sealing materials and mechanisms that normally maintain system vacuum. Also, the carbon used in adsorption systems may have less capability to adsorb alcohol and ether vapors than hydrocarbons. Vapor control efficiencies of thermal oxidation systems may be degraded when processing oxygenated gasolines and M85 due to a leaning of the overall stoichiometry of the vapors being processed with these fuels, creating a higher potential for flameouts. In any event, a flameout poses two very serious fire hazards. First, the probability is very likely that vapors in the flammable range will be present when relighting the units; therefore correct safety procedures are essential. Second, the fuel vapors collected from the tank truck loading process would then be emitted directly to the open air. Consult vapor control system manufacturers for proper and correct operating procedures when using oxygenated gasolines under normal and flameout conditions.

Refrigeration vapor control system efficiency may actually benefit from the use of oxygenated gasolines and M85. The alcohol content of these fuels would act to reduce frost build-up on the condenser coils of these systems, thereby increasing the condenser's effectiveness in condensing fuel vapors and recovering them as product.

5.3.4 Impact on Flame Arresters

The glycol-water solutions used in hydroseal flame arresters may become diluted with alcohol from oxygenated gasolines and M85. As noted in API Publication 4498, if enough alcohol is pulled into solution with the glycol-water mixtures, the overall solution may become flammable.

Matrix-type flame arresters may experience a faster rate of obstruction when using oxygenated gasolines and M85 because the alcohols in these fuels tend to act as a solvent on dirt, rust and hydrocarbon residues in the system. As a result, these debris are loosened and carried through the system. Obstructed flame arresters decrease system performance and lose their effectiveness since the obstructing material is likely to be combustible and saturated with fuel vapor. Such material is likely to be ignited by a flashback and continue burning thereafter, as noted in API Publication 4498. Periodic maintenance should be considered to keep flame arrestors clean and unobstructed.

The presence of alcohol in the glycol-water mixture can be determined by monitoring the liquid specific gravity on a routine basis. If the specific gravity is less than one, consider changing out the mixture.

6 Service Stations

The retail service station operations addressed in this publication are tank truck unloading into underground tanks, underground storage tank maintenance and cleaning, and vehicle refueling. Oxygenated gasolines and M85 have potential tank truck unloading fire-safety hazards similar to those for base gasoline. Storing and handling oxygenated gasolines containing methanol, ethanol and cosolvents at service stations is addressed in API Recommended Practices 1626 and 1627.

6.1 TANK TRUCK UNLOADING INTO UNDERGROUND STORAGE TANKS

Underground storage tanks typically contain significant amounts of vapors at the start of the refilling process, taking the vapor space beyond the rich flammability limit even when tanks are essentially empty. In addition, the in-tank turbulence created from the filling process tends to create fuel vapor, especially in those tanks without long drop tubes that extend to near the bottom of the tank. The possibility of air entering the tank when fill lines or vapor lines are opened is very slight, since the gasoline vapors in the tank are heavier than air and the vapor pressure is usually greater than air.

Oxygenated gasolines present the same fire-safety hazards as base gasoline. Proper safety practice includes grounding the truck and bonding it to the tank by means of the loading hose or bonding cable, as specified in API Recommended Practice 2003.

6.2 UNDERGROUND STORAGE TANK MAINTENANCE

6.2.1 General

Three primary areas of underground tank maintenance are impacted by oxygenated gasolines. These include tank bottoms removal, vapor-freeing, and interior tank surface cleaning.

Proper fire-safety practice typically requires the removal of all liquid fuel product from these tanks as well as the ventilation (that is, vapor-freeing) of fuel vapors remaining in the tank before the start of any maintenance procedures. Tanks typically remain closed while maintenance preparations are conducted outside the tank. Occupational Safety and Health Administration (OSHA) regulations addressing hot work or confined space entry require testing for oxygen and benzene (or other toxics such as tetra ethyl lead where appropriate) in addition to hydrocarbon vapors, both before entering the tank and while work is in progress. If the maintenance procedure to be performed requires cutting access holes to enter the tank, or hot work inside the tank, the tank should be completely vapor-free (0% LFL) or totally inerted before cutting commences. Typical industry safety practices, as specified in API Recommended Practices 1604 and 1631, and OSHA requirements should be followed when performing maintenance inside tanks.

6.2.2 Tank Bottoms Removal

Tank bottoms that appear to be primarily water may be flammable if they have come in contact with oxygenated gasolines. Water tank bottoms will extract alcohol from oxygenated gasolines which could in turn make these bottoms flammable, as noted in Douthit, et al, SAE Paper 881667.

Water bottoms removal is typically achieved through the use of a vacuum truck, portable pump or tank truck take-off pump. Normally a closed connection is made between the vacuum truck or pump and the underground tank fill pipe to pump out product through the fill pipe and into the truck cargo tank. During water bottoms removal, venting of trucks and underground tanks to an area free of people and ignition sources should be done following industry practices.

Spills of tank bottoms constitute fire hazards from ignition of vapors and from contact with hot surfaces. Tank bottoms from oxygenated gasolines will likely contain significant amounts of alcohols and ethers that could make the bottoms flammable. Likewise, these bottoms represent a fire-safety hazard when exposed to hot surfaces. Tank bottoms from oxygenated gasolines should always be treated as flammable.

The fire hazard potential of liquid spills during tank bottoms removal is generally expected to be the same for oxygenated gasolines and M85 as for base gasoline. Care should be taken to prevent tank bottoms containing oxygenates from getting into the ground water.

6.2.3 Vapor Releases

Vapor releases from the vapor-freeing of underground tanks may result from underground storage tank maintenance. Vapors from oxygenated gasolines and M85 represent the same fire-safety hazard as the vapors from base gasoline. Some states may have regulations preventing release of vapors from underground storage tanks.

6.2.4 Interior Surface Cleaning

Oxygenated gasolines represent the same fire-safety hazard as base gasoline when cleaning or repairing the interior of underground tanks. The increased solvency power of oxygenated gasolines, alcohols, ethers, and M85 may decrease tank interior deposits. However, if the tank was used to store base gasoline in the past or is currently storing oxygenated gasoline, deposits, rust, or bottoms will contain gasoline and result in fire-safety hazards similar to base gasoline even after all product has been removed.

Once tank bottoms have been removed and the vapor space freed of fuel vapors, the interior surface of the underground tanks can be cleaned or repaired. OSHA and API standards and guidelines governing entry into confined spaces, hot work, and permit requirements should be consulted and followed when performing interior tank maintenance on underground tanks. However, fuel vapors may be released during such procedures from deposits and scale left on the walls of the tank or from residues left in crevices inside the tank. The same practices and procedures for cleaning tanks that contained base gasoline may generally be used for tanks that contained oxygenated gasoline.

A potential fire-safety hazard exists when cutting access holes in metal tanks or welding inside or outside metal tanks as the surface of the tank is heated up and fuel vapors are released. The same practices and procedures for performing hot work on tanks that contained base gasoline are generally considered appropriate for tanks that contained oxygenated gasoline.

6.3 VEHICLE REFUELING

6.3.1 General

Oxygenated gasolines impact the fire-safety characteristics of vehicle refueling practices in three areas:

a. electrostatic charge accumulation in dispenser filters.
b. fuel vapor releases.
c. fuel spills.

6.3.2 Electrostatic Charge Accumulation

Oxygenated gasolines represent the same level of concern for electrostatic charge build-up as base gasoline. M85 represents a unique case; while methanol is much more conductive than base gasoline, the dispenser filters developed for M85 are finer than those for base or oxygenated gasolines, and thus tend to create additional potential for electrostatic charge accumulation, as noted in Henry, *Fuel Reformulation,* Vol. 3, No. 1. As the filter accumulates particles, the propensity to accumulate electrostatic charge also increases. Some M85 dispensers may have a higher flow rate than base gasoline dispensers to compensate for the larger volume of M85 to be dispensed. Larger flow rates also increase the propensity to accumulate electrostatic charge in fuel dispensing systems. For M85 dispensers, it is essential that only the specified filters be used and, to lessen the potential for electrostatic build-up, that they be changed regularly before becoming obstructed. The discharge of static electricity inside a filter can cause them to leak fuel in extreme cases, leading to safety and environmental concerns.

6.3.3 Vapor Releases

Oxygenated gasolines and M85 represent the same hazards for ignition of vapors during vehicle refueling as for base gasoline.

6.3.4 Fuel Spills

Oxygenated gasolines and M85 represent the same hazards for ignition of fuel spills during vehicle refueling as for base gasoline.

6.3.5 Stage II Vapor Recovery Systems

Both balance and assist types of Stage II vapor recovery systems have been designed to operate safely and reliably using base gasoline. Neither oxygenated gasolines or M85 have properties that are expected to significantly affect the fire-safety hazards of Stage II systems. No changes in operating procedures are recommended when using oxygenated gasolines or M85. However, M85 has different materials compatibility requirements compared to straight or oxygenated gasolines. Using M85 in systems designed for base gasoline may result in degradation of system components that will affect operation.

APPENDIX A—TYPICAL FUEL PROPERTY DATA

Property data for base gasoline and the most widely used oxygenates are presented in Table A-1. These data are presented as a guide to fire safety issues relative to gasoline. Precise property data for oxygenates and oxygenate blends should be requested from the supplier and have parallel measurements taken. All personnel dealing with fuels should have Material Safety Data Sheets to refer to for each specific fuel and blend.

Table A-1—Properties of Base Gasoline and Oxygenates

Properties and Characteristics	Base Gasoline	Neat Methanol	Denatured Ethanol	M85	MTBE	ETBE	TAME	TAEE	DIPE	TBA	IPA
Boiling Temperature, in °F	80–439[a]	149	80[b]	NA	131	161[c]	187	214	155	181	180
Flash Point, in °F	–45	52	<10°F[d]	–32	–14	–3[e]	12[f]	15[g]	–18[h]	52	53
Vapor Pressure, Reid, in pounds per square inch	7 to 15[i]	4.6	4.5	7 to 9	7.8 11 to 13[j]	4.0	1.5	1.2	4.9	1.8	1.8
Vapor Density Relative to Air (Air = 1.0)	3.4:1 to 5.0:1[k]	1.1:1[l]	1.6:1[m]	1.2:1 to 2.0:1[n]	3:1[o]	3.5:1	NA	NA	3.5:1	2.6:1[p]	2.1:1
Flammability Limits, vol% in air	1.4 to 7.6	6 to 36	3 to 19	5.7 to 34	1.6 to 8.4	1.0 to 6.8[q]	1 to 7.1	NA	1.4 to 21	2.4 to 8.0	2.0 to 12
Electrical Conductivity, in picoSiemen per meter	1	4.4×10^7	1.4×10^5	3.0×10^7	1.21×10^3[r]	NA	NA	NA	NA	NA	NA
Autoignition Temperature, in °F	495	867	689	725 to 896	705	580	NA	NA	829	892	750
Latent Heat of Vaporization, in Brtitish thermal units per pound	150	506	396	450	154[s]	134	147	NA	148[t]	258[u]	320
Flame Visibility[v]	1	2	3	1	1	NA	NA	NA	NA	NA	NA
Solubility in Water, wt% @ 77°F	negligible; <0.1%	100	95	70 to 90	4.3	2.0	1.2	0.4	1.2	100	100

Notes:

NA = Not available in the literature at the time of publication of this report

a. American Petroleum Institute, *Alcohols and Ethers: A Technical Assessment of Their Application as Fuels and Fuel Components,* Second Edition, API Publication 4261, July 1988.
b. Estimated based on 5 volume percent gasoline denaturant.
c. Piel, William J., "Expanding Refinery Technology Leads to New Ether Potential," presented at 1992 National Conference on Clean Air Act Implementation and Reformulated Gasolines, Washington, DC, October 1992.
d. Chevron USA Material Safety Data Sheet for Ethanol–Fuel Grade, 575 Market St., Room 2900, San Francisco, CA 94105-2856.
e. ARCO Chemical Company, Material Safety Data Sheet, Ethyl T-Butyl Ether, March 24, 1993.
f. Chevron Environmental Health Center, Material Safety Data Sheet, Tertiary Amyl Methyl Ether, August, 16, 1991.
g. Evans, T.W., and K.R. Edlund, "Tertiary Alkyl Ethers, Preparation and Properties," *Industrial and Engineering Chemistry,* vol. 3, no. 10, October, 1936.
h. Exxon Chemical Company, Material Data Safety Sheet, Diisopropyl Ether, January 14, 1993.
i. 7 represents summer limit in California; 15 represents winter limit in ASTM Class E areas.
j. ASTM P232, *Specification for Fuel Methanol,* 1993, for summer and winter grades of M85.
k. Exxon Company, Material Data Safety Sheet, Exxon Unleaded Gasoline, October 8, 1987.
l. Machiele, Paul A., "Flammability and Toxicity Tradeoffs with Methanol Fuels," SAE Paper No. 872064, presented at International Fuels and Lubricants Meeting and Exposition, Toronto, Ontario, November 2-5, 1987.
m. Cargill, Materials Safety Data Sheet, Fuel Alcohol, March 29, 1993.
n. Sun Company, Inc., Material Safety Data Sheet, June 17, 1993.
o. ARCO Chemical Company, MTBE product information brochure, 1988.
p. Wells, G. Margaret, *Handbook of Petrochemicals and Processes,* Gower Publishing Company, Limited, 1991.
q. ARCO Chemical Company, *Oxygenates for Future Fuels,* 1990.
r. ARCO Products Company, MTBE Product Safety Bulletin, February 1993.
s. Prezelj, M. "Pool Octanes Via Oxygenates," *Hydrocarbon Processing,* Vol. 66, September 1987.
t. *Oil and Gas Journal,* May 25, 1992, p. 39.
u. *Handbook of Chemistry and Physics,* 62nd Edition, 1981, The Chemical Rubber Company Press, Inc.
v. Visibility key: 1 = visible under all conditions; 2 = invisible in daylight; 3 = difficult to see in daylight.

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