

METHANOL SAFE HANDLING TECHNICAL BULLETIN

Using Physical and Chemical Properties to Manage Flammable Liquid Hazards Part 1-A: How to Use the Technical Bulletin

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INTRODUCTION

This is part one of a three-part Technical Bulletin on how to use physical and chemical properties to identify, assess, and control hazards associated with commonly used flammable liquid and gaseous fuels. The three parts complement each other, but can also be used independently, according to the level of information needed by the user.

Part 1 of this Bulletin provides information for eight fuels ranging from gaseous hydrogen to biodiesel, and is divided into two sections. Section 1-A serves as the introduction to the table and contains the glossary of terms and acronyms. Section 1-B is the actual fuel properties data table.

The table in Section 1-B listing fuel properties is divided into five sections, as follows:

- 1.) General Information
- 2.) Liquid Properties
- 3.) Vapor properties
- 4.) Flammable Properties
- 5.) Sources of Information

The first section of this document contains information that is generally useful for handling, shipping, and responding to releases and spills. Sections 2 through 4 compare selected properties of one fuel with another by listing parameters in tabular format. The information source for each item of data is listed in Section 5.

Parts Two and Three of the Technical Bulletin develop a foundation for using selected physical and chemical properties to determine the character, and severity of methanol hazards compared to those of other commonly used gaseous and liquid fuels.

Virtually all methanol users have experience handling gasoline and or diesel, so the properties of methanol are compared to those of gasoline and diesel. Users will see that hazard severity is determined by two factors: 1.) properties of the chemical or substance, and 2.) the circumstances under which the chemical or substance is being transported, stored and used.

SELECTED FUELS

The fuels include Hydrogen gas (H₂), compressed natural gas, propane (a liquefied gas), three Class IB Flammable Liquids (methanol, ethanol, and gasoline), and two Class 2 combustible liquids (No. 2 diesel, and biodiesel). Parameters listed for methanol and ethanol are for neat (i.e., pure) materials, not for fuel blends. Parameters for

fuel blends must be determined for each specific blend.

SOURCES OF INFORMATION

Information in the tables was derived from a combination of copyright-protected publications, and from various internet sources available as of March 31, 2011. Information beyond that included in the tables can be obtained by accessing the listed web pages and/or by conducting expanded internet searches using your own guidewords. The authors and the Methanol Institute make no representation as to the accuracy, quality or completeness of information obtained from the sources cited and take no responsibility for its use. Users are encouraged to use the internet; however, data should be verified by a second source when possible.

GLOSSARY OF TERMS AND ACRONYMS

(Sources of the indexed definitions are tabulated at the end of the glossary.)

Adiabatic Flame Temperature (see also Peak Flame Temperature) - the highest possible flame temperature presuming there is no loss of heat to from the flame to the surroundings. This is a calculated value that assumes that all of the heat released as heat of combustion is directed toward raising the temperature of the flame. The actual flame temperature will be much cooler than the value calculated as the adiabatic flame temperature, because in reality a portion of the heat of combustion is transferred to the surroundings via convective and radiant heat transfer.⁽¹⁾

API- American Petroleum Institute

ASME- American Society of Mechanical Engineers

Autoignition Temperature- the minimum temperature of a liquid necessary to initiate the self-sustained combustion of its vapor in the absence of an ignition source.⁽²⁾

BLEVE or Boiling Liquid Expanding Vapor Explosion- The phenomena in which the rapid buildup of internal pressure within a container, tank, or pressure vessel which is relieved by explosion and bursting of the container. BLEVEs can cause containers to 'rocket' away from the site of the explosion due the force of the explosion.⁽²⁾

Boiling Point Temperature- The temperature at which the vapor pressure of a liquid substance equals the average atmospheric pressure: i.e., 14.7 psia or 760 mmHg.⁽²⁾

CAS Number- The American Chemical Society's Chemical Abstract Service number. Each chemical compound is assigned a unique number.⁽³⁾

Coefficient of Volumetric Thermal Expansion- The change in the volume of a liquid per degree of change in temperature.⁽²⁾

Density- The property of a substance that measure its compactness; the mass of a substance divided by the volume it occupies.⁽²⁾

DOT- U.S. Department of Transportation

DOT Guide Number (see also UN and UA Numbers)- The four digit hazard code assigned by the U.S. DOT.⁽³⁾ Typically, the DOT Guide Number and the UN Number are the same. If there is no DOT Guide Number or UN Number, then a NA Number is assigned.

DOT Hazard Class and Division- The category of hazard DOT assigns to a hazardous material such as explosives, compressed gases, flammable and combustible liquids, flammable solids, oxidizers and organic peroxides, poisonous and toxic materials, infectious substances, radioactive materials, corrosive materials, and miscellaneous hazardous materials.⁽¹¹⁾

DOT Number- Companies that operate commercial vehicles hauling passengers or cargo in interstate commerce and/or intrastate haulage of hazardous materials must be registered with the Federal Motor Carrier Safety Administration (FMCSA) and must have a DOT Number. The DOT Number serves as a unique identifier for the company when compiling incident reports and accident history.⁽⁵⁾

DOT Packaging- regulated hazardous materials for export require UN/DOT compliant packaging.

DOT Packing Group- Mitigating the risks associated with shipment of hazardous materials may require application of safety precautions during shipment, storage and use. Packing groups are used to determine the degree of protective packaging required for dangerous goods during transportation. Group I is great danger; group II is medium danger; and group III is least danger.⁽⁶⁾

Electrical Conductivity (see also Specific Electrical Conductance)- The measure of how well a material allows movement of an electrical charge. It is the ratio of the current density to the electric field strength. The SI derived unit of measure is Siemens/meter (S/m). A unit of Siemens is equivalent to the older unit for the inverse of an ohm, known as “mho.” Conductivity (also called specific conductance) of moderately conductive liquids such as methanol is frequently expressed in units of micro Siemens per centimeter ($\mu\text{S}/\text{cm}$). Conductivity of dielectric liquids such as gasoline and diesel are often expressed in units of pico Siemens per centimeter (pS/cm). A unit Siemens is equivalent to 1×10^{12} pico Siemens. A unit micro Siemen is equivalent to 1×10^6 pico Siemens.⁽¹²⁾

Enthalpy of Combustion (see also Heat of Combustion)- The exothermic thermal energy that is released by a combustion reaction.⁽²⁾

Flame Temperature- The temperature of a flame. Flame provides a general indication of the rate of the combustion reaction. Liquids which are characterized as burning with a high flame temperature have higher reaction rates than those characterized by a low flame temperature.⁽⁷⁾

Flammability Limits- The volume or mole percent concentration of a gaseous fuel in air at which combustion can occur. Flammability limits are both an upper and a lower bound.

Flammability Range- The numerical difference between a flammable substance’s lower and upper explosive limits in air.⁽²⁾

Flash Point Temperature- The minimum temperature at which the vapor of a liquid or solid ignites when exposed to sparks, flames, or other ignition sources.⁽²⁾

Freezing Point Temperature- The temperature at which the liquid and solid states of a substance coexist at one atmosphere (atm) of pressure.⁽²⁾

Fuel in Vaporized Stoichiometric Mixture- The volume percent of vaporized fuel available to a combustion reaction which occurs at stoichiometric concentration.

Hazard- A characteristic of a compound, chemical, or material which has the potential of causing harm and damage if not controlled and appropriately managed.

Heat Capacity (see also Specific Heat or Specific Heat Capacity)-The amount of heat needed to raise either one gram of a substance one degree Celsius or one pound of substance one degree Fahrenheit.⁽²⁾

Heat of Combustion (see also Enthalpy of Combustion)- The heat evolved to the surroundings when a compound is burned to yield carbon dioxide and water vapor.⁽²⁾

Heating Value- The theoretical amount of heat that can be released by a combustion reaction if the fuel and oxidants are converted with 100% efficiency to CO₂ and H₂O vapor. Two values are given heat value: a higher heating value (HHV) and a lower heating value (LHV). HHV is used for situations in which all of the heat (heat of reaction, the sensible heat of product gases, and the heat of condensation of water vapor) is recovered and utilized to perform work. HHV is essentially the same as the thermodynamic heat (enthalpy) of combustion. The LHV is used if a portion of the sensible heat of the gases and the heat of condensation of water vapor is not recovered to perform work. The process industries typically use the lower heating value.^(1,8)

ICC- International Code Council

IEEE- Institute of Electrical and Electronics Engineers

ISA- International Society of Automation (formerly Instrument Society of America)

Latent Heat of Vaporization- The energy to transform a given quantity of a material into a gas.

Liquid Flammability Class- A system of classification used by NFPA and ICC which groups liquids into categories based upon boiling point and flash point temperature. Methanol, ethanol, and gasoline are type IB flammable liquids. By comparison, diesel is a combustible liquid.

Lower Flammability Limit (see also lower explosive limit)- The concentration of a gas or vapor in air below which a flame will not propagate upon exposure to an ignition source. If the fuel/air mixture is said to be too lean, there is insufficient fuel to support sustained combustion.⁽²⁾

Mass Burning Rate- The loss in mass per unit time by materials burning under specified conditions.⁽⁹⁾

Minimum Ignition Energy- The smallest amount of energy of a piloted ignition source which can ignite a mixture of fuel in air when the concentration of the fuel is between the lower and upper flammable limits. Four sources of heat energy are: ⁽¹⁾ chemical, ⁽²⁾ electrical, ⁽³⁾ mechanical, ⁽⁴⁾ nuclear.⁽⁷⁾

NACE- National Association of Corrosion Engineers

NEC- National Electrical Code

NFPA- National Fire Protection Association

OSHA- U.S. Occupational Safety and Health Administration

Peak Flame Temperature (see also Adiabatic Flame Temperature)- the theoretical maximum temperature a flame can reach assuming no heat is transferred to the surroundings.

Reid Vapor Pressure (RVP)- A commonly used measure of vapor pressure for gasoline, defined as the absolute vapor pressure exerted by a liquid at 100oF as determined by the test method ASTM D-323. The test method

does not apply to liquefied petroleum gases such as propane. RVP is the absolute vapor pressure. True Vapor Pressure (TVP) is the partial vapor pressure.⁽¹⁰⁾

Specific Electrical Conductance (see Electrical Conductivity)

Specific Gravity- The mass of a given volume of matter compared to the mass of an equal volume of water.⁽²⁾

Specific Heat (see also Specific Heat Capacity or Heat Capacity)- The ratio of the heat capacity of a substance to the heat capacity of water at the same temperature.⁽²⁾

Specific Heat Capacity (see Specific Heat or Heat Capacity)

STCC Number (Standard Transportation Commodity Code) - The unique 7-digit code assigned to commodities transported by rail. The STCC number must be shown on all bills of lading.⁽¹³⁾

Stoichiometric Air to Fuel Ratio- The ratio of the theoretical amount of air (expressed as moles or mass) to the amount of fuel expressed in the same units which contains sufficient oxygen to allow full and complete combustion of 100% of the hydrogen and carbon contained within the fuel.⁽¹⁾ Oxygen-to-fuel ratio: oxygen/Fuel = $(1 + x/4)$ where $x = H/C$ of the fuel

$$\text{Air-to-fuel ratio: } A/F = (100/21)(O/F)$$

Stoichiometric Flame Speed- The speed of the flame front at the stoichiometric air-to-fuel ratio.

Stoichiometric Mixture- A mixture of air and fuel which has a chemical composition equivalent to the stoichiometric air to fuel ratio.

Thermal Conductivity- The ability of a material to conduct heat. Liquids with high thermal conductivity conduct heat more readily than liquids with low thermal conductivity.⁽¹⁾

UA Numbers- North American Numbers are identical to UN Numbers. If a material does not have a UN Number, it may be assigned an UA Number; these are usually four-digit numbers starting with 8 or 9.⁽⁴⁾

UN Numbers- United Nations Numbers are four digit numbers used worldwide to in international commerce and transportation to identify hazardous chemicals, or classes of hazardous materials.⁽⁴⁾

Upper Flammability Limit (see also upper explosive limit)- The concentration of a gas or vapor in the air above which it cannot burn when exposed to an ignition source. If the fuel is said to be too rich to burn above the UFL, the number of moles of air is insufficient to support combustion.

Vapor Pressure (see also True Vapor Pressure TVP)- The pressure exerted within a confinement vessel by the vapor of a substance in equilibrium with its liquid; a measure of a substance's propensity to evaporate.⁽²⁾

Viscosity- The quality of resistance to flow.⁽²⁾

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