METHANOL
INSTITUTE

METHANOL SAFE HANDLING MANUAL

5TH EDITION

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1 INTRODUCTION TO THE MANUAL

This chapter explains the purpose of the manual and provides an introduction to the methanol value chain. The Methanol Institute's Product Stewardship policy and contact information are also included.

1.1 PURPOSE OF THE MANUAL

We at the Methanol Institute intend this manual to serve as a guidance document for methanol distributors and users like you. The purpose of the manual is to promote the safe handling of methanol in order to protect your health and that of your co-workers, your workplace, the environment, and your community.

You may be a wastewater treatment plant operator in India, a biodiesel plant manager in Canada, a Health and Safety Coordinator at a formaldehyde plant in Mexico, a tanker truck driver at a chemical distribution warehouse in Algeria, a research engineer developing a fuel cell in New Zealand, an antifreeze production supervisor in East Siberia, or a shipping terminal manager in China. You and your colleagues in the worldwide methanol supply chain together speak dozens of languages and are located in practically every country in the world.

This manual is designed to be a primary resource for information on methanol specifically for you who are responsible for its safe handling. It presents current information on methanol's properties, potential environmental and health and safety hazards, safe handling practices, emergency response procedures, product and distribution stewardship, and risk communication.

The manual's chapter organization and content are intended to provide you with convenient access to practical information. Key facts and useful references are highlighted in the text. Additional technical data, such as methanol's chemical, physical, and thermodynamic properties, can be found in the appendices. The reference section presents a list of scientific and technical resources for more in-depth research.

For additional convenience, we have included a glossary of scientific terms and commonly used acronyms to help you navigate through the regulatory and technical language.

In addition to the manual, we have a companion Methanol Safe Handling Video available, and we also have Fact Sheets available on a number of topics related to methanol safe handling. These include tainted alcohol poisoning, methanol fire detection extinguishment, a crisis communication guidebook and more. All of our safe handling materials are available on our website at: https://www.methanol.org/safe-handling/

1.2 THE METHANOL VALUE CHAIN

Methanol is a product with many useful characteristics that allow it to serve as a fuel or fuel additive, a chemical feed stock, a solvent, a refrigerant, and a component or intermediate in many consumer goods. Methanol is also a hazardous chemical with significant toxic, flammable, and reactive properties that can produce deleterious impacts on human health and the environment when not properly handled.

Natural sources of methanol include volcanic gases, vegetation, microbes, and insects, and it is also manufactured from a variety of inorganic and organic sources. Most methanol is produced from natural gas in large, integrated chemical manufacturing plants located in regions where hydrocarbon feed stocks are plentiful, such as the Persian Gulf, the Caribbean, South America, Africa, and Russia. In China, in particular, most methanol is produced from coal. Although methanol is consumed throughout the world, the largest users are in regions that have high industrial development, such as Western Europe, North America, and Asia (Japan, China, Taiwan, and South Korea). World methanol demand in 2019 was an estimated 83,000,000 metric tonnes.

Due to the geographical distance between the major manufacturing centers and the principal users, as much as 80% of the world's annual methanol production is transported between continents by trans-ocean shipping. Methanol is received and stored in marine terminals and trans-shipped via truck, rail, and barge to chemical production facilities and bulk distributors, where it is stored in tank farms and repackaged into smaller containers. Tanker trucks and trailers complete the distribution network, delivering methanol to the wide range of final users in the methanol value chain.

More recently developed industrial uses of methanol include its application as a denitrification agent in wastewater treatment plants and as a reagent and solvent in biodiesel production facilities. New applications of methanol are emerging, as a marine and road transport fuel, as a fuel for industrial boilers, kilns and cookstoves, and with technological innovations, such as fuel cells for vehicles and consumer electronic products.

Methanol is amenable to recycling by removing impurities through distillation and introducing the recovered material back into the process. Waste methanol has high-caloric value and can be used to recover energy through thermal destructive processes that generate heat to fuel other reactions.

1.3 METHANOL INSTITUTE PRODUCT STEWARDSHIP POLICY

As the global trade association for the methanol industry, product stewardship is our primary concern.

The Methanol Institute's Product Stewardship Committee is responsible for methanol health and safety initiatives, including product risk evaluation, exposure risks throughout the supply chain, education, and training on proper methanol handling. The product stewardship tools developed by the committee and its individual members will benefit the global methanol industry. The committee will closely coordinate with other working committees to provide maximum support to Methanol Institute initiatives.

1.4 METHANOL INSTITUTE CONTACT INFORMATION

The Methanol Institute's headquarters are located in Singapore, with U.S. offices near Washington, D.C. and offices in Brussels and Beijing. For additional information or to find out more about the Institute and its programs, please contact:

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1.5 ABOUT THE AUTHORS

The Methanol Institute's Product Stewardship Committee commissioned the authors of the original manual, Alliance Consulting International, with the preparation of the second edition and now fifth editions. They are an environmental and health and safety professional services firm based in San Diego, California. The project team consists of Enrique Medina (MS, CIH, Environmental specialist, editor, and project manager), and Robert R. Roberts (MS, MBA, Process Engineering and Reliability specialist). For additional information on Alliance Consulting International, please contact:

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The Methanol Institute commissioned Wellon Safety Solutions Inc. with revising the Methanol Safe Handling Manual for this fourth edition. Revisions consist primarily of updated and more detailed information regarding process safety management (PSM), as well as providing specific guidance for PSM application for the safe handling of methanol. Wellon Safety Solutions is an EHS and Process Safety consulting firm based in Calgary, Alberta. For additional information, please contact:

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The Methanol Institute commissioned SP Technical Research Institute of Sweden with revising the Methanol Safe Handling Manual Fire Safety chapter for the fourth edition. Revisions consist primarily of updated and more detailed information regarding general fire safety information as well as fire detection, extinguishment with sprinkler and foam, extinguishment with inert gas, and first fire response routines. SP Technical Research Institute of Sweden is located in Borås, Sweden. For additional information, please contact:

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1.6 DISCLAIMER

As part of its commitment to methanol product stewardship, the Methanol Institute has prepared this Manual. Our intention is to improve the awareness of safe and environmentally sound practices for the handling of methanol throughout the global distribution chain. The information, procedures, recommendations, and data presented in this Manual are informational only, and the Manual is designed to provide general guidance only. The Methanol Institute and the report authors assume no liability whatsoever with respect to the accuracy and completeness of the information, procedures, recommendations, and data presented in this Manual and disclaim all liability arising out of the use of such information, procedures, recommendations, and data. All users of this Manual must still use their own independent judgment and discretion in ensuring that they handle methanol safely and communicate appropriately. In doing so, they must develop the specific systems that best fit their management structure, product lines, location, and other factors that are unique to the user. We encourage you to research the local codes and regulations that may be applicable to the handling of flammable and hazardous materials such as methanol. This Manual is not a substitute for applicable laws and regulations, nor does it alter the obligation of the user to comply fully with federal, state, provincial and local laws.

2 METHANOL GENERAL INFORMATION

This chapter summarizes the character of methanol as a chemical compound, the life cycle or value chain of methanol, and both established and emerging uses of methanol.

2.1 WHAT IS METHANOL?

Methanol is a colorless alcohol, hygroscopic and completely miscible with water, but much lighter (specific gravity 0.8). It is a good solvent, but very toxic and extremely flammable. This simple single-carbon alcohol is a volatile solvent and a light fuel.

Methanol, also known as methyl or wood alcohol, is a colorless organic liquid at normal temperature and pressure (NTP: 72o F and 1 atm). Though correct, this description is a small part of what a handler must know and understand in order to transport, store, and use methanol safely.

Methanol is a remarkably useful material that means different things to different users. To some, methanol is a fuel, to others a fuel additive, to still others a chemical feed stock, a solvent, a refrigerant, or a component of antifreeze. Emerging applications of methanol include its use as a vehicular and marine fuel, a source of protons for direct methanol fuel cell technology and as a turbine fuel for electric power generation.

The particular hazards of methanol that matter most to your facility depend in large part on how methanol is received and stored, how it is used, where it is used, and how much is stored and used at any given time. Failure to control hazards associated with a small amount of methanol can be problematic with virtually no consequence; loss of control of a large quantity can be catastrophic. Section 2 of this manual provides an overall view of methanol for both large and small quantity handlers, transporters, and users.

Five overriding considerations are important when handling methanol:

1. Methanol is a flammable, easily ignited liquid that burns and sometimes explodes in the air.

2. The molecular weight of methanol vapor is marginally greater (denser) than that of air (32 versus 28 grams per mole). As a result, and depending on the circumstances of a release or spill, methanol liquid will pool and vapor may migrate near the ground and collect in confined spaces and low-lying areas. It is expected that methanol vapor, being near neutral buoyancy, will dissipate readily from ventilated locations. Do not expect it to dissipate from non-ventilated locations such as sewers and enclosed spaces. If ignited, methanol vapor can flash back to its source.

3. In certain specific circumstances, methanol vapor may explode rather than burn on ignition. Methanol containers are subject to Boiling Liquid Expanding Vapor Explosion (BLEVE) when heated externally.

4. Methanol is a toxin; ingestion of a small amount (between one and two ounces, approximately 10 to 30 milliliters, or less than a 1/4 cup) may cause death; lesser amounts are known to cause irreversible blindness. Do not swallow methanol liquid, do not breathe methanol vapor, do not walk in pooled liquid, and do not allow vapor or liquid to contact skin. Methanol absorbs through the skin and other tissues directly into the blood stream.

5. Methanol is totally miscible in water and retains its flammability even at very high concentrations of water. A 75v% water and 25v% methanol solution is considered to be a flammable liquid. This has important consequences for firefighting.[1] Methanol is a chemical solvent, which has important implications for materials selection and also firefighting.

The methanol molecule contains a single carbon, and is thereby the simplest alcohol that can be derived from normal, saturated hydrocarbons – namely, methane (CH4), ethane (C2H6), and propane (C3H8). The two- and three-carbon-derived alcohols are ethanol and propanol, respectively.

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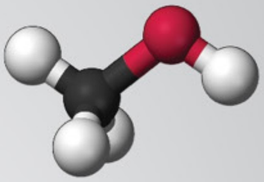
[1] Refer to Methanol Institute Safe Handling Technical Bulletin "Using Physical and Chemical Properties to Manage Flammable Liquid Hazards: Parts 1A, 1B, 2 and 3."

WHAT IS METHANOL?

Methanol, CH3OH, is a clear and colorless liquid produced from natural gas, coal and a wide range of renewable feedstocks. Also known as “wood alcohol”, methanol is naturally occuring and biodegradable.



To some, methanol is a fuel for cars, trucks, buses, and ships, to others a chemical feedstock for solvents, refrigerants, and even antifreeze. Emerging applications for methanol include its use as a hydrogen carrier for fuel cell technology applications, a denitrification agent for wastewater treatment, and as a turbine fuel for electric power generation.

From paints and plastics, furniture and carpeting, to car parts and windshield wash fluid, methanol is a chemical building block used in making hundreds of products that touch our daily lives.

- MDF Baseboard Molding

- PET Plastic Bottles
- Decorative Laminates

Other Uses:
- Clothing
- Fertilizer
- Fiberglass Insulation Binder
- Silicone Sealants
- Plywood Structural Panels
- Electrical Molding Components
- OSB Structural Panels - Roof
- Roofing Adhesive
- Vinyl Adhesives

- Paints

- Urethane Foam

- Polyester Carpet

- Coating Polyols

- Particle Board

- Polyurethane Door Skins

- Clean Fuels
- Paints
- Polyester Carpet & Fabric
- Thermoset Bumper & Energy Absorber
- Light Lens
- Tire Core Adhesives
- Body Panels
- MDF/MDI Door Panels
- Safety Glass Laminate
- Polyurethane Dashboard Foam
- Windshield Washer Fluid
- Acetyl Thermoplastics: Gears, Pumps, Mouldings, Coumpounds, Distributer Caps, Fuses

- Rigid Foam Door Insulation

- Nylon Carpets

- Textile Treatments

- Polyurethane Mattress Foam

- Computer Disks

- Aerosols
- Disinfectants
- Fragrances
- Solvents
- ASA Medication

METHANOL INSTITUTE

The chemical names for alcohols come from the names of the corresponding hydrocarbon groups. Accepted naming convention drops the “e” ending and adds “ol.” Common alcohols – methanol (CH3OH), ethanol (C2H5OH), and propanol (C3H5OH) – have similar physical and chemical properties, but very different toxicity hazards. As the number of carbon atoms in alcohol molecules increases, the length of the straight carbon chain increases, the molecular weight of the alcohol molecule increases, freezing point temperature decreases, and boiling point temperature increases.

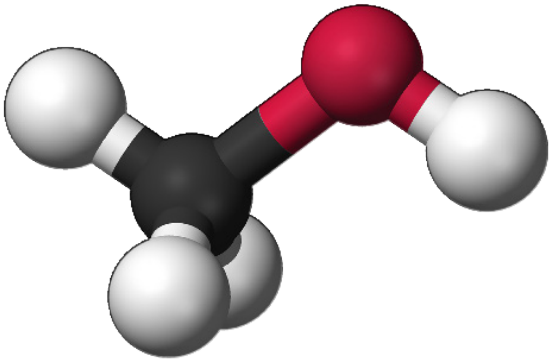


Figure 1. Methanol CH_3OH

Alcohols are structurally similar to water. Some properties of alcohols, specifically of methanol, resemble properties of water. Both water and methanol are polar molecules. If mishandled, methanol poses hazards to life safety. It is flammable, toxic, reactive with alkali metals and strong oxidants, and 100% miscible in water. These properties necessitate specific measures in handling storage, as discussed in more detail in future sections.

Table 1 lists the structural formulas, systematic names, common names, and solid melting and boiling point temperatures for three representative alcohols.

If mishandled, methanol poses hazards to life safety. It is flammable, toxic, reactive with alkali metals and strong oxidants (e.g., bromine, bromates, chlorates, chromates, etc.) and is 100% miscible in water. These properties necessitate specific measures in handling storage, as discussed in more detail in future sections.

Table 1. Three Representative Alkane-Derived Alcohols

Molecular Structure	**Systematic Name**	**Common Name**	**Liquid Freezing Point**	**Liquid Boiling Point**
CH_3OH	Methanol	Methyl Alcohol; Wood Alcohol[2]	-144°F (-97°C)	149°F (65°C)
CH_3CH_2OH	Ethanol	Ethyl Alcohol; Grain Alcohol[3]	-175°F (-115°C)	172.4°F (78°C)
$(CH_3)_2CHOH$	2-Propanol (Isopropanol)	Isopropyl Alcohol	-194.8°F (-126°C)	206.6°F (97°C)

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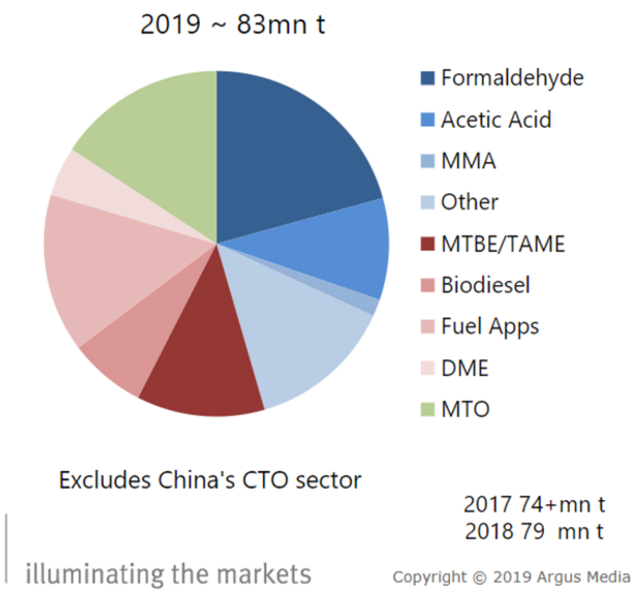
[2] Prior to 1926, methanol was referred to as "wood alcohol." During this period, methanol was produced by destructive distillation of wood.

[3] Grain alcohol, or ethanol, is produced by fermentation of grain. Typically, small amounts of methanol are produced along with ethanol. Because methanol is a potent poison, it is necessary to separate the methanol before consuming the ethanol.

2.2 THE METHANOL LIFE CYCLE (VALUE CHAIN)

Methanol is produced, stored, and shipped in enormous quantities. Global methanol production continues to expand at high speed, led by the US and China. Worldwide, over 90 methanol plants have a combined production capacity of about 110 million metric tons (almost 36.6 billion gallons or 138 billion liters) and 2019 methanol demand is estimated (excluding China's CTO sector, at 83 million metric tons).

Table 2.



Excludes China's CTO sector

2017 74+mn t
2018 79 mn t

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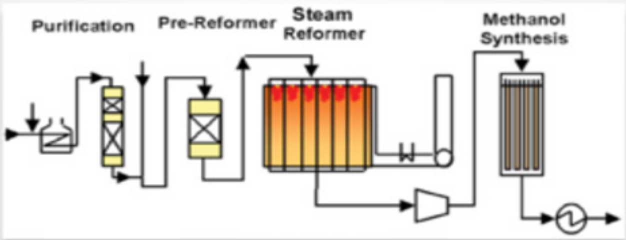
2.2.1 METHANOL MANUFACTURE

Methanol producers are typically located in regions of the world that produce an excess of natural gas, areas that mine large amounts of coal, and/or industrialized countries that can access natural gas in large quantity at relatively low shipping cost. Natural gas supplies are increasing as a result of new drilling and hydro-fracturing technology, which allow development of previously unrecognized low-cost reserves. Another market trend is caused by the cost of manufacturing methanol from natural gas versus other sources such as coal. Because it is less expensive to manufacture methanol from gas than from coal, high-cost coal-to-methanol producers are curtailing production, particularly in China, in order to take advantage of lower-cost imported methanol (Saudi Arabia, New Zealand, Malaysia, and Indonesia). Table 2 shows global methanol supply and demand balance.

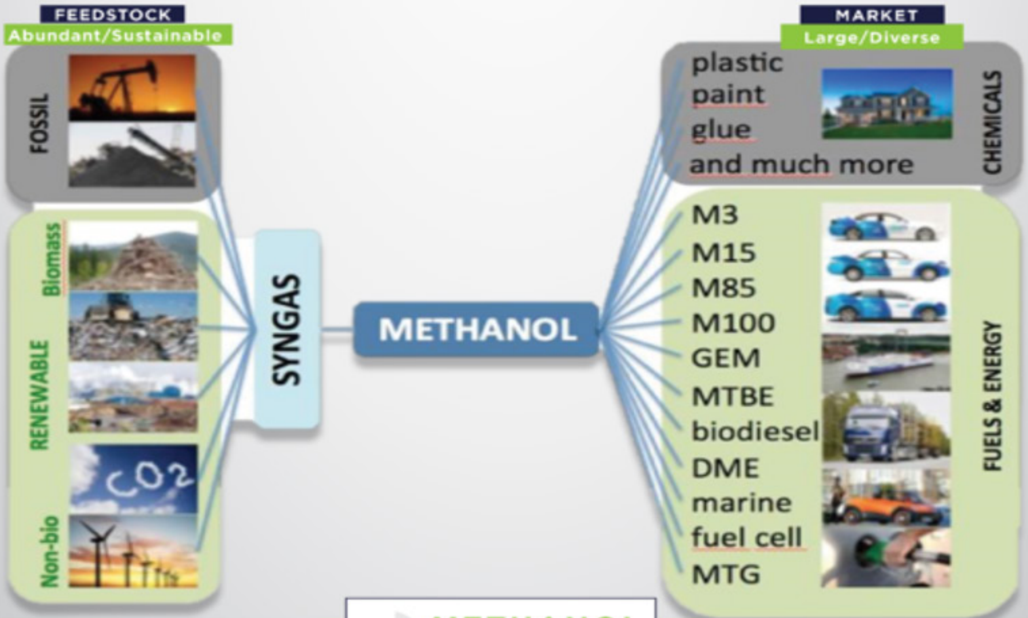
METHANOL:
PRODUCTION & SUPPLY

The typical feedstock used in the production of methanol is natural gas. Methanol can be made from renewable resources such as wood, muncipal solid wastes, renewable electricity, waste CO2, and even sewage. The production of methanol also offers an important market for the use of flared natural gas.

In a typical plant, methanol is made by mixing natural gas with steam, heating this mixture and passing it over a catalyst in a steam reformer. The gas/steam is transformed to produce "synthesis gas," which is then pressurized and coverted to crude methanol over a catalyst, and finally distilled to remove water and yield pure methanol.



More than 90 world-scale methanol plants have the capacity to produce over 110 million metric tons per year or 36.6 billion gallons/138 billion liters of methanol annually.



The global methanol market in the foreseeable future will likely be driven by supply and demand in China as China's high-cost, coal-based sources go offline, and by energy-related applications in the transportation sector and the power sector. Methanol is experiencing increased application as a replacement for gasoline in China and around the world.

Demand for fuel oxygenates such as Methyl Tertiary Butyl Ether (MTBE) has increased as has demand for formaldehyde and acetic acid. Other increases in demand appear to be coming from increased use of methanol as a gasoline replacement, as marine fuel and fuel for industrial boilers, cookstoves and kilns, primarily in China, and for biodiesel, and demand for Dimethyl Ether (DME), a liquid fuel similar to Liquefied Petroleum Gas (LPG) has fallen due to low-cost petroleum.

Originally, methanol was produced by destructive distillation of wood; it is now produced largely from natural gas in large, integrated chemical manufacturing plants. In some regions – particularly China – methanol is produced from the gasification of coal. Because of the western world's dependence on hydrocarbon fuels, and manufacture of derivative products, methanol is produced in regions where feedstock is plentiful (Persian Gulf, the Caribbean, South America, Africa, and New Zealand). Methanol is consumed in regions that have a high level of industrial development. By contrast, methanol fuel and fuel additives are in high demand in regions with developing economies. North America, Western Europe, and a handful of Asian countries (Japan, China, Taiwan, and South Korea) consume methanol as chemical feedstock, and in the case of China, as a replacement fuel. These regions manufacture derivative products: formaldehyde, olefins, resins, methylamines, methyl chlorides, silicones, dimethyl terephthlate (DMT), terephthalic acid (TPA), and methyl methacrylates.

Technology for production of methanol will likely continue to evolve throughout this century as feedstocks change, low-pressure and low-temperature catalysts improve, applications for methanol change, and market demand increases. Continued technological improvements are expected in catalyst efficiency and catalyst tolerance of feed stream impurities. Improved catalysts may increase the variety of feed materials that can be used to manufacture methanol, and lower manufacturing process energy requirements.

2.2.2 SUSTAINABLE PRODUCTION

Sustainable production of methanol derives from three specific chemical characteristics:

1. Methanol comprises the widely abundant and almost ubiquitous methyl and hydroxyl groups.
2. Methanol is chemically simple, and is readily synthesized from a variety of carbon-containing materials, through production from some of these materials is more expensive than from others.
3. Methanol is a fundamental building block for a wide variety of useful materials: fuels, glues, plastics, solvents, antifreeze, and others.

In small amounts and low concentrations, methanol is a naturally occurring material. It is a natural byproduct of most bacterial- driven bio-decomposition cycles. Chemical plants have the ability to replicate and accelerate these natural processes. As a result, methanol, or more appropriately, bio-methanol, can be manufactured from natural materials even more easily and efficiently than ethanol, the next-larger alcohol molecule, and from less-expensive non-food- stuff feedstock. For more information on Renewable Methanol, see MI's Renewable Methanol Report here: https://www.methanol.org/wp-content/uploads/2019/01/MethanolReport.pdf

MI MEMBER CARBON RECYLING INTERNATIONAL'S EMISSIONS-TO-LIQUIDS TECHNOLOGY IS THE DIRECT SYNTHESIS OF CARBON DIOXIDE TO METHANOL.

2.2.2.1 RECYCLING

Methanol is an eminently recyclable material. As a solvent, it can be readily separated from contaminates by distillation. Similarly, excess reactant can be recovered at the end of a process, refined, and recycled back into the process.

2.2.2.2 REUSE

Because methanol is a basic building block in a large number of chemically complex materials such as plastics, it can be recovered from these materials by chemically destructive processes, which decompose complex inorganic molecules into their simple components.

2.2.2.3 WASTE MANAGEMENT

Methanol is a commonly used solvent in many organic reactions, and the resulting spent methanol is considered a hazardous waste in the United States. Distillation of the spent solvent to recover methanol for recycling is a standard process. However, some contaminants may be too difficult, hazardous, or expensive to remove. In such cases, spent methanol waste may find use as secondary fuel for energy recovery.

In the future, new processes with new catalysts will be used for recovery of waste organic materials. As with the denitrification application in sewage water treatment plants, described in a subsequent section, methanol will be used to reduce waste from existing processes and reuse waste from other waste streams.

2.3 THE USES OF METHANOL

Methanol markets have changed during the course of the past 20 years as usage and demand patterns are continuing to shift. Evolving global economic, energy, and environmental realities will continue to drive the methanol market in the foreseeable future. During the first quarter of 2008, crude oil prices spiked over $140 U.S. per barrel. At the same time, natural gas (methane) prices (in the United States in particular) lagged behind crude oil prices. Use of food crops to produce ethanol fuel has been blamed in part for driving supply and demand of staple food items. These circumstances provided an increased incentive to use methanol as a replacement for ethanol as a direct additive to motor fuel to reduce air emissions, and perhaps eventually as an alternate for gasoline in automobiles. While crude oil prices are currently at lower levels, the cyclical nature of the global oil market means higher prices are likely to return in the future.

Other new fuel/energy applications for methanol are emerging, such as marine fuel applications, diesel substitution, methanol-fueled turbine engines, biodiesel, and direct methanol fuel cells. In addition, applications, such as wastewater treatment, are using increasing quantities of methanol for denitrification.

Currently, formaldehyde manufacture accounts for about 34% of methanol demand for production of urea-formaldehyde and phenol-formaldehyde resins, glues, and adhesives. These are used extensively as bonding agents in particleboard, plywood, and fibrous wood panels. At present, the distribution of methanol demand is changing radically. This is expected to continue during the next decade as a greater percentage of methanol production is used for energy applications.

2.3.1 CHEMICAL INTERMEDIATES

Methanol is a basic building block for chemical synthesis and is, therefore, the starting point for primary, secondary, and tertiary derivatives. Formaldehyde is the primary product, followed by acetic acid. Figure 2 summarizes the role of methanol in the production of intermediate chemical feedstock.

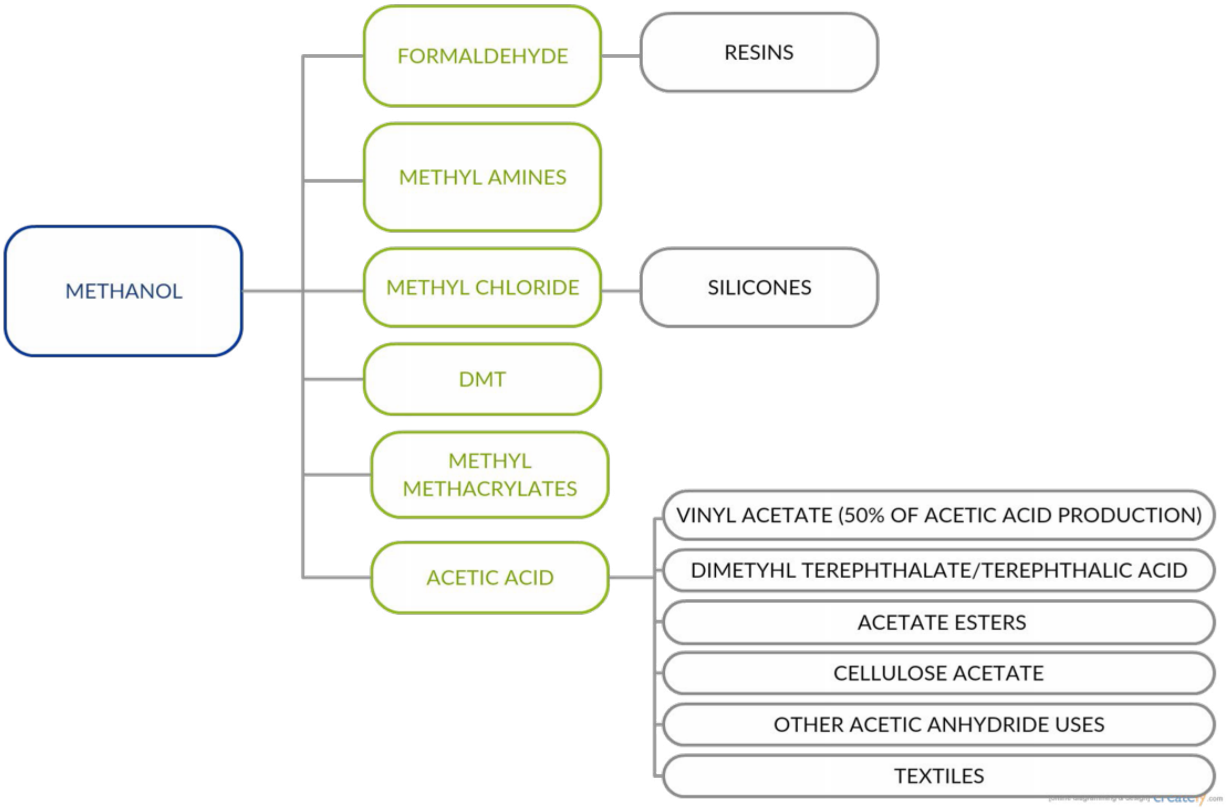
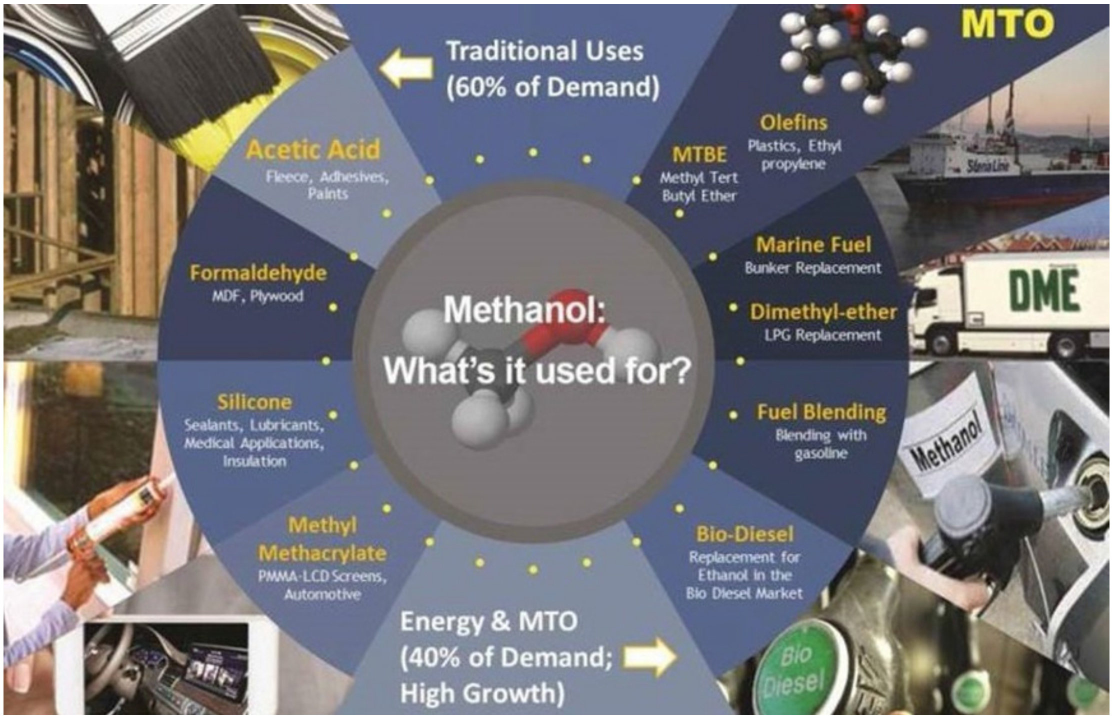


Figure 2. Methanol as Intermediate Chemical Feedstock

2.3.2 FUEL APPLICATIONS

Supplementing and eventually replacing conventional motor fuels with methanol received widespread attention during the spikes in crude oil prices of the 1970s. In the 1980s, interest was again generated in alternate sources of energy and specifically in alternate motor fuels.



Methanol was recognized at that time as a potential replacement for crude-oil-derived gasoline. During the intervening years between the 1970 and the 2010 price spike, various agencies and organizations have assessed the hazards, challenges, and benefits of using methanol as a motor fuel. A study by the United States Environmental Protection Agency (EPA) [63] concludes that methanol is a safer motor fuel than gasoline. Other studies have concluded that hazards posed by the motoring public's use of methanol are greater than those of gasoline. An important factor often not considered in the discussion is the proportion of methanol used in a fuel blend. Most current blends envisioned for vehicle fuel range from 5-15% up to 100% pure methanol. As methanol becomes widely available as a motor fuel.

The question of public safety when using methanol as a vehicle fuel centers on its potential for causing vehicle fires, as compared to gasoline.

According to a National Fire Protection Association (NFPA) study [43], the incidence of vehicle fires in the United States has decreased by 45% between 1980 and 2006 to the lowest level in 20 years. Vehicle fires were identified as being responsible for 15% of all civilian deaths and 12% of all property losses. Interestingly, only 3% of vehicle fires involved collisions, which accounted for over half the deaths. Over half of the fires were due to vehicle component failure, such as fuel system leaks, loose wiring connections, or cracked insulation. The type of fuel is not the main factor in vehicle fire incidence. Proper vehicle maintenance is the best prevention against a fire, according to the NFPA.

Methanol, used as an automotive fuel, has multiple desirable safety features:

- Methanol flame is low temperature and non-luminous; therefore, methanol fires generate substantially less radiant heat than gasoline fires, which have higher flame temperatures and burn with luminous flames. In fact, the U.S. EPA has estimated that if all our cars were fueled with methanol, the incidence of vehicle fires would be reduced by 90%, saving hundreds of lives per year.
- Because of low-radiant heat generation, methanol fires spread more slowly than gasoline fires. Likewise, allowable approach distance is closer, so portable extinguishers can be used more effectively to quench the fire. When using a portable extinguisher, it is necessary to aim at the base of the flames, not at the flames themselves.
- The concentration of methanol in air necessary for combustion is approximately four times greater than that for gasoline. Coincidentally, the vapor pressure of methanol at a specified temperature is lower. At a predetermined temperature, methanol releases less vapor than gasoline. In other works, methanol must be raised to a higher temperature in order to generate vapor concentrations (>6 v%) necessary to support combustion in air.
- Methanol vapor is near neutral buoyancy; therefore, vapors are more likely to dissipate and less likely to flow along the ground and accumulate in low-lying areas than those of gasoline. Nevertheless, methanol vapor is reported to sometimes accumulate in low-lying areas.
- Large methanol pool fires are best extinguished with alcohol- resistant foam; however, small fires can be extinguished with portable extinguishers and/or water spray, provided the volume of water is at least 4 (and preferably 5) times the volume of the methanol pool. Secondary containment must be capable of holding a volume 4-5 times larger than that of the methanol pool.

These considerations also apply to normal transportation modes and especially to automobile fires. In fleeing from an automobile gasoline fire, the factors of time to escape, temperature, safe standoff distance, rate of fire propagation, and ease of flame suppression are critical life safety considerations. This is particularly true of methanol/gasoline-blended fuels. Considerations for tank farms and fuel terminals need to be even more detailed.

The driving public may elect to use methanol and/or methanol blends as alternatives to gasoline. This change is anticipated to have both pros and cons. An anticipated benefit is that driver-occupant safety will be increased. Another potential benefit is that of reducing the already low likelihood of fuel station fires. A disadvantage is that the complexity of responding to tanker truck, rail tanker, and fuel distribution facility fires will increase. Responders must be better trained, better managed, and equipped with equipment such as Alcohol-resistant Aqueous Film Foam (AR-AFFF) foam, which is not available in all circumstances.

A recent study [49] identifies a fundamental driving force for making the change from gasoline to methanol as the abundance of and variety of sources for obtaining methane gas. One difficulty in making this transition is the high energy necessary to generate hydrogen gas required for methanol synthesis using existing technology. The technical feasibility of using methanol as a fuel was addressed by the Methanol Conversion Group [67]. A general finding is that direct substitution of methanol for gasoline is technically feasible.

Should the world crude oil supply-demand situation, or regulatory actions requiring greater vehicle efficiency require substantial changes in fuel consumption, fuel formulation, and vehicle design and operation. Methanol will likely be an important factor in that change, placing greater responsibility for acceptable standards of product stewardship on methanol transporters, handlers, and users.

2.3.3 BIODIESEL FUEL PRODUCTION

Biodiesel is diesel fuel that has been sourced from biodegradable materials, specifically vegetable waste, or rendered oils, rather than from petroleum distillate. There are many reasons for making biodiesel, which range from saving money to "going green." Biodiesel allows recycling of waste material and replacing a consumable resource with a renewable resource. It also diversifies the fuel supply base away from solely petroleum-based fuels. Regardless of the motivation, biodiesel production involves using neat (100% pure) alcohol, typically either methanol or ethanol.

Biodiesel is made by reacting vegetable oils and animal fat[4] with pure methanol or 200-proof ethanol in the presence of a sodium or potassium hydroxide catalyst. The chemical process is called transesterification. The objective is to convert fat molecules in the oils into an ester, biodiesel, and the remainder into glycerol, a byproduct that can be processed to make soap, or disposed of as waste, depending on circumstances. Once dried, glycerol can also be burned as fuel or potentially used as an additive in livestock feed.

When methanol is used to process bio-waste material into biodiesel, it produces a hydrocarbon fuel with properties similar to diesel fuel. Conversion can be accomplished on scales that range from 30-gallon capacity trash-can-sized batches, to continuous processes operated intermittently, to continuously operated plants with capacities ranging from 4 million to 100 million gallons (15000 to 378000 cubic meters) per year. Typically, people using methanol to produce biodiesel in small-scale batch applications are not trained chemists. Operators are likely unaware of the hazards and regulatory compliance necessary to manufacture fuel safely and legally. These individuals may not be trained or experienced in handling concentrated hazardous chemicals such as

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[4] Emphasis is placed on using vegetable oils because animal fat spoils. Spoilage, in addtion to being unpleasant, reduces the yield of the conversion process.

lye (sodium/ potassium hydroxide, Na/KOH) and methanol.

Operators of intermittently operated continuous processes will likely be familiar with precautions and laws that accompany production of biodiesel, but they may or may not have the proper equipment and procedures and training necessary for self-protection and efficient chemical handling.

Small-scale operators of continuous processes likely have access to people trained in chemistry and chemical safety and are likely interfacing with regulatory agencies regarding health and safety regulations, process safety, chemical reporting, and waste disposal.

Waste oil is acidic. A mixture of sodium/potassium hydroxide is added to nearly pure methanol and mixed until conversion to sodium/potassium-methoxide, a very strong base, is complete. The methoxide is then reacted with additional methanol and the vegetable or waste oil in a reactor until esterification is complete. At this point, the reactor will contain two raw products: a light-colored upper layer of methyl esters floating on top of a heavier and darker glycerol product. Reaction products are separated by either decanting the biodiesel away from the glycerol, or draining the glycerol away from the methyl esters.

Approximately 30% by volume of the original methanol reactant remains un-reacted and can be recovered by vacuum distillation and recycled. After distillation, the biodiesel is water-washed, separated from the wash water, and finally dried to obtain the finished biodiesel product.

A variety of precautions must be observed:

- Methanol must be stored in a dedicated location, where it is protected from heat and ignition sources. All electrical systems must be fully enclosed and explosion proof. In order to prevent the methanol from absorbing moisture, it must be stored in a sealed container. If the container is sealed, there should be an allowance for thermal expansion; otherwise, large changes in temperature may cause the methanol to expand and rupture the container.

- Methanol must be stored in a bermed, diked or bunded, well-ventilated area, which, if designed in accordance with NFPA 30 [45], shall be capable of containing at least 110% of the volume of the largest methanol storage tank in the contained area. Best practice dictates considerably more than 110%. Following a leak inside the containment area, the resulting methanol pool should be completely covered with alcohol-resistant foam. If the containment area is adequately sized, the methanol spill can be diluted with at least four parts water to one-part methanol to reduce the risk of fire. Insufficient freeboard within the bermed area can result in overflow of the berm and a so-called "running fire." Running fires are difficult to control.

- It is desirable to preheat the waste oil prior to reaction with methoxide. This must be done carefully to prevent oil spattering and accidental ignition when the methanol hydroxide reactant is added.

- Care must be taken in handling methanol, adding hydroxide, mixing hydroxide, and then introducing the methoxide into the waste oil.

- Temperature control throughout the process is critical to safe and efficient operation. If the temperature rises too high, and agitation is too vigorous, then fire and/or explosion are possible. If the temperature is too low and agitation too gentle, then the reaction will not go to completion.

- The potential for spills is consistent throughout the process. A closed reactor, whether batch or continuous, is preferable to a reactor that is open to the atmosphere.

2.4 EMERGING USES OF METHANOL

Previously mentioned applications account for most of the world's current methanol consumption. Methanol's use is anticipated to increase due to new applications in emerging technologies and increased demand in developing and developed countries during the 2016 to 2020 time frame.

Five of these new uses are discussed here:

1. De-nitrification of wastewater treatment plant organic-laden effluent.
2. Fuel in methanol-fired turbine engines.
3. Fuel in direct and reformed methanol fuel cells.
4. Natural gas hydrate inhibition and mitigation in intermediate and deep water offshore hydrocarbon production.
5. Marine Fuel Applications.

As regulations increasing road transport vehicle efficiency, and reducing pollutants such as SOx, NOx and Particulate Matter (PM) in marine environments, come into force, it is likely that additional pressure will be placed on developing alternate modes of transportation and power sources, including fuel cells, methanol-fired turbine engines and methanol fueled marine powerplants.

2.4.1 WASTEWATER DENITRIFICATION

Wastewater effluent from municipal waste treatment plants characteristically contains high levels of nitrogen in the form of nitrates and ammoniated compounds (NH3 – anhydrous ammonia, NH4OH – ammonium hydroxide, etc.). Nitrogen is an excellent fertilizer, which enhances plant growth in soils and water. Overactive plant growth may damage ecosystems if the effluent is released into natural waters, such as streams, rivers, lakes, and even the ocean. Methanol denitrification is a simple, effective, and comparatively inexpensive method of removing excess nitrogen and inhibiting plant growth.

In the broadest sense, denitrification is removal of nitrogen and nitrogen compounds from soil and water media. The intent is to reduce the amount of fertilizer available to plant life, and thereby slow the growth rate of algae. This is necessary in circumstances in which a body of water is receiving a combination of excess organic and nitrogen nutrients. In this situation, plant growth may become excessive to the point of depleting dissolved oxygen below the threshold concentration necessary to support water column ecology. The environmental effects may be devastating.

Denitrification is a natural process, which occurs within surface water, ground water, and near surface soils. Within the context of wastewater effluent conditioning, denitrification is a liquid phase biochemical reduction reaction which is facilitated by the presence of methanol. Under anaerobic (oxygen free) conditions, microorganisms such as bacteria convert nitrogen-containing compounds, (for example, ammonium (NH4-), ammonia (NH3), nitrates (NO3-1), nitrites (NO2-1), and proteinaceous organic nitrogen) into elemental nitrogen (N2). The overall chemical reaction is

$$6\ NO3^{-1} + 5\ CH_3OH_{(l)}\ 4\ \ 5\ CO_{2(g)} + 3\ N_{2(g)} + 7\ H_2O_{(l)} + 6\ OH^{-1}_{(l)}.$$

Elemental nitrogen atoms combine and form a gas (N2(g)) which escapes into the atmosphere, thereby reducing availability of nitrogen within the wastewater discharge. Limiting the amount of nitrogen available as fertilizer slows down plant growth. Oxygen uptake likewise decreases, and dissolved oxygen becomes more available throughout the water column.

If the effluent is left untreated, the contained organic material combines with oxygen, thereby depleting dissolved oxygen within the natural waters that receive the effluent. Without sufficient oxygen, aquatic animal life suffocates and dies. In short, methanol is added to wastewater plant effluent to preserve wildlife ecology and protect the environment.

The metabolic energy necessary for microorganisms to break the nitrogen-oxygen chemical bond can be obtained from a carbon-containing biodegradable substrate material, such as methanol, or from dissolved oxygen (O2(g)). By forcing anoxic conditions, the reduction conversion reaction is forced to occur at the nitrogen-oxygen bond, rather than the oxygen-oxygen bond, thus purging nitrogen and preserving oxygen within the system.

Presence of excessive quantities of nitrogen compounds enhances growth of algae and other water plants, and essentially cokes even large bodies of water with nitrogen-fertilized plant material. The issue of excessive plant growth upsetting waterway ecology can become so severe, even in large bodies of water, that waste treatment plant effluent is a U.S. Environmental Protection Agency (EPA) regulated discharge. Addition of methanol, a water-soluble biodegradable liquid, at process plant denitrifying filters, can provide a well-dispersed form of solubilized carbon, which is used by a host of organisms to denitrify the effluent. Hundreds of waste treatment plants are currently using denitrification to meet increasingly stringent EPA regulatory limits for nitrogen in waste treatment plant effluent with excellent results. This can be done at significantly lower cost than some alternative technologies.

There are over 150 existing major wastewater treatment plants (over 1 million gallons per day flow) designed for use of methanol in the United States. One of these, the Blue Plains Wastewater Treatment Facility in Washington D.C., has been able to reduce the amount of nitrates entering Chesapeake Bay from 20 tons per day to 10 tons per day, with a resulting 30% decrease in nitrogen levels within the Bay. This has been accomplished at a cost of U.S. $0.50 to $0.60 per pound of nitrogen removed, which is 12% of previously reported costs.

2.4.2 METHANOL FUEL CELLS

At present, there are about a dozen fuel cell technologies. Direct and reformed methanol fuel cells are discussed here because they constitute technologies that uses methanol as fuel. (2.3.2-1 to 2.3.2-5)

Fuel cells use hydrogen as a fuel to produce clean and efficient electricity that can power cars, trucks, buses, ships, cell phone towers, homes and businesses. Methanol is an excellent hydrogen carrier fuel, packing more hydrogen in this simple alcohol molecule than can be found in liquefied hydrogen.

Methanol can be "reformed" on-site at a fueling station to generate hydrogen for fuel cell cars, or in stationary power units feeding fuel cells for primary of back-up power. On-board reformer technology can be used on fuel cell vehicles, allowing quick 3-minute fueling and extended range (from 200 km with hydrogen to 800 km on methanol).

As a simple molecule with no carbon-to-carbon bonds, Direct Methanol Fuel Cells can be used for some applications, where methanol reacts directly on the fuel cell's anode to strip hydrogen atoms to fuel DMFC systems.

Direct methanol fuel cells are electrochemical cells, which produce electricity and function somewhat like conventional lead acid car batteries, but with exotic catalysts, special materials, advanced technology, and slightly elevated temperature and pressure operating conditions.

Direct methanol fuel cells function in a manner similar to, but distinct from, that of a lead acid battery. They use a polymer membrane instead of an aqueous electrolyte. The membrane serves the purpose of an electrolyte and transfers hydrogen ions (H+) or protons, produced at the anode to the surface of the cathode. In direct methanol fuel cells, hydrogen ions are generated by direct oxidation of methanol (CH3OH) at a catalyzed anode. The oxidation reaction generates hydrogen ions, which diffuse through the membrane to the cathode. Electrons from the anodic oxidation reaction circulate through an external electrical circuit as current, and carbon dioxide (CO2) is generated at the anode as a gaseous waste product.

Oxidation-reduction reactions necessary to generate hydrogen ions at the anode and water at the cathode occur in the vapor or liquid phase, depending on cell design. A mixture of steam and methanol is injected under pressure and at elevated temperature into the anode compartment. An anode with a highly specialized catalytic coating enhances the kinetics of a direct chemical reaction, which breaks the carbon-hydrogen bonds of methanol molecules into hydrogen ions, and re-combines carbon with oxygen in the form of carbon dioxide (CO). A solid polymer membrane transports hydrogen ions generated at the anode to the cathode. The cathode, also a pressurized gas chamber, contains compressed air. Oxygen within the air reacts with the hydrogen ions on the catalyzed surface of the cathode to complete the reduction portion of the reaction by forming water vapor. Using highly advanced catalyst and polymer materials a direct methanol fuel cell essentially burns methanol at the anode and reduces hydrogen ions at the cathode, generating an electrical current and forming carbon dioxide and water vapor.

Anode (Methanol) noble metal catalyzed oxidation rxn:	$CH_3OH+H_2O\text{ (steam) }4\ CO_2+6H^++6e^-$
	↓
Polymer Electrolyte conveys H^+ (Protons) from anode to cathode:	$6H^+$
	↓
Cathode (Oxygen as Air) reduction rxn:	$6H^++3/2O_2+6e^-\ 4\ 3H_2O$

Methanol fuel is an easily handled liquid, and the products of the oxidation-reduction reaction are water and carbon dixoide absent NOx and SOx contaminants.

Operating temperature is between 60-130°C with a typical operating temperature near 120°C. Operating pressure may be somewhat elevated and may be manipulated to achieve optimum performance for a given set of conditions. Operating efficiency is expected to approach 40%.

Direct methanol fuel cells are an outgrowth of indirect fuel cells, which use hydrogen (H2) as the fuel rather than methanol. Direct methanol cells provide several advantages compared to indirect fuel cells. In direct methanol fuel cells, the fuel is liquid and easily stored and transferred. In indirect fuel cells, hydrogen is used directly or is generated by chemical stream reforming. Storage of hydrogen gas is difficult and potentially hazardous; addition of a steam reformer increases the complexity of the cell.

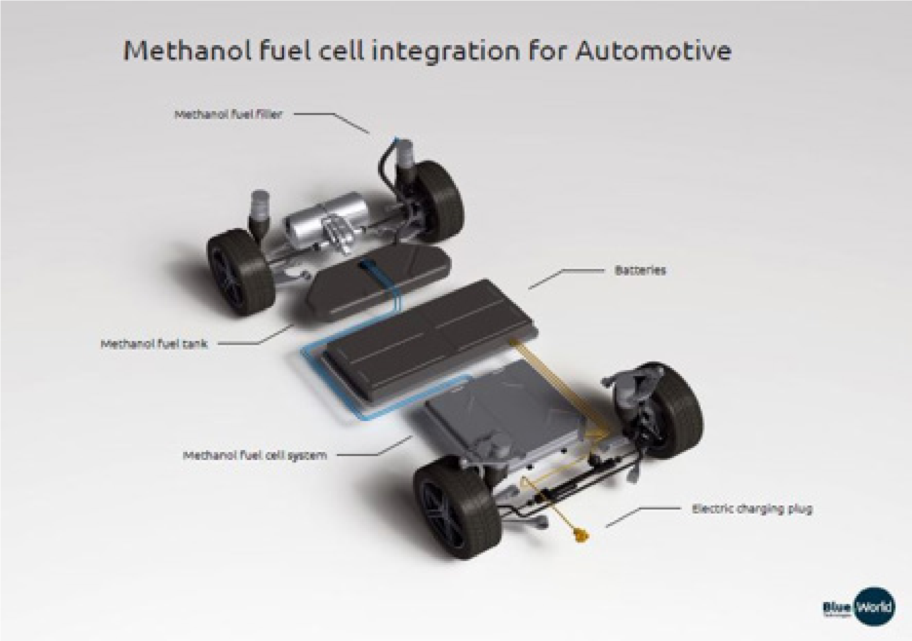
Direct methanol fuel cells and indirect cells are essentially the same, except that methanol substitutes for hydrogen as a source of protons, and the anode of the direct methanol fuel cell is a noble metal catalyst. Both types of cells have a polymer membrane that transfers protons from the anode to the cathode, and both produce water as a waste material. Both cells also generate an electrical current by an oxidation reaction which occurs at the anode. The cathode side of the fuel cell consists of air (21 v% oxygen and 79 v% nitrogen). Hydrogen ions diffuse through an electrolytic proton membrane and react with oxygen in the air at the cathode to form water.

Current configurations emphasize a modular approach in which fuel cell components and entire fuel cells are easily exchanged, and stacking multiple units satisfies power needs. An application that appears to be growing in popularity is using direct methanol fuel cells to charge batteries, which in turn power electronic equipment. This approach is being tested by the military for field operation of electronics, and by Toshiba for personal electronics such as cell phones, smart phones, laptop computers, and other portable electronic items.

Manufacturers are developing modularized component-based configurations, which can be exchanged to replenish various cell components as they become depleted or wear out.

The International Civil Aviation Organization has approved use of DMCs to power passenger personal devices, such as laptop computers, while on- board airplanes. Several development companies have direct methanol fuel cells commercial productions at this time.

Hurdles to even more widespread commercialization appear to be methanol crossover from the anode to the cathode, and the catalytic activity of the anode and cathode surface materials. Crossover has two deleterious effects on cell performance. The first is polarization of the cathode, which reduces effective voltage; the second is loss of fuel resulting in reduced power capacity. A better understanding of the various factors such as pressure of oxygen on the cathode side of the cell is ongoing and appears to be creating more favorable results.



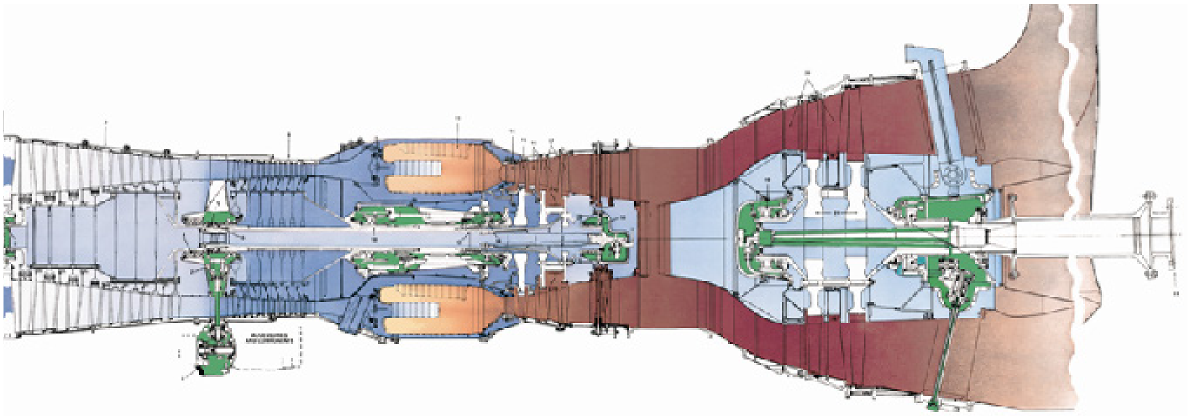
One of the more exciting applications of fuel cell technology may be replacement of batteries in hybrid automobiles. Regardless of whether this is done with direct or indirect methanol fuel cells, methanol provides the advantage that a fully electric, a hybrid, or an engine-powered vehicle could use a single fuel to power the engine and the motor. Refueling would be similar to that for gasoline, and would serve for all types of automobiles.

2.4.3 TURBINE ENGINES

Stationary turbines are typically fueled with natural gas or distillate jet fuel, both of which are products refined from crude oil. These fuels contain sulfur and nitrogen, which cause air quality compliance issues. Air quality within the United States is regulated by the EPA under auspices of local air quality management districts.

Within the United States, nitrogen and sulfur oxides (NOx and SOx) emissions from fixed sources are monitored and strictly regulated to control air quality. The cost and operating restrictions forced by these regulations are considerable. Industries that use substantial amounts of direct-fired equipment, such as heaters, furnaces, and boilers, have incentive to find alternate ways of obtaining process heat and electrical power without incurring penalties associated with fuel contaminates and polluting oxides.

Low NOx burners and air monitoring systems have been retrofitted to most furnaces, heaters, and boilers within the United States. Low NOx burners may pose a safety hazard if the replacement burners are upsized to increase heating capacity of direct-fired equipment.



Turbine users and manufacturers began investigating combustion technology, which could replace natural gas and distillate fuels with methanol, as early as 1971. Methanol contains no sulfur or nitrogen and burns at a lower temperature, thereby substantially improving stack gas air quality.

Air monitoring requirements for methanol-fueled turbines are less than those for natural gas and distillate fueled turbines. Air quality control has become an increasingly expensive operating issue as air quality standards have become increasingly more stringent.

There are multiple disadvantages of firing with refined hydrocarbon fuels: capital cost of monitoring equipment, increased operating cost, cost of uncertainty and penalties associated with non-compliance, shortened mean time between failures and associated increased maintenance cost, shortened life of turbine components, and increased lifetime cost associated with system unavailability. Taken together, methanol may have significant economic and operating advantages over conventional fuels.

There are technical and economic considerations in switching from natural gas or distillate to methanol. These considerations are much the same as those associated with substituting methanol for gasoline in internal combustion engines. Some considerations have been successfully resolved for automobiles, which presumably can likewise be resolved for turbine service.

As evidence of this, GE has published written indication that the use of methanol as a turbine fuel is feasible and, in fact, offers some advantage over using natural gas and distillate fuels.

The principal technical considerations are discussed below.

- Methanol has a low heating value compared to natural gas and currently used distillate turbine fuels. A greater volume of methanol must be combusted in order to produce the same base load output (brake horsepower) as that of natural gas or distillate fuel. Turbine fuel storage, and transfer and combustion systems may need to be modified to accommodate appropriately larger fuel volume. Testing indicates that turbine operability and performance with methanol fuel is equivalent to that of natural gas and distillate; air quality is superior.

- Methanol has low lubricity. Distillate has inherent lubricity because of the nature of the carbon-hydrogen molecules that comprise the fuel and the presence of small amounts of sulfur. Testing is in progress on additives that will increase methanol lubricity.

- Methanol has a low flash point (very low vapor pressure at low temperature), which affects cold weather starting and operation and the need for explosion safeguards. Cold weather starting issues can be circumvented by starting up with conventional fuels. The explosion issue requires modification of engine configuration. Testing is being done for several methods of resolving the explosion issue.

- Methanol liquid is electrically conductive compared to natural gas and distilled fuels. Conductivity increases corrosion of alloys commonly used to handle natural gas and distillate fuel. This is particularly true for aluminum and titanium alloys. Additives are being tested to inhibit corrosion. Alternatively, commonly used materials may be replaced with more corrosion-resistant materials. Aluminum and titanium alloys should not be used in methanol or methanol vapor service without a rigorous mechanical integrity program.

- Methanol is a solvent, which attacks some plastics, resins, and fiberglass compounds. A variety of compatible materials are available to replace incompatible materials. Special care must be taken in selection and storage of gaskets, "O" rings, and other parts that prevent leakage.

- Methanol absorbs water from the atmosphere. Unlike gasoline, neat methanol and gasoline-methanol blend fuels absorb moisture from the air. Moisture absorbed by neat methanol is fully miscible, and is retained as a single phase that does not affect combustion. Moisture absorbed by gasoline- methanol blends forms an immiscible phase, which sinks, thereby accumulating in the bottom of tanks and piping low spots. If the amount of water is small, presence of an immiscible phase has little or no effect on the combustion properties of the blended fuel. Large amounts of water-phase material interfere with combustion, and in extreme circumstances may result in flameout.

2.4.4 OFFSHORE PLATFORMS

Wellhead crude and natural gas products consist of a mixture of hydrocarbon and water. The water is derived from down-hole hydrocarbon bearing strata. So-called "Produced Water" is water consisting of formation water, injection water, and condensed water vapor. It also includes trace amounts of chemical additives, which perform a variety of functions, such as inhibiting hydrate formation, capturing water vapor, preventing scale formation, controlling corrosion, preventing bacteria growth, breaking and coagulating oil water emulsions, preventing foaming, and removing deposited paraffin. Hydrate and dehydration additives are used primarily in production of natural gas; however, they are also used in crude production when hydrocarbon is accompanied by large amounts of associated gas and water.

In general, the amount of produced water increases throughout the life of a well, and the amount of hydrocarbon decreases. In this circumstance, the likelihood of hydrate formation increases, and risks associated with hydrates increase, as wellhead yield becomes less. As a result, gas wells are usually shut down at the onset of substantial amounts of water. Effective use of methanol can reduce hydrate risk, thereby extending well production life. This is typically an economic decision based on the break-even point of product revenue and the cost of hydrocarbon production, including increased amounts of methanol inhibitor.

Costs associated with treatment of produced water are a small percentage of the overall cost of natural gas production. However, incorrect or inadequate treatment may compromise equipment performance, thereby increasing operating cost. Likewise, mean time between equipment failure is decreased by exposure to untreated wellhead product, with resulting increases in maintenance cost and shortening of equipment service life. The above is particularly relevant to formation of natural gas hydrate or clathrate in subsea natural gas piping, valves, and equipment.

Methane hydrate, methane clathrate, hydro-methane, methane ice, "fire ice," and natural gas hydrate are synonyms for a solid clathrate compound that traps a large amount of methane within its crystal structure of frozen water, thereby forming a porous ice-like solid.

A typical composition of methane clathrate hydrate is 1 mole of methane for every 5.75 moles of water at an observed density of 0.9 g/cm3. One liter of methane clathrate contains 168 liters of methane gas at standard temperature and pressure. Clathrates contain sufficient amounts of methane to ignite and burn in air, hence the name "fire ice."

At high pressure and moderate temperature, hydrate forms a solid which adheres to the inside surfaces of piping and equipment. If hydrate formation is not mitigated, then undersea gathering lines and flow transfer lines may plug and interrupt fluid flow. Chunks of hydrate that break away from pipe walls may mobilize in the fluid stream thereby interfering with production, damaging equipment, and in extreme cases causing catastrophic piping failure.

Piping failure may necessitate blocking in the wellhead, loss of product, and release of hydrocarbon directly into the water column.

Hydrate formation can be controlled mechanically with thermal insulation and heat tracing to avoid temperature conditions necessary for hydrate formation, and by chemical means where the freezing point is lowered below minimum operating temperature.

Chemical hydrate inhibitors serve the same function as antifreeze in an automobile engine cooling system. Addition of ethylene glycol (and more commonly methanol) at the wellhead and, in some cases, in the well lowers the freezing temperature of water, thereby preventing formation of the clathrate structure. Methanol is most frequently the preferred additive due to the higher cost of ethylene glycol. About half as much ethylene glycol is required to achieve the same level of protection as that provided by methanol. Ethylene glycol remains in the produced water, which facilitates recovery and reuse. About half of the methanol additive vaporizes to the gas phase and is non-recoverable; the other half of the methanol remains dissolved in the produced water, which facilitates recovery and recycling.

Except in warm shallow water, offshore production of natural gas requires use of either methanol or ethylene glycol to avoid hydrate formation. Methanol is being used extensively in Gulf Coast intermediate and deep-water production, where flow pressures may be high and temperatures low.

2.4.5 MARINE FUEL

The global shipping industry is facing increasingly stringent emissions requirements. Starting January 2020, the new Marpol Annex VI fuel regulation came into effect in the maritime industry. The regulation caps the sulphur content in bunker fuel to 0.5% for all commercial shipping vessels, down from the previous 3.5% (except for Emission Control Areas). The new limit, agreed in October 2016, represents an ongoing effort of the International Maritime Organization to protect the environment and reduce air pollution.

In 2018, the shipping industry used about 3.5 million barrels of high sulphur residual fuel (sulphur content >0.5%) per day, accounting for approximately half of global demand. Under the 2020 regulation, marine vessels either need to install exhaust gas cleaning systems (known as scrubbers) or switch to low sulphur distillate fuels, low sulphur fuel oils, or alternative fuels such as methanol or LNG.

For the existing fleet of some 100,000 commercial vessels plying the world's oceans, and the 2,000 new keels laid each year, the option of adding dual-fuel capability for diesel-LNG (liquefied natural gas) or diesel-methanol is increasingly seen as the smart course. While there are already some 50-60 ships ready to use LNG as a bunker fuel, interest in the use of methanol fuel, as a considerably less expensive alternative to LNG, is quickly gaining speed, as new build dual-fuel methanol tankers enter service.

- Methanol is plentiful, available globally and could be 100% renewable - There are over 75 million tons of methanol being produced annually, and depending on the feedstock used in its production, it can be 100% renewable as well.

- Current bunkering infrastructure needs only minor modifications to handle methanol - Methanol is very similar to current marine fuels such as heavy fuel oil (HFO) as it is also a liquid. Existing storage, distribution and bunkering infrastructure can handle methanol with only minor modifications necessary due to methanol being a low-flashpoint fuel.

- Infrastructure costs are modest compared to alternative solutions - Installation costs of a small methanol bunkering unit have been estimated at around € 400,000, and a bunker vessel can be converted for approximately € 1.5 million. In contrast, an LNG terminal costs approximately € 50 million, and an LNG bunker barge 30 million.

- Conversion costs will drop dramatically as experience mounts - The main reference point on conversion costs comes from conversion of the Stena Germanica. Being the first of its kind, the Stena Germanica retrofit entailed much design work on new technical solutions, safety assessments and adaptation of rules and regulations. It has been estimated that a second retrofit will cost only 30% to 40% of the Stena Germanica conversion.

- Current engines have performed well on methanol and upcoming technologies will further improve this performance - Thus far, methanol ships have been powered by diesel engines modified to run on both methanol and marine diesel. Converted methanol engines have performed as well as, or better than, diesel engines in both field and lab tests. Methanol-optimized engines currently in development are expected to perform even better than the current converted engines.

- Shipping and chemical industries have a long history and ample experience in handling methanol safely - has been shipped globally, and handled and used in a variety of applications for more than 100 years. From a health and safety perspective, the chemical and shipping industries have developed tested procedures to handle methanol safely. These have been codified in the Methanol Safe Handling and Safe Berthing Bulletin and Checklists available on MI's website. MI's Methanol as a Marine Fuel Report can also be viewed on the website.

- Methanol is biodegradable - From an environmental point of view, methanol performs well. Methanol dissolves rapidly in water and is biodegraded rapidly. In practice, this means that the environmental effects of a large spill would be much lower than from an equivalent oil spill.

2.4.6 METHANOL SPECIFICATIONS

Additional information and specifications for methanol are available on the Internet at the International Methanol Producers and Consumers Association (IMPCA).

3 TRANSPORTATION AND STORAGE OF METHANOL

This chapter summarizes the safety issues related to methanol storage and transportation from manufacturing centers to end users.

3.1 METHANOL TRANSPORTATION

Geography and demographics of the methanol market require heavy reliance on transportation in order to move methanol product from manufacturers to consumers. Methanol is manufactured in several regions of the world and used in other, separate regions. Lack of proximity between manufacturing and use requires that as much as 80% of the world's annual methanol production is transported between continents. The safety, reliability, and integrity of trans- ocean shipping, dockside transfer, and marine terminal storage constitute a large portion of the potential loss exposure resulting from accidental and unmitigated release that is borne by the methanol industry.

Process safety management (PSM) is typically applied to chemical manufacturing and processing facilities. However, PSM practices can (and, some might argue, should) be used to safely manage methanol transportation and distribution activities as well. PSM is described in detail in Chapter 5 of this manual.

3.1.1 OCEAN-GOING TRANSPORT

Methanol is pumped from dockside storage tanks into sealed cargo holds of tanker ships. Delivery to dockside storage may be by pipeline, barge, rail, or truck.

Trans-oceanic transport is similar to that for other hydrocarbon liquids, such as crude oil, gasoline, diesel, and fuel additives such as MTBE. Double-hulled vessels are commonly used by shippers, and will likely become the standard as world production increases. Special provisions for tanker shipment are: cleanliness (to prevent contaminating the methanol), methanol leak detection, appropriate firefighting equipment (including alcohol-resistant foams) and pump, piping, hose, and gasket materials that are suitable for methanol service.

Accidental releases into open ocean are to be avoided, but are considered to pose less of a threat to the environment than crude oil, bunker fuel, gasoline, or diesel fuels. Solubilization of pure (100%) methanol in water is rapid and complete. The accompanying dilution reduces methanol concentrations to a level that is nontoxic to marine life in less than one mile, even for large catastrophic releases. More safety information is available through MI's MI's Methanol Safe Berthing Technical Bulletin & Checklist.

3.1.2 RAIL TRANSPORT

Precautions for rail transport are much the same as those for ethanol, gasoline, MTBE, jet fuel (kerosene), and distillate. This includes grounding for protection against static discharge.

Specially designed tanker cars are equipped with provisions for pressure relief in order to accommodate thermal expansion during transit and short-term (less than 30 days) side-lining during switching and temporary holding. Rail transport is considered to be safe, as long as methanol is contained within an upright tanker car.

In the event of derailment, first responders should treat methanol as highly flammable and highly toxic. The 2016 edition of the Emergency Response Guidebook (ERG2016) [19] recommends an immediate isolation distance of 150 feet (50 meters) in all directions. So-called "running fires" may be expected with large-volume releases. Flashback can be expected. Running fires are particularly hazardous if allowed to flow into sewers and drains. In the event of accidental release as a result of derailment or some other circumstance that compromises containment, ERG2016 recommends that responders isolate and consider evacuating in all directions from the release to a radial distance of one-half mile (800 meters).

Methanol tanker cars are known to BLEVE (Boiling Liquid Expanding Vapor Explosion, an instantaneous tank failure and catastrophic release and ignition of vapor) when involved in flames and/or when subject to high radiant heat flux.

3.1.3 TANKER TRUCK TRANSPORT

Comments relating to rail tank cars apply equally for tankers attached to tractor haul trucks and for tank trailers towed by tractor haul trucks. Methanol transport by truck haulage is subject to substantially the same precautions as are routinely exercised for gasoline transport.

3.2 METHANOL STORAGE

Storage of methanol is subject to substantially the same provisions as those used for gasoline storage. Methanol is routinely stored in tank farms consisting of above-ground, floating roof tanks and smaller, internally baffled floating baffle tanks. Tanks must be grounded to avoid hazards associated with static discharge. Ignition control may be by nitrogen padding, natural gas padding, or by designation of a hazard zone with ignition control.

Because methanol is commonly stored with other solvents and feed stocks, all piping and valves subject to carrying methanol should be consistently labeled, and direction of flow should be indicated. All storage materials, including totes and drums, require berming and adequate ventilation. Berming should be stabilized by compacting, by use of suitable methanol resistant fabric, or with concrete. Because of the solvent properties of methanol, hydrocarbon residuum, asphalt, and road oil are not suitable as berm cover/stabilization materials.

Methanol burns with a non-luminescent flame, which may be invisible in bright sunlight. Responders should be equipped with infrared devices that allow remote heat and relative temperature detection. It is highly desirable to have this capability overhead in an emergency response helicopter, if at all possible.

3.2.1 DOCKS AND MARINE TERMINALS

Storage facilities at docks and marine terminals are typically floating roof tanks, dedicated to methanol handling. Internal floating roofs are preferred to avoid contamination. Facilities may be equipped with leak detection and alarms. Appropriate suppression and spill response capability is important and is likely required by insuring parties.

The larger concern is for unattended tank leaks. American Petroleum Institute codes, standards, and recommended practices should be referenced to obtain specific information regarding tank construction, inspection, and maintenance.

3.2.2 TANK FARMS

Tank farms at facilities such as refineries and chemical plants likely have dedicated methanol storage and handling systems. Typically, tanks are above ground, and piping is above ground and overhead in pipe racks. In general, fire protection for gasoline tanks is sufficient for methanol tanks, provided extra precaution is made for containment berm volume, leak detection, toxic hazard, and availability of alcohol-compatible fire suppression foam.

3.2.3 PORTABLE CONTAINERS

Totes and drums can be problematic. The methanol industry has gone to considerable lengths to design and fabricate satisfactory totes that are easily obtainable. Because the number of users of tote and drums far outnumbers the number of facilities with dedicated bulk storage and handling systems, this manual stresses the importance of safe methanol handling for tote and drum containment.

It is strongly suggested that handlers consult methanol providers concerning their selection of primary containment. Unlike tank farms, where personnel seldom have direct contact, users of totes and drums are typically subject to spillage, need for immediate response, and subsequent cleanup.

The following provisions are suggested for tote, drum, and can users:

- Methanol should be purchased only from reputable sources. The Methanol Institute provides a service to link methanol customers with methanol suppliers. Visit the MI web site at www.methanol.org, and click on the "Methanol Source Requests" link under the "Contact" heading. Complete and submit this online form, providing information on your methanol needs, and your information will be shared with MI members representing the leading global methanol producers and distributors. These suppliers will then contact you directly to discuss price and supply.

- Providers should be consulted regarding the intended application and circumstances of use before committing to a sales contract. Many merchant chemical companies are equipped and willing to extend their services in order to assure safe use of the chemicals they sell.

- After agreeing on facilities and provisions for receiving, storage, and local transfer, establish, equip, and train a local response team in the actions that are necessary and prudent in the event of a spill.

- Certain aspects of methanol handling require special provisions and protective measures. These include the following:

◊ As much as possible, methanol should be stored and used in a dedicated area that is specifically marked off and appropriately labeled. This area should have safety measures readily available to employees working in the area. The area should be designated as a hazardous area, and protective measures should be immediately available in the event of spillage, exposure, and ignition.

◊The area designated for methanol handling should be equipped with an effective audible alarm, which will summon assistance in a timely manner.

◊ Use positive materials identification for gaskets, filters, hose material, and similar supplies.

◊ Replace gaskets, hoses, and “O” rings periodically, before they are expected to degrade or fail.

◊ Ensure that procedures are in place to ground, and periodically verify grounding.

◊ Ensure that procedures are in place to protect from water uptake and accumulation.

◊ Ensure that provisions and procedures are in place to prevent spilled methanol from entering drains, manholes, and confined spaces.

◊Ensure that procedures and provisions are in place for preventing methanol entry into the water table or aquifers.

◊Ensure that procedures and equipment are in place for personnel protection and exposure mitigation. This should include eye wash and shower stations.

◊ Ensure that procedures and equipment are in place for leak detection and alarm.

- Guidelines and considerations relating to handling and storage of methanol in small tanks, totes, and drums are provided in the following regulatory and best practice documents:
    - ◊ IFC Chapter 57.
    - ◊ NFPA 30.
    - ◊ OSHA CFR 49 1910.119 and other regulations pertaining to hazardous materials.
    - ◊ Policies and procedures must also address safety considerations raised in a Hazard and Operability Study (HAZOP), performed prior to delivery of the first tanker truckload, tote, or drum of methanol.
    - ◊ ISO 9001: 2015 - Quality Management Systems.
    - ◊ Methanol Drum Transport Handling and Storage.

3.2.4 ELECTRICAL CLASSIFICATION

Electrical equipment within the proximity of methanol storage and handling must be explosion proof to meet National Electrical Code (NEC) requirements [42]. Positive pressure may be required to ensure that methanol-free areas, such as smoking rooms and control systems and electrical switch gear, are protected.

3.2.5 GROUNDING AND BONDING

Grounding is especially important in protecting methanol from accidental ignition resulting from static discharge. Methanol is an electrically conductive, polar compound. In general, methanol storage is not expected to accumulate static charge. However, circumstances such as a tank with a non-conductive liner can change the rate of charge accumulation.

It is recommended that grounding straps be equipped with carbide- tipped clamps to ensure electrical contact through non-conductive surface coatings, such as paint. Tanks and storage vessels should be fitted with dip-tube-filling to protect against ignition from static electricity generated as a result of liquid falling through air.

Grounding is required for lighting systems, pipe racks, pumps, vessel, filters, and all other equipment near and potentially within range of methanol vapor. Tall towers and other equipment subject to lightning strike must be equipped with lightning arresters.

Hoses must be grounded. In methanol loading and unloading situations, the possibility of spark generation due to accumulation of static electricity is less than with materials such as low sulfur diesel. Methanol is not a static accumulator. Electrical conductivity of methanol is relatively high when compared to that of most fuel materials. Nevertheless, velocity limits should be placed on transfer operations that involve high pressure drop, hydraulic impacts, and erosion concerns. Refer to API and NFPA publications for specific guidance.

Bonding is a measure intended to dissipate static electricity generated during fluid transfer through a conductive or nonconductive material. It involves making a connection between a grounded object and an ungrounded object. Methanol transfer operations should be bonded and grounded.

Metal containers (cans, drums or totes) and the associated fill equipment pump should be bonded together and grounded during methanol transfer operations. Fill pipes or hoses should be conductive and should be bonded to the filling system. Bonding should be done with a 1/8-inch bare stainless steel cable[5] connected to a clamp with hardened steel points and screws or a strong spring that will penetrate paint, corrosion, and accumulated materials. Apply the bonding clamp on the top chime of drum containers prior to removing the bung. Extend the pipe to within one inch (25 mm) of the bottom of the container. Start pouring slowly (at less than one meter per second or a container fill rate of less than 2 inches or 5 cm of fluid level rise per minute) until the container is filled to a level equivalent to two pipe diameters up the side of the fill pipe.

In recent years, attention has been drawn to the hazard of using personal electronic items, such as cell phones, laptop computers, etc., in environments subject to potentially explosive atmospheres, e.g., gasoline stations, and fueling terminals. The energy necessary to ignite gasoline vapors (0.2 mJ at the optimum mixture ratio for combustion) is similar to the energy produced by static electricity and by sparks generated by low-voltage electrical devices when they are turned on. It is not considered good practice to operate electronics such as cell phones and laptop computers in a potentially flammable atmosphere.

Be aware of the following:

- Mobile phones can ignite fuel fumes from gasoline, ethanol, methanol, propane, and compressed natural gas (CNG).
- Mobile phones that light up when switched on or when they ring release enough energy to provide a spark capable of igniting hydrocarbon vapors.
- Mobile phones should not be used (should be turned off) in filling stations, fuel terminals, or when filling portable containers, fueling lawn mowers, boats, etc.
- Mobile phones should not be used (should be turned off) around materials that generate flammable or explosive fumes (e.g., solvents, chemicals, gases).

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[5] A 1/4” to 3/8” flexible, bare bronze cable can be used for large grounding and bonding clamps.

The same precautions apply for laptop computers, flashlights, battery lanterns, and other battery-operated devices that are not rated as explosion proof. As a general rule, electronic devices should not be used within 20 feet (7 meters) of a potentially explosive atmosphere [40]. This distance is sufficient to provide a buffer of distance between the potential source of ignitable fumes and the device. Increase this distance to 50 feet (17 meters) for pressurized liquid gases, such as propane.

When dispensing from a metal container, the container and the associated fill equipment, including dip pipes, conductive hose, and pump, should be bonded together and grounded. Plastic-lined metal containers with epoxy or phenolic coatings less than 2 mm thick can be treated as metal containers. If the liner is more than 2 mm thick, the container should be treated as non-conductive. When handling methanol, treat non-conductive containers as if both the container and the methanol are non-conductive.

Plastic containers cannot be grounded and should not be used for Class I Flammable liquids, such as methanol, without expert review, as per NFPA 30, Flammable and Combustible Liquids. If a plastic container must be used, follow the same procedure as for metal containers.

Consult the following standards and references for additional information regarding issues pertaining to preventing accidental ignition:

- ASTM E681 describes a standard test method for determining flammability limits.
- Perry's Chemical Engineers' Handbook, 6th Edition, McGraw- Hill Book Company, San Francisco, Sec. 3, pp. 256-257, 1984.
- NFPA-325, *Guide to Fire Hazard Properties of Flammable Liquids*, Gases and Volatile Solids, 1994.
- Glassman, I., Combustion, 2nd Edition, pp. 321-313, pp. 486-489, 1987.
- NFPA 30A, *Code for Motor Fuel Dispensing Facilities and Repair Garages*, 2015.

- NFPA 30A, *Code for Motor Fuel Dispensing Facilities and Repair Garages*, 2015.

- UFC, Article 52, *Motor Vehicle Fuel-Dispensing Stations*, 1997.

- NEC, Chapter 5, Articles 500-504, 2008. These articles define requirements for intrinsically safe electronic devices in Class I, Division 1, and Class 1, Division 2 area hazardous locations.

- ANSI/UL 1203 *Explosion-proof and Dust-Ignition-proof Electrical Equipment for Use in Hazardous (Classified) Locations.*

- ANSI/UL 913 *Intrinsically Safe Apparatus and Associated Apparatus for Use in Class I, II, and II Division 1, Hazardous Locations.*

- UL 1604 *Electrical Equipment for Use in Class I and II, Division 2, and Class III Hazardous (Classified) Locations.*

- DOD-HDBK-263, Electrostatic Discharge Control Handbook.

- IEC 60050-426:1990, IEC 60079-4:1975, IEC 60079-4A:1970, IEC 60079-20:199.

4 HEALTH AND SAFETY

This chapter describes the toxicological properties of methanol; routes and symptoms of exposure; and effective control strategies, safety precautions, and first aid measures.

4.1 EXPOSURE TO METHANOL

Toxic exposure can occur by inhalation (breathing in vapor), ingestion (swallowing liquid), or dermal contact with methanol vapor or liquid. If liquid methanol is present, then methanol vapor in concentrations above toxic limits might also be present.

4.1.1 ROUTINE SOURCES OF EXPOSURE

Humans are exposed to methanol from many sources. Not only does methanol occur naturally in the human body, but humans are exposed routinely to methanol through air, water, and food. Food is the primary source of exposure for the general population. It is generally believed that dietary sources contribute to the observed background blood methanol concentrations. Methanol is widely found in small concentrations in the human diet from fresh fruits, vegetables, commercial beverages like fruit juices, beers, wines, and distilled spirits. The food additives Aspartame (an artificial sweetener) and DimethylmDicarbonate (DMDC) (a yeast inhibitor used in tea beverages, sports drinks, fruit or juice sparklers), as well as wines, release small amounts of methanol when metabolized in the human body. Table 4 illustrates examples of methanol levels in common foods and beverages, compared to background levels in the human body.

Table 4. Methanol Levels in Foods and Beverages and in Blood

SAMPLE	METHANOL LEVEL
Fresh and Canned Fruit Juices (Orange and Grapefruit Juices)	1-640 mg/l (average of 140 mg/l)
Beer	6-27 mg/l
Wines	96-329 mg/l
Beans	1.5-7.9 mg/kg
Lentils	4.4 mg/kg
Carbonated Beverages	~56 mg/l
Human Body Background Level	0.5 mg/kg (0.73 mg/l in blood)

Non-dietary potential exposure to methanol (primarily through inhalation) can result from using certain consumer products, such as paints, windshield washer fluids, antifreeze, de-icers, and adhesives that contain methanol as a solvent. Methanol is also used in fuel cells that power consumer electronic devices such as laptop computers and cellular phones. Fuel cell-powered vehicles may also use methanol as a hydrogen carrier fuel. These relatively new uses of methanol may become more common in the future.

STUDIES HAVE SHOWN THAT THE U.S. GENERAL POPULATION HAS A BACKGROUND BLOOD METHANOL CONCENTRATION OF BETWEEN .025 TO 4.7 MG/L IN BLOOD (MILLIGRAMS PER LITER IN BLOOD). IN CONTROLLED STUDIES, HUMANS BREATHING AIR CONTAINING 200 PPM (PARTS PER MILLION) METHANOL HAD BLOOD LEVELS BELOW 10 MG/L.

Most routine environmental exposures to methanol vapor in the air are significantly below occupational exposures. Typical environmental exposures to methanol in the air in rural areas are below 0.0008 ppm and approaching 0.03 ppm in urban areas. Methanol is currently used to a limited extent as an alternative fuel, primarily in a mix of 85% methanol and 15% gasoline, otherwise known as M85. Methanol's proposed use as a substitute for petroleum fuels may result in greater environmental releases to the air through vehicle emissions and at fueling stations.

Occupational (workplace) exposure is likely to cause the highest daily exposure to methanol. Occupational exposures typically occur through inhalation of methanol vapors during production or use. About 70% of the methanol produced in the United States is used as feedstock for the production of other organic chemicals and a variety of consumer prod ucts, including windshield washer fluid. It is also used in the treatment of wastewater and sewage. Occupational exposure to methanol may occur during its production, or result from its presence in refrigeration systems and as a component in the production of formaldehyde, MTBE, acetic acid, and other industrial chemicals. The Occupational Safety and Health Administration (OSHA) Time-Weighted-Average (TWA) Permissible Exposure Limit (PEL) to methanol is 200 ppm for an 8-hour day and 40-hour week.

CONCENTRATIONS OF METHANOL VAPORS MEASURED IN THE BREATHING ZONE OF WORKERS DURING REFUELING OF METHANOL-POWERED TRANSIT BUSES ARE GENERALLY LESS THAN 10 PPM. CONCENTRATIONS OF METHANOL VAPORS MEASURED IN THE BREATHING ZONE OF MECHANICS CHANGING FUEL FILTERS (2-MINUTE PROCEDURE) FOR THESE BUSES AVERAGED APPROXIMATELY 50 PPM.

4.1.2 ACCIDENTAL SOURCES OF EXPOSURE

Less common scenarios that are part of general population exposures include the use of methanol-containing fuels as solvents and accidental spillage. Another type of potential accidental exposure to methanol warrants mention. Each year, several thousand cases of accidental ingestion of gasoline are reported to United States poison control centers. Analysis of the data found that 39% of accidental ingestions involve teenage and young adult males, and 36% involved children under 6 years old. Almost all of the former cases occurred during the course of (mouth) siphoning to transfer fuel from one container to another. Most of the latter cases occurred when the children found a used beverage container in which gasoline was stored. With gasoline, the primary toxicity hazard lies in the possibility of regurgitating the fuel and aspirating the vomitus, which can induce chemical pneumonitis. However, if M85 were substituted for gasoline in these situations, methanol would considerably increase the potential for serious morbidity or mortality. Skin contact with methanol solutions can also lead to rapid absorption and appearance of signs of toxicity. Cases of methanol poisoning in children exposed dermally have been reported.

The following table illustrates some of the potential methanol exposure routes and the added methanol body burden expected from the exposure for a 154 lb (70 kg) person.

Table 5. Added Body Burden of Methanol [32]

EXPOSURE/DOSE	ADDED BODY BURDEN OF METHANOL
Background body burden in humans	35 mg*
Skin contact of hand in liquid methanol, 2 min	170 mg
Inhalation, 40 ppm methanol for 8 hr	170 mg
Inhalation, 150 ppm for 15 min	42 mg**
Inhalation, ingestion of 12 oz (0.34 liter) of aspartame sweetened diet beverge	21 mg
Ingestion of 0.2 ml of methanol	170 mg
Ingestion, 0.7-3 oz (25-90 ml) of methanol	Lethal (~21000-70000 mg)

*Estimated from methanol body burden of 0.5 mg/kg body weight for a 70 kg person

**Assuming 100% absorption in lung (60%-85% more likely)

4.1.3 ROUTES OF EXPOSURE

Methanol's primary routes of entry into the body are by inhalation, absorption through the skin as a result of contact, eye contact, and ingestion by either eating or drinking.

4.1.4 METHANOL METABOLISM

Methanol is easily and rapidly absorbed by all routes of exposure and distributes rapidly throughout the body. Humans absorb 60%-85% of methanol that is inhaled. A small amount is excreted by the lungs and kidneys without being metabolized. The rate of metabolism for methanol in the body is 25 mg/kg-hr, which is seven times slower than for ethanol and is independent of concentrations in the blood. Humans metabolize methanol into formaldehyde as the first step. The formaldehyde is then converted to formate (which can be toxic at high concentrations) and finally, to carbon dioxide and water. The half-life of methanol elimination in expired air after oral or dermal exposure is 1.5 hours. Due to their limited capability to metabolize formate to carbon dioxide, humans accumulate formate in their bodies from high-dose methanol exposure. If formate generation continues at a rate that exceeds its rate of metabolism, methanol toxicity sets in. Background levels of methanol in the human body will not result in formate accumulation or adverse health effects. Studies have shown that short-term inhalation exposure to 200 ppm methanol results in blood methanol concentrations of less than (10 mg/l) with no observed increase in blood formate concentration.

Human metabolism of methanol:

$$\text{Methanol} \xrightarrow{\text{Step 1}} \text{Formaldehyde} \xrightarrow{\text{Step 2}} \text{Formate} \xrightarrow{\text{Step 3}} CO_2 + H_2O$$

4.1.5 EFFECTS OF EXPOSURE

Methanol is a poison. This means that it can cause severe and sometimes fatal acute toxic effects from a single exposure. Therefore, the principal concern is with acute exposure through any primary route of entry. The signs and symptoms of methanol exposure do not occur immediately. The time lag between exposure and onset of symptoms may cause misdiagnosis of the cause, particularly in persons who are unaware they have been exposed, or who are unaware of the toxic nature of methanol and the differences between methanol, ethanol, and isopropyl alcohol.

4.1.5.1 GENERAL SYMPTOMS

Regardless of the route of exposure, the toxicity of methanol is the same. Signs of systemic toxic effects may be delayed between 8 and 36 hours after initial exposure. Methanol is irritating to the eyes, the skin, and the respiratory tract. It also strips the natural oils and fat from the skin, causing skin to become dry and cracked. It can cause permanent damage to the optic nerve and central and peripheral nervous system with just a single acute exposure. Other signs and symptoms of methanol poisoning include headache, dizziness, vomiting, severe abdominal pain, back pain, difficulty breathing, cold extremities, lethargy, and lack of coordination. Eye exposure can also cause a burning sensation accompanied by tearing, redness, and swelling. Direct contact with the liquid may cause conjunctivitis and corneal burns. High exposures may result in blindness, organ failure and death.

4.1.5.2 ACUTE EFFECTS

The effects of acute, high-dose methanol exposure have been well characterized in human cases of alcohol poisoning and in animal studies. Generally, the affected individual experiences a short period of intoxication with a mild depression of the central nervous system, followed by a pe riod in which no symptoms of intoxication or toxicity are noted (commonly 12 to 14 hours). This is followed by physical symptoms of poisoning, such as headache, nausea, vomiting, loss of equilibrium, severe abdominal pain, and difficulty in breathing. These symptoms can be followed by coma and death. Other hallmarks of acute methanol toxicity are disturbances of the visual system and accumulation of acid in the body. Methanol exposure results in vision effects that range from excessive sensitivity to light, to misty or blurred vision, to dramatically reduced visual acuity and total blindness.

THE AMOUNT OF METHANOL THAT CAN CAUSE SEVERE METHANOL EXPOSURE IS VERY SMALL: ASSUMING THAT 100% METHANOL FUEL IS SWALLOWED, THE LETHAL DOSE IS LESS THAN ONE TEASPOONFUL (4 ML) FOR A ONE-YEAR OLD INFANT, ONE AND ONE HALF TEASPOONS (6 ML) FOR A 3-YEAR-OLD CHILD, AND LESS THAN ONE ¼OF A CUP (10-30 ML) FOR AN ADULT.

4.1.5.3 CHRONIC EFFECTS

In contrast to the effects of acute, high-concentration exposure, relatively little is known about the effects of chronic, low-dose methanol exposure. Based on the limited number of case reports and epidemiological studies, the effects of prolonged exposures to methanol are similar to those of acute exposure: visual and central nervous system disorders. Repeated direct skin contact with methanol can cause dermatitis with dryness and cracking. Other symptoms of chronic exposure include eye irritation, headache, giddiness, insomnia, gastrointestinal problems, and especially visual difficulties.

According to the Organization for Economic Cooperation and Development's (OECD's) Screening Information Data Set, methanol is a candidate for further work on human health effects due to potential hazardous properties, including neurological effects, central nervous system (CNS) depression, ocular effects, reproductive and developmental effects, and other organ toxicity. Rapid metabolism and excretion are noted depending on the dose.

Methanol is not currently listed by any international consensus body or government agency (e.g., IARC, NTP, NIOSH, ACGIH, or OSHA) as being a carcinogen. EPA's Integrated Risk Information System (IRIS) is conducting a human health hazard and dose- response assessment of methanol. EPA's Integrated Risk Information System (IRIS) conducted a human health hazard and dose-response assessment of methanol. The final IRIS Toxicological Review of Methanol (Non-cancer) released in September 2017 established a reference dose for oral exposure of 2 mg/kg-body weight/day of methanol, and an inhalation reference concentration of 20 mg/m3. IRIS did not make a determination as to the carcinogenicity of methanol to humans.

In 2012, the State of California added methanol to a list of chemicals known to the State to cause reproductive toxicity under its Proposition 65.

There is concern for adverse developmental effects in fetuses if pregnant women are exposed to methanol at levels that result in high blood methanol concentrations greater than 10 mg/l. Blood methanol levels of 10 mg/l or greater are not expected to result from normal methanol PEL. However, this value is not intended to represent the highest "safe" blood concentration.

4.2 EXPOSURE CONTROL

4.2.1 ENGINEERING CONTROLS

Where possible, automatically pump liquid methanol from drums or other storage containers to process containers to minimize the potential for exposure. Methanol should always be kept within closed systems and not left open to the atmosphere. Refer to Sections 3.2 (Methanol Storage) and Chapter 5 (Managing Methanol Safely: Process Safety) for more information.

4.2.1.1 VENTILATION

The building ventilation system should provide fresh air for normal operation and should take into consideration the possibility of a leak. In some cases, natural ventilation may be adequate; otherwise, mechanical ventilation systems should be provided. Ventilation requirements should be determined on a site-specific basis, but the ultimate target is to ensure that methanol concentrations in air do not reach or exceed 200 ppm.

When possible, enclose operations and use proper local exhaust ventilation at the site of methanol transfer, use, or release. The type of ventilation will depend on factors such as dead air spaces, temperature of the methanol process, convection currents, and wind direction. These factors must be considered when determining equipment location, type, and capacity. If mechanical ventilation is installed, spark-proof fans must be used.

4.2.2 EXPOSURE MONITORING

Methanol has a faintly sweet alcohol odor but does not make its presence known until a concentration of 2000 ppm or above is reached, which is ten times higher than the safe limit for human exposure of 200 ppm. Because the odor of methanol is a poor indicator of concentration, it is essential that some quantitative measure of exposure be determined. This is necessary to ensure that the health of workers is not impaired and to determine compliance with any applicable regulations.

Methanol vapor concentrations can be measured using direct- reading gas detection tubes, such as colorimetric detection tubes, or with electronic instruments, such as portable gas monitors. Gas monitors can provide continuous readings of methanol concentrations, and alarms can also be set at specified concentrations. TWA personal exposure concentrations can also be measured using an air sampling pump with silica gel sorbent tubes.

Portable Gas Monitor

Gas Detection Tubes

(Courtesy of Drägerwerk AG with permission)

Currently, the OSHA PEL and the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) for methanol are set at 200 ppm [3]. Both values are based on an 8-hour TWA exposure. The ACGIH short-term exposure limit for methanol is 250 ppm, and it contains a skin notation. The National Institute for Occupational Safety and Health (NIOSH) has also set the 10-hour TWA recommended exposure limit at 200 ppm. The OSHA PELs are set to protect workers against the health effects of exposure to hazardous substances, such as methanol. PELs are regulatory limits on the amount or concentration of a substance in air that is not to be exceeded in the workplace. They may also contain a skin designation, which serves as a warning that skin absorption should be prevented in order to avoid exceeding the absorbed dose received by inhalation at the PEL level. The ACGIH TLVs are guidelines used by industrial hygienists and other health and safety professionals in making decisions regarding safe levels of exposure to various chemicals found in the workplace. Both the PEL and the TLV are maximum levels of exposure that the typical worker can experience without adverse health effects.

ACGIH also publishes Biological Exposure Indices (BEI) for a number of chemicals. BEI determinants are an index of an individual's "uptake" of a chemical. Most BEIs are based on a direct correlation with the TLV, although some relate directly to an adverse health effect. The BEI for methanol in urine collected at the end of the shift is 15 mg/l.

4.2.3 PERSONAL PROTECTIVE EQUIPMENT

Exposure to methanol can occur via inhalation, skin absorption, contact with the eyes, or ingestion, whenever methanol is used or handled. The level of risk of exposure to methanol will dictate the appropriate level of personal protective equipment required. At a minimum, safety glasses with side shields or safety goggles and task-appropriate gloves are recommended. Depending on the situation, additional personal protective equipment may be required.

4.2.4 RESPIRATORY PROTECTION

Respiratory protection should be selected based on hazards present and the likelihood of potential exposure. Air purifying respirators with organic vapor (OVA) cartridges are not appropriate protection against methanol vapors due to the very short service life of the OVA cartridge. In addition, the odor threshold of methanol can vary between 100 and 1500 ppm, so the OVA cartridge may not provide an adequate warning of when breakthrough of methanol vapors occurs and the respirator is no longer providing protection from methanol exposure.

The use of a supplied air respirator with a full face piece operate in a pressure-demand or other positive-pressure mode is the recommended respiratory protection. Evaluation of the appropriate type of respirator should also factor in the need for eye protection. Fit testing and regular maintenance programs for respiratory equipment are required whenever use of respiratory protection is required for a specific job task. The following table is a guide for whether respiratory protection is required or not, when the air concentration of methanol is known.

Table 6. Respiratory Protection Guide

AIR CONCENTRATION OF METHANOL	RESPIRATORY PROTECTION
<200 ppm	No protection required. Skin and eye protection may still be needed.
200 ppm or greater	Protection required if the daily time-weighted-average (TWA) exposure is exceeded or if there are additional routes of exposure (skin, eyes, ingestion). A supplied air system must be used if protection is needed.
>200 ppm sustained	A supplied air breathing apparatus (SCBA) system must be used (i.e., positive-pressure SBCA).

4.2.5 CHEMICAL-RESISTANT CLOTHING/ MATERIALS

Chemical-resistant clothing/materials should be worn if repeated or prolonged skin contact with methanol is expected. These may include anti-static rubber boots, resistant gloves, and other impervious and resistant clothing. Chemical-resistant materials include butyl rubber and nitrile rubber. Use chemical goggles when there is a potential for eye contact with methanol, including vapor. A full faceshield may be worn over goggles for additional protection, but not as a substitute for goggles.

Table 7 serves as guidance for proper personal protective equipment, depending on the situation presented.

Table 7. Personal Protective Equipment Selection

LOW RISK OF VAPOR/ LOW RISK OF VOLUME SPLASH	**HIGH RISK OF VAPOR/LOW RISK OF VOLUME SPLASH**	**HIGH RISK OF VAPOR/ HIGH RISK OF VOLUME SPLASH**
Fire Retardant Clothing	Full Chemical Resistant Suit	Full Chemical Resistant, Impermeable Suit
Gloves (Silvershield or Disposable Nitrile)	Chemical-Resistant Rubber Gloves	Checmical-Resistant Rubber Gloves
Safety Glasses with Side Shields	Full Face Supplied Air Respirator	SCBA or Compressed Air Breathing Apparatus (CABA)
Full Boot Cover	Chemical-Resistant Anti-Static Rubber Boots	Chemical-Resistant Anti-Static Rubber Boots

4.3 SAFETY PRECAUTIONS

4.3.1 ROUTINE OPERATIONS

Safety precautions are required both for toxicity and flammability. Vapor pressure and vapor flammability are such that discharge of static electricity can ignite vapor concentrations that are within the flammable range.. Therefore, grounding and bonding should always be applied when there is a potential for static electricity, and is required for all equipment. Carbide-tipped clamps (to ensure good contact through paint) and dip tube filling are generally used to guard against ignition from static electricity.

The following is a recommended list of additional safety precautions. Special or high-hazard operations may require additional precautions and are addressed in the next section.

- Smoking must be prohibited.
- Vehicle access should be strictly controlled.
- Ventilation must be sufficient to cope with the maximum expected vapor levels in buildings.
- Positive pressure may be required for methanol-free areas, such as control, switch and smoking rooms.
- Storage tank vents to atmosphere should be sized for fire-heated emergency vapor release.
- Electrical equipment must be explosion-proof to meet national electrical code requirements.
- Alcohol-resistant Aqueous Film-forming Foam (AR-AFFF) with 6% foam proportioning (with water) equipment is advised for use on methanol fires.
- Dry chemical extinguishers should be accessible for small fires. An adequate supply of handheld and wheeled types should be available.
- Fire Hydrants should be strategically placed with adequate hose diameter, sufficient hose length, and appropriate misting nozzles.
- Small spills should be remediated with sand, earth, or other non-combustible absorbent material, and the area then flushed with water. Larger spills should be diluted with water and diked for later disposal.
- Lighting should be grounded. Tall vessels and structures should be fitted wit h lightning conductors that are securely grounded.

4.3.2 SPECIAL OR HIGH HAZARD OPERATIONS

Confined space entry and hot work are high hazard operations that require special safety provisions.

4.3.2.1 CONFINED SPACE ENTRY

Many workplaces contain spaces that are "confined" because they hinder the activities of workers who must enter, work in, and exit them. A confined space has limited or restricted means for entry or exit, and it is not designed for continuous occupancy by workers. Examples of confined spaces include, but are not limited to, underground vaults, tanks, storage bins, manholes, pits, silos, process vessels, and pipelines. In addition, confined spaces often contain an atmosphere that is oxygen-deficient, toxic, or combustible, therefore requiring them to be classified by OSHA as "permit-required" for entry. Deaths in confined spaces have occurred in the workplace because the atmosphere within the confined space was not tested prior to entry and/or continually monitored. Confined space entry procedures must comply with all applicable Federal and local codes and regulations.

In addition to the potential for an oxygen-deficient atmosphere, accumulation of methanol vapors in confined spaces may lead to explosion if ignited. The Lower Explosive Limit (LEL) of methanol is 6% (60000 ppm) by volume, which is 10 times the Immediately Dangerous to Life or Health (IDLH) concentration, and the Upper Explosive Limit (UEL) is 36% (360000 ppm) by volume. At concentrations in air less than the LEL, there is insufficient methanol vapor to propagate a flame. At concentrations in air greater than the UEL, there is excess methanol and insufficient oxygen to propagate a flame. The LEL and UEL of methanol correspond to a temperature range of 54°F to 106°F (12°C to 41°C). In this temperature range, methanol will burn. Since methanol vapor concentrations in the explosive range are toxic, keeping the air concentration safe for health also makes it safe from fire. However, keeping it safe from fire does not necessarily make it safe to breathe.

In confined spaces, ventilation systems may be necessary in order to keep airborne concentrations of methanol below the LEL and below permissible exposure limits. Before entering a confined space where methanol may be present, check to make sure that an explosive concentration does not exist.

4.3.2.2 HOT WORK

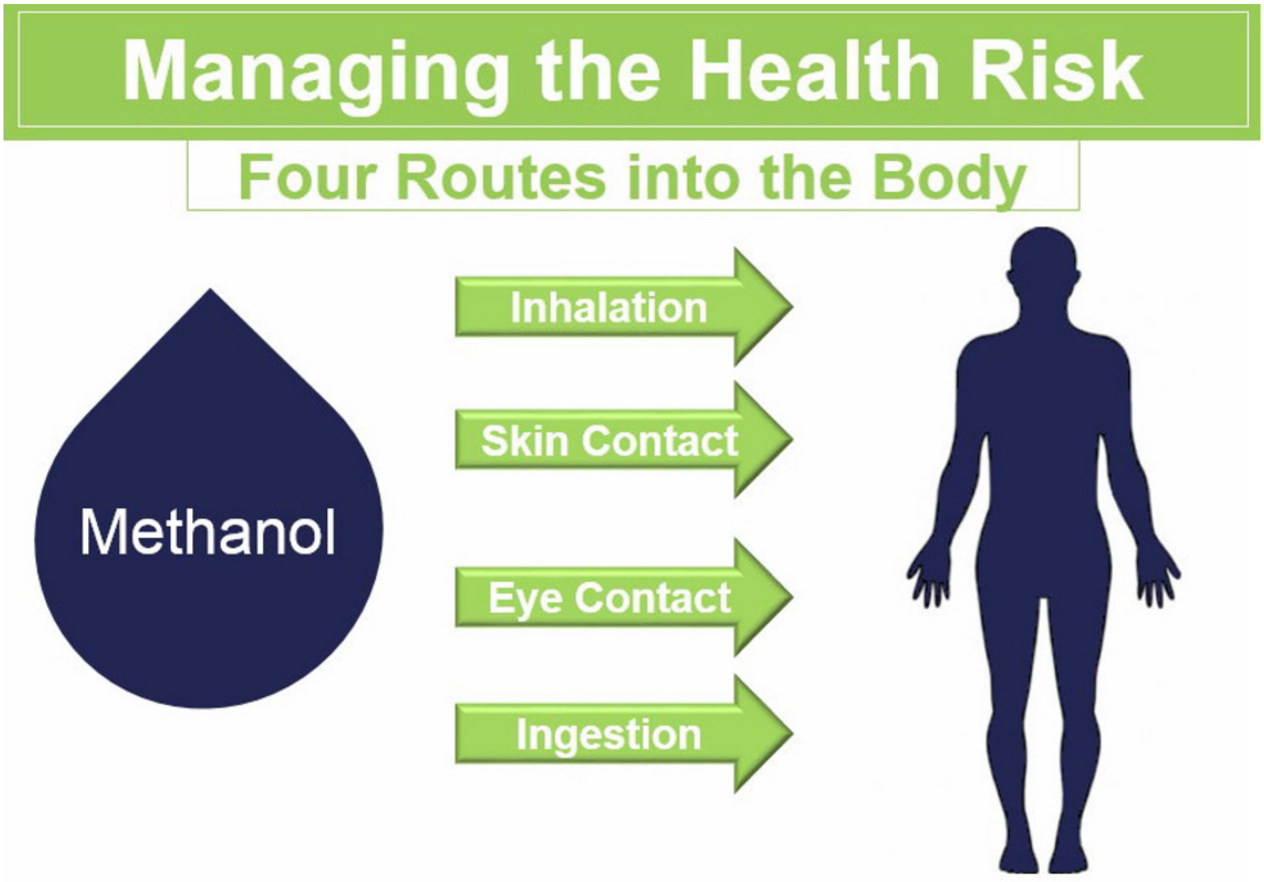
Hot work is any activity that creates heat, flame, sparks, or smoke. Examples of hot work include, but are not limited to, welding, brazing, soldering, cutting, heat treating, grinding, and using power-actuated tools. Methanol is extremely flammable and has the potential to ignite and burn when hot work is performed near sources of methanol vapors.

Methanol is defined by the NFPA and OSHA as a Class 1B flammable liquid, or by the United Nations as a flammable liquid (UN Hazard Class 3). It releases vapors at or below ambient temperatures. When mixed with air, methanol can burn in the open. The specific gravity of unmixed methanol vapor is 1.1 compared to air at 1.0. Methanol vapors are marginally heavier than air and may travel short distances (yards or meters) along the ground before reaching a point of ignition and flashing back. The distance of travel depends on circumstances of release. Turbulent release as a flashing liquid that is depressurizing or as a liquid jet release promotes rapid mixing with air; non-turbulent release from a liquid pool retards mixing with air.

Pure methanol has a low flash point of 54°F (11°C) and a wide flammability range (6-36. vol%). Flash point is defined as the minimum temperature at which the vapor pressure of a liquid is sufficient to form an ignitable mixture with air near the surface of the liquid. Flammability range is the concentration range within which a mixture of air and methanol vapor is capable of igniting, providing availability of an ignition source. The extent of the flammability range means that methanol vapor can be ignited throughout a wide range of concentrations in air [33]. The minimum ignition energy (MIE) for methanol in air is slightly lower than that of gasoline. Local hot spots can exceed the flash point and methanol can be ignited. Methanol burns with a clear blue-colored, non-luminous flame that may be difficult to see in bright sunlight. Methanol may be on fire and you may not be able to discern the hazard of a fire by looking for a flame.

The hazards associated with hot work can be reduced by implementing an effective hot work program that includes prior work authorization, safe welding practices, and a fire watch.

4.4 FIRST AID MEASURES



First aid is the immediate temporary treatment given to an exposed individual before the services or recommendations of a medical professional are obtained. Prompt action is essential. If necessary, medical assistance must be obtained as soon as possible. A Safety Data Sheet (SDS) for methanol or materials containing methanol should be carefully reviewed for information on first aid measures.

4.4.1 INHALATION

In case of inhalation of methanol vapors, first remove the individual to fresh air if it is safe for you to do so, and keep him or her warm and at rest. Monitor for respiratory distress. If difficulty in breathing develops or if breathing has stopped, administer artificial respiration or cardiopulmonary resuscitation (CPR) immediately and seek medical attention. If trained to do so, administer supplemental oxygen with assisted ventilation, as required.

4.4.2 SKIN CONTACT

In case of contact with skin, immediately use an emergency eyewash or safety shower, and flush the exposed area with copious amounts of tepid water for at least 15 minutes. Contaminated clothing and shoes should be removed under the shower. Wash the area thoroughly with soap and water. Seek medical attention if irritation or pain persists or if symptoms of toxicity develop. Wash contaminated clothing and shoes before reuse.

4.4.3 EYE CONTACT

In case of contact with eyes, immediately irrigate the eyes with copious amounts of tepid water for at least 20 minutes. The eyelid should be held apart during the flushing to ensure all accessible tissue of the eyes and the lids are in contact with water. Obtain medical attention.

4.4.4 ACCIDENTAL INGESTION

Ingestion of methanol may be life threatening. Onset of symptoms may be delayed for 8 to 36 hours after ingestion. Do not induce vomiting. Get medical attention immediately. The individual should remain under close medical care and observation for several days.

Treatment of methanol poisoning is well established: administer alkali, ethanol, and hemodialysis. Alkali is administered to combat the accumulation of formate in the blood. Ethanol is administered because ethanol competes with methanol for the enzyme that metabolizes methanol to formate. When ethanol and methanol are both present, the enzyme preferentially metabolizes ethanol. Dialysis is used to enhance the removal of methanol and its toxic products from blood. An antidote (in the form of an injection, fomepizole) is also available to treat methanol poisoning.

4.4.5 MI REFERENCE MATERIALS

Through the Institute's work in combating bootleg/adulterated alcohol poisoning, MI has developed a number of reference materials. More information on bootleg/adulterated alcohol poisoning and MI and our partners' materials can be found at www.methanol.org/ safe-handling/

5 MANAGING METHANOL SAFELY: PROCESS SAFETY

This chapter summarizes the Process Safety Management (PSM) approach to managing hazardous materials. PSM is by no means the only system used successfully to manage chemical hazards; however, it has proven to be effective in the many years during which it has been formally in effect, starting in the US and later expanding to other countries, provided the principles are applied diligently and intelligently.

Many organizations provide guidance or requirements for a comprehensive Process Safety Management System (PSMS). The first organization to formally establish PSM guidance was the Center for Chemical Process Safety (CCPS), a division of the American Institute of Chemical Engineers (AIChE). The AIChE has been involved in process safety and loss control issues since the early 1970's and established the CCPS in 1985. The CCPS, through AIChE, first published formal PSM guidelines in 1989 in its book titled Guidelines for Technical Management of Chemical Process Safety.

Based directly on the PSM guidelines from the CPPS, the US Occupational Safety and Health Administration (OSHA) developed regulation 29 CFR 1910.119, Process safety management of highly hazardous chemicals, which came into effect in 1992 [63]. According to provisions set forth in this regulation, methanol is classified as a highly hazardous material and must be managed in the US under the PSM regulation if the equipment in which it is contained (tanks, process piping, etc.) is connected to the process and consists of at least 10,000 lbs (equivalent to 4535 kg; about 1,510 US gallons or 5740 Litres, depending on temperature).

Since that time, several organizations have followed suit with provision of guidance for PSM. For example, the International Electrotechnical Commission (IEC) provides excellent and detailed standards regarding functional safety that can be used to supplement the OSHA guidance.

Relevant information can also be obtained from the Organization for Economic Cooperation and Development's (OECD) Guiding Principles for Chemical Accident Prevention, Preparedness, and Response

[53], the European Directive on the Control of Major Accident Hazards Involving Dangerous Substances (Directive 96/82/EC), the Association Française de Normalisation (AFNOR), Deutsches Institutfür Normung E.V. (DIN), International Organization for Standardization (ISO), American Petroleum Institute (API), and the American Society of Mechanical Engineers (ASME), amongst others.

Although traditional safety management systems and PSM have been in place in some organizations for many years, many companies continue to experience challenges with safety performance and results. To promote process safety management excellence and continuous improvement throughout industry, the CCPS developed next-generation PSM guidance known as risk-based process safety (RBPS). This framework was published by CCPS in 2007 in its book Guidelines for Risk Based Process Safety [34].

This latest evolution of PSM guidance from the CCPS not only supports compliance with regulatory requirements but helps organizations move away from a compliance mindset and towards using risk information and leading indicators to predict safety performance. Risk-based process safety management promotes use of risk information to determine the appropriate level of effort and resources required to manage risks.

As it is the most evolved PSM guidance to date, this Methanol Manual encourages use of CCPS risk-based PSM as the basis for a system that should be implemented in one form or another to maintain a safe and economically robust chemical processing industry.

Regardless of where you reside in the methanol production and distribution chain, when you take delivery of methanol, it will have traveled a long distance and been administered to by many hands. A large number of those hands have focused on the safe production, storage, and transport of your methanol, from raw well-head methane gas to the facility that filled and delivered the tank, tote, drum, or container that holds your methanol.

Literally millions of dollars have been expended in preventing accidental release within every aspect of the manufacturing process and in every step of the distribution chain. This effort has been made to protect life safety, environmental quality, and capital assets. Harm, degradation, and damage can result from direct exposure to the hazards inherent to methanol.

As a user, one aspect of your stewardship is to use this chemical in a safe and responsible manner. You are expected, and have legal responsibility within most countries, to continue this chain of custody, applying best engineering and management practice in every aspect of care and custody.

PSM uses a descriptive rather than a prescriptive command and control approach to regulating hazardous materials. This was chosen in order to give process operators and chemical handlers maximum autonomy in determining how to best operate and maintain their respective uses in a safe, responsible, and efficient manner. From the perspective of this manual, it is inconsequential whether your facility is or would be regulated by PSM regulations. The point is not regulation, but responsibility. The basic structure laid out in the CCPS risk-based PSM provides an effective framework for safe manufacture, storage, and use of hazardous chemicals. You are encouraged to make good use of these principles.

Process safety is founded on the principle that knowledge is power, power enables control, and control is a fundamental management function. The intent of PSM is to know, understand, and control hazards of chemicals, process technology, and equipment used in chemically based activities, large and small.

Risk-based PSM consists of 20 management elements. Each element addresses a particular aspect of the process necessary to safely manage chemical hazards. Each element stands alone, but also projects into and strengthens every other element. Each element of PSM is applied over and over (under OSHA PSM, the sequence operates on five-year cycles). With each successive cycle, facility management and staff should become more adept at establishing routines and improving facility operations.

The remainder of this chapter summarizes the intent and provides more details of each element of the risk-based PSM.

5.1 DEFINITIONS

Process Safety

A blend of engineering and management skills focused on preventing catastrophic accidents, particularly explosions, fires, and toxic releases, associated with the use of chemicals and petroleum products [35]. Management of process safety is focused on the prevention of major incidents that can result in large numbers of injuries or fatalities or significant environmental impact.

Risk-Based Process Safety (RBPS)

The prioritization of process safety and its management based on consideration of the level of hazard and risk, the resources available and the organization's process safety culture. According to the CCPS, "(t)he RBPS approach … focuses more resources on higher hazards and risk." [34]

Process Safety Management (PSM)

The management of safety risk associated with processes involving hazardous chemicals, materials, or energy.

Process Safety Management System (PSMS)

A documented system to manage process hazards and risks associated with chemical and petroleum processes. The Center for Chemical Process Safety (CCPS) defines it more formally as a management system that is focused on prevention of, preparedness for, mitigation of, response to and restoration from catastrophic releases of chemicals or energy from a process associated with a facility [34].

5.2 INTRODUCTION TO PROCESS SAFETY MANAGEMENT

The concept of process safety arose following a number of major incidents that occurred at chemical and petroleum processing facilities in the 1970's and 1980's. Organizations began to realize that these catastrophic events were not able to be prevented through the traditional focus of environment, health and safety (EHS) which aims to protect individual workers from harm.

Process safety has a greater focus on technology with the purpose of ensuring that hazardous materials are contained within process equipment and major incidents that can impact large numbers of people are prevented.

Governments have taken notice and, in several jurisdictions, have put in place prescriptive regulations requiring companies to establish process safety management systems. One example is the US regulation administered by the Occupational Safety and Health Administration (OSHA), 29 CFR 1910.119, Process safety management of highly hazardous chemicals, which came into effect in 1992.

A well-established EHS management system (EHSMS) will include some of the practices that would be included under process safety management. However, other activities that form part of a comprehensive PSMS will remain absent. In order to further improve the management of hazards and risks, companies should develop a PSMS that overlaps the EHSMS in some areas.

Not all aspects of a PSMS are applicable to all operations, locations or personnel, though some elements will be equally applicable in intent if not in degree. The PSMS allows a tailoring of location-specific process safety activities. Taking a risk-based approach considers the intersection of risks, resources and culture at each location.

The ultimate objectives of a comprehensive PSMS are to:

- prevent releases of hazardous materials and energy,
- maintain processing equipment in safe operating condition, and
- build a strong process safety culture.

Prevention of releases equates to minimizing injuries, illnesses, environmental impacts and property damage from chemical and petroleum processes.

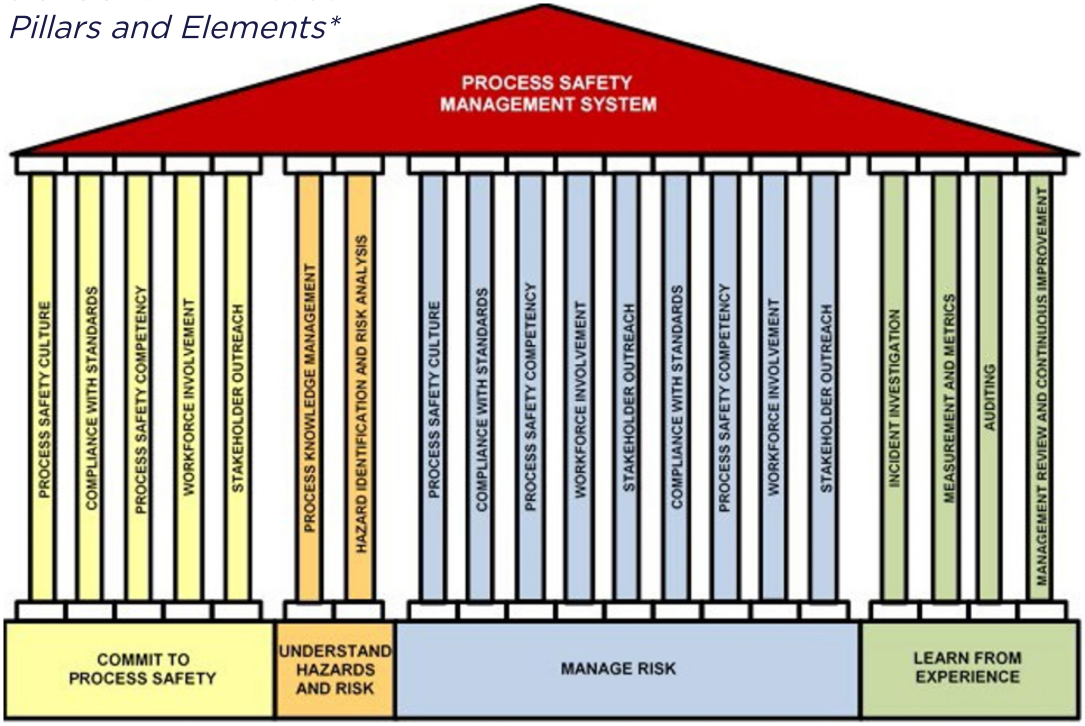
CCPS has defined twenty elements of process safety management that are logically grouped under four main areas or pillars:

- Commit to Process Safety
- Understand Hazards and Risks
- Manage Risk
- Learn from Experience

The twenty PSM elements and their relation to the four pillars are shown in Figure 3 below.

Risk-based process safety practices in the CCPS guidelines are designed to comply with all requirements of US regulations for process safety management. However, regardless of jurisdiction, each company must ensure that its implemented PSM system and practices fully comply with local regulatory obligations.

*Figure 3: CCPS Risk-Based PSM Pillars and Elements**



*CCPS *Risk Based Process Safety Overview*, 2014

5.3 COMPARISON - CCPS RISK - BASED PROCESS SAFETY VS OSHA REGULATIONS

Regulators, including in the US, used the original guidance from CCPS in 1989 as the basis for the development of PSM regulations. As noted in the previous section, the more advanced risk-based PSM guidelines from 2007 are designed to allow continuing compliance with regulations already in effect.

At the time of writing this manual, OSHA is in the process of reviewing and revising its PSM regulations to include additional PSM elements, in part based on the CCPS risk-based PSM guidelines. The following table* presents the relationship between CCPS risk-based PSM elements and current US OSHA PSM elements.

Table 8. CCPS vs OSHA PSM Elements

CCPS RISK-BASED PSM ELEMENT	OSHA PSM ELEMENT
Commit to Process Safety	
1. Process Safety Culture	
2. Compliance with Standards	1. Process Safety Information
3. Process Safety Competency	
4. Workforce Involvement	4. Employee Participation
5. Stakeholder Outreach	
Understand Hazards and Risks	
6. Process Knowledge Management	1. Process Safety Information
7. Hazard Identification and Risk Analysis	2. Process Hazard Analysis
Manage Risk	
8. Operating Procedures	3. Operating Procedures
9. Safe Work Practices	9 Hot Work Permits & 3. Operating Procedures
10. Asset Integrity and Reliability	8. Mechanical Integrity
11. Contractor Management	6. Contractors
12. Training and Performance Assurance	5. Training
13. Management of Change	10. Management of Change
14. Operational Readiness	7. Pre-Startup Safety Review
15. Conduct of Operations	
16. Emergency Management	12. Emergency Planning and Response
Learn from Experience	
17. Incident Investigation	11. Incident Investigation
18. Measurement and Metrics	
19. Auditing	13. Compliance Audits
20. Management Review and Continuous Improvement	

*Adapted from CCPS "Guidelines for Risk Based Process Safety", Table 1.8

5.4 PSM ELEMENTS - DESCRIPTIONS AND APPLICATION TO METHANOL SAFE HANDLING

5.4.1 PROCESS SAFETY CULTURE

The CCPS defines Process Safety Culture as the combination of group values and behaviors that determines the manner in which process safety is managed. How an individual or organization behaves when no one is looking reflects the strength of the culture.

Adherence to the following key principles will help an organization develop and maintain a strong process safety culture:

- Establish process safety as a core value
- Provide strong, knowledgeable leadership
- Establish and enforce high standards of performance
- Maintain a sense of vulnerability, i.e., a high awareness of hazards and their potential consequences
- Empower individual workers to fulfill their safety responsibilities with appropriate balance of responsibility, authority, accountability, and resource use
- Ensure open and effective communications
- Establish a questioning and learning environment
- Foster mutual trust
- Provide timely response to issue and concerns

In addition, the organization should provide ongoing monitoring of process safety performance with an aim of continuous improvement of the culture.

5.4.2 COMPLIANCE WITH STANDARDS

A wide range of standards, codes, regulations and laws affects the way that companies carry out their work activities, not only for companies that manufacture or handle methanol but for many other chemical and petroleum products as well. At a minimum, work must be carried out in compliance with relevant regulations and laws. Codes and standards, while typically establishing another minimum level of performance, are often enshrined in local regulations, e.g., National Fire Codes. External and internal standards can also be adopted as either best practices or required practices. Companies should generally require adherence to both internal and external standards of practice across the organization.

A number of countries currently have regulations in place that directly relate to process safety. Details on some of these regulations follow.

United States

Federal regulations in the US specifically address requirements for process safety management. The most significant regulations are administered under the Occupational Safety and Health Administration (OSHA – Code of Federal Regulations 29) and the Environmental Protection Agency (EPA – Code of Federal Regulations 40).

OSHA 29 CFR 1910.119 *Process Safety Management of Highly Hazardous Chemicals* describes criteria for determining whether the regulation applies to a given company and the specific PSM system that a company must have in place to meet requirements.

EPA 40 CFR 68 *Chemical Accident Prevention Provisions* describes requirements for preventing and safely managing chemical accidents. Subpart D directly aligns with OSHA PSM requirements, while other sections include requirements for emergency response and risk management plans.

Canada

There is no regulation in Canada that specifically addresses PSM requirements. However, the Criminal Code of Canada was amended in 2004 to increase organizational and personal liability for chemical accidents; Law C-21 was enacted to allow these amendments. Criminal liability has been extended to organization “representatives” that may include directors, officers, employees, contractors and others.

Law C-21 establishes criminal liability for organizations and individuals when they fail to take reasonable steps to prevent workplace accidents that affect workers or the public. In other words, in the event of an accident, Canadian regulators will be looking for evidence of due diligence and may be expected to reference US OSHA 29 CFR 1910.119 as an industry best practice. Subject to Law C-21, failure to show due diligence in process safety could result in significant fines and jail terms.

United Kingdom

UK safety legislation covers both traditional worker safety (e.g., use of PPE, slips, trips and falls, working at heights, confined space entry) and process safety. The enforcing authority for all health and safety legislation is the Health and Safety Executive (HSE).

Although not explicitly referred to as “process safety regulations”, process safety legislation in the UK, such as the Control of Major Accident Hazards (COMAH) Regulations, is aimed specifically at those industries identified as having a major accident potential which could result in significant on-site and off-site effects to employees, members of the public and the wider environment. The regulatory framework seeks to protect people and the environment from, and limit the consequences of, major accidents occurring within establishments covered by COMAH.

The COMAH Regulations were most recently updated in 2015 and are referred to as COMAH 2015. More detailed information is available at http://www.hse.gov.uk/comah/index.htm

European Communities

The European Communities has regulations in place that are very similar to the UK regulations described above and were also updated in 2015. The regulations are referred to as the Chemicals Act (Control of Major Accident Hazards Involving Dangerous Substances) Regulations 2015, S.I. No. 209 of 2015.

China

In order to address the occurrence of major industrial accidents, the Chinese national standard on Identification of Major Hazard Installations (GB 18218 2009) was released in 2000 and then amended in 2009. Subsequently in 2010, the State Administration of Work Safety (SAWS) released its first Process Safety Management regulation in China, AQ/T 3034-2010 Guidelines for Process Safety Management of Chemical Corporations. The regulation came into effect in 2011.

This regulation adopted twelve of the fourteen OSHA PSM elements, excluding Trade Secrets and Employee Participation. Although the title states “Guidelines”, AQ/T 3034-2010 references additional regulations that support requirements in the guideline.

In 2013, SAWS published a detailed guidance document to further strengthen company practices regarding process safety management (SAWS III [2013] No. 88).

In addition to PSM-specific regulations such as those described above, there are numerous other regulations, codes and standards that have either direct or indirect relevance to process safety requirements. The three tables below present many other types of regulations, codes and standards that must be considered when establishing PSM systems and practices.

Depending on the country or jurisdiction where a company is operating, not all of the regulations, codes and standards in the tables will apply at every location that handles methanol. There may also be additional relevant items that are not in the tables. Codes and standards in particular only become requirements when referenced in regulations or by-laws or when specified as part of standard practice requirements by a company. The tables are not intended to imply that all external codes (e.g., NFPA codes) and standards (e.g., NIOSH) must be followed in all situations.

Table 9. Examples of Additional Regulatory Requirements

Pressure Equipment Regulations
National, Provincial or State Engineering Regulations
Facility Operating Permits*
Safety Regulations
Environmental Regulations
Workers Compensation Regulations

**Operating permits normally require regulatory approval and typically specify requirements / limits on facility construction, operation, layout, equipment, storage capacity, incoming materials, process methods, wastes streams, emissions control, disposal methods, etc.*

Table 10. Examples of Codes

Pressure Equipment
National Fire Protecting Association (NFPA) Codes
American Petroleum Institute (API) Codes and Standards
Fire Codes
Building Codes
Electrical Codes
Boiler Codes
Fuel Codes
Environmental Codes
Codes of Ethics (e.g., company or professional orgnaization)

Table 11. Examples of Standards of Practice

American Conference of Government Industrial Hygienists (ACGIH)
National Institute of Occupational Safety and Health (NIOSH)
National Standards Association (e.g., ANSI, CSA)
Company Safety Manuals
Company Engineering Standards
Standard Operating Procedures (SOPs)
Safe Work Practices (SWPs)

5.4.3 PROCESS SAFETY COMPETENCY

The term "process safety competency" refers to organizational competency in process safety management, not individual competency which is managed through the Training and Performance Assurance PSM element. Organizational competency in PSM is a measure of the collective effectiveness of the process safety-related activities carried out across the company.

Process safety competency is the ability of an organization to successfully manage process hazards and risks, develop and retain process safety knowledge, ensure that knowledge is available to those who need it and consistently apply what has been learned.

To achieve a high level of process safety competency, each of the elements of the PSMS must be effectively implemented and well-maintained, with the highest level of competency being attainable in a process safety culture focused on continuous improvement.

All of the PSM elements may not have equal importance in ensuring an effective PSMS. Relative importance will be dependent upon the risks that must be managed at a given operating location. For example, while communication with stakeholders is important, a site may choose as a priority in a new PSMS to focus on hazard identification and risk analysis first. A risk assessment may help to prioritize the elements in the PSMS. Overall process safety competency may then be determined from a weighting of competencies for each of the individual PSM elements.

While all PSM elements and effective practices contribute to building competency, the level of competency is demonstrated through reviews of the PSMS. Audits, metrics and management review all are used to assess the level of process safety competency in PSM, while improvements made based on results of these reviews will further enhance competency.

For companies that handle methanol or other hazardous chemical products, there are a number of process safety practices that, when implemented and managed effectively, will increase the level of process safety competency across the organization. Following are several examples.

Project Reviews for Lessons Learned

Following a significant project, e.g., building a new tank farm, a review should be carried out to collate lessons learned from the project. A Lessons Learned Report should be distributed to all people involved with that project or who may become involved in a similar project. Lessons learned should be formally used in the planning and design of the next similar project.

Adherence to Established Standards

Application of established standards and codes of practice to company processes ensures consistent practices and reduces the likelihood of incidents and the potential for regulatory non-compliance. PSM competency improves as compliance with codes and standards improves. A company should identify and strictly apply standards and codes related to process safety during the design, construction and operation of its facilities, for example:

- processing piping specifications;
- tank construction, inspection and repair standards;
- NFPA codes;
- NIOSH permissible exposure limits; and
- local or regional safety performance metrics reporting.

Process Knowledge Management

While some organizations may depend on the knowledge of specific individuals to meet their company objectives, a company with process safety competency ensures that process knowledge is documented and maintained. Thus, as personnel changes occur, knowledge is not lost.

Requirements should be in place for development, retention, maintenance and accessibility of process knowledge. Numerous types of information and records are described in section 5.4.6 that collectively constitute process knowledge and, consequently, improve competency in PSM.

Progression planning and organizational MOCs also facilitate retention of process knowledge when individuals move to other positions.

Standard Operating Procedures (SOPs)

Operators at company facilities normally use SOPs to operate equipment and perform work. Following SOPs drives consistent practices that have been established to minimize incidents and maximize worker safety. In many cases, individual operating locations develop their own SOPs for the specific equipment and processes at that location.

Process safety competency will be improved where SOPs are standardized across multiple company sites that use similar equipment or have similar processes.

Preventive Maintenance (PM)

Equipment failures can have a variety of impacts including environmental releases, worker exposures, equipment damage or downtime. All of these impacts have financial implications for a company, in addition to potential injuries / illnesses or environmental damage. PM is aimed at preventing unexpected equipment failures through planned inspections, testing and maintenance activities.

Although PM programs have inherent costs related to planned downtime, labour, parts and supplies, effective PM programs can be justified when compared to the losses from unplanned failures.

Company PM programs typically focus on critical equipment and any other situations subject to regulation, e.g., transportation equipment. These PM programs improve equipment reliability and reduce failures, therefore improving the process safety competency of the organization. Further enhancement of process safety competency is possible where effective PM programs are expanded to include additional equipment.

Management of Change (MOC)

An effective MOC process will require a multi-disciplinary review of planned changes for inherent or added risk that can then be managed through the implementation of the change. Where these risks are understood and controlled, likelihood of incidents is reduced and improved process safety competency results. Process safety competency is further enhanced when MOC review is not restricted to certain types of change only but when all types of change undergo an MOC review.

Refer to the descriptions of each of the PSM elements in this section for further details of PSM practices that enhance process safety competency.

5.4.4 WORK FORCE INVOLVEMENT

A process safety management system can only be truly effective with the direct participation of employees from all parts of the organization, from management to operators, maintenance workers to safety personnel, engineers to human resources personnel. The strength of each individual PSM element, and therefore the overall process safety competency of a company, is directly impacted by the degree of workforce involvement.

The guiding principle regarding workforce involvement is that the employees are the persons who must have the most detailed knowledge regarding the process in order to operate and maintain process system equipment safely and efficiently. In effect, all aspects of a process safety management system belong to facility employees while employers have the responsibility and the duty of creating, supporting, and funding the system and verifying that the system functions as anticipated and produces the intended result.

The following are examples of the many ways that various company employees can become directly involved in process safety.

Process Knowledge Management

To help guide the development of a company's PSM system, a committee could be formed, consisting of representatives from each department, e.g., Operations, Maintenance, EH&S, Engineering, Management, HR, and so on. Each committee member would consider potential impact on his or her department, how PSM practices might best be implemented and resource requirements. Members would provide input into the development of each PSM element or review drafts as they are prepared and provide feedback for improvement.

Day-to-Day Involvement in the PSMS

Operations personnel and other employees will participate in the PSMS on a daily basis through various activities, for example:

- complying with all company and regulatory requirements during the execution of work tasks (*see section 5.4.2 Compliance with Standards*);

- following standard operating procedures and safe work practices (*see sections 5.4.8 Operating Procedures and 5.4.9 Safe Work Practices*);
- performing maintenance activities (*see section 5.4.10 Asset Integrity and Reliability*);
- mentoring less experienced workers;
- participating in process hazards analyses and job task observations (see section 5.4.7 Hazard Identification and Risk Analysis); and
- participating in PSM audits (*see section 5.4.19 Auditing*).

Safety Meetings

Most companies will hold regular safety meetings of various types, such as:

- Regular (e.g., monthly or quarterly) safety meetings for all personnel at the facility. Attendance should be taken and meeting minutes recorded that reflect topics discussed and any actions arising from the meeting.
- Department safety meetings where issues specific to a department are discussed. As above, attendance should be taken and minutes recorded.
- Daily toolbox or tailgate meetings held at operating locations to review work plans for the day (or shift), hazardous work that may be occurring and share any other concerns with the coming shift. All operators should be required to participate in these meetings.

Hazard Reviews

(see sections 5.4.7 Hazard Identification and Risk Analysis and 5.4.13 Management of Change)

Multi-disciplinary teams are brought together to perform hazard reviews when the needs arise, from a simple review conducted during an Management of Change review to a detailed hazard and operability (HAZOP) study involving experienced employees from several functional groups.

Management of Contractors

(see section 5.4.11 Contractor Management)

Management should conduct reviews to ensure the contractors working on their facilities meet defined minimum requirements relating to safety, insurance and workers compensation. Operators would oversee the activities of contractors while performing work on site.

Appropriately trained personnel could manage the company's online contractor screening system and work with Operations to assist contractors with maintaining acceptable status within that system.

Employee Training

(see section 5.4.12 Training and Performance Assurance)

Companies can provide a wide variety of training for employee development, ranging from required training for specific job functions, through required and voluntary safety training, to soft skills training for career development and success. Training programs may be available as online training modules, classroom sessions (in-house or provided by a third party) or formal education.

Managers may establish annual training and development plans for their employees who, in turn, participate in training as required or desired.

Management of Change (MOC) Process

(see section 5.4.13 Management of Change)

As a process applicable to all operating divisions of the company and to all groups responsible for projects relating to operations, MOC includes a number of areas for direct involvement.

- Operations or project employees – These personnel usually have the right and responsibility to initiate a change request, at least through initial discussions with his or her supervisor.

- An initiator of a change – This person prepares and submits an MOC request for review by a multi-disciplinary team. The respective supervisor or manager should approve the change request prior to submission of the MOC.

- MOC Review Team – This is a multi-disciplinary team typically consisting of knowledgeable employees representing EHS and Engineering, as well as other groups such as Operations or Maintenance as required. MOC reviews should be conducted on a regular basis.

- Operations and/or project personnel – These may be different workers from the person who initiates a change request. They implement approved changes and include any requirements resulting from the MOC review.

Pre-Startup Safety Reviews (PSSRs)

(see section 5.4.14 Operational Readiness)

Personnel from various disciplines may participate in a PSSR, depending on its complexity. This may range from an Operator performing a basic PSSR following routine maintenance or a simple replacement-in-kind, to a review team that may include Engineering, EHS, Operations and Maintenance personnel in preparation for a startup of a new facility.

In addition, employees involved in PSSRs may provide feedback to improve PSSR checklists used when conducting reviews.

Emergency Response

(see section 5.4.16 Emergency Management)

Operations personnel will usually participate in the development of site-specific Emergency Plans and are trained to respond appropriately to site emergencies. All facility employees should participate in emergency drills and exercise relevant to their workplaces.

Incident Management

(see section 5.4.17 Incident Investigation)

Employees are normally directly responsible for reporting incidents and near misses when they occur. In most cases, EHS and personnel from the group involved in an incident jointly conduct an incident investigation, identify root causes and develop corrective actions. Involved personnel then implement corrective actions as necessary.

Trained employees will manage the company's incident reporting and management system.

Senior management should review monthly incident summaries and provide recommendations and direction for improving safety performance across the company.

PSM Auditing

(see section 5.4.19 Auditing)

Similar to PSSR team structure, personnel from various disciplines may participate in a PSM audit, again depending on its complexity. Team members may include employees from Engineering, EHS, Operations or others as appropriate.

Various personnel may be responsible for implementing improvement actions in response to audit findings.

Management PSM Reviews

(see section 5.4.20 Management Review and Continuous Improvement)

Management participates in PSM not only through day-to-day management of PSM-related activities but also through regular (e.g., annual) reviews of PSM metrics and the overall health and performance of the system.

5.4.5 STAKEHOLDER OUTREACH

The ultimate objective of stakeholder outreach is to develop and maintain good relationships with appropriate stakeholders over the life of a facility and share appropriate information about the facility's operations. This can be achieved by:

- identifying individuals or organizations that may be affected by a company's operations;
- engaging these stakeholders in a dialogue about process safety and the company; and
- providing information about the facility's processes, hazards and risks and their management.

Stakeholders might be internal (e.g., employees) or external (e.g., local community, industrial neighbors, first nations / aboriginal groups, regulatory authorities). Sharing information with stakeholders can be critical to the success of the organization. Discussing process safety with industry peers promotes improved process safety across industry. Proactively sharing information with communities and regulators builds trust which enhances the facility's licence to operate, while regulators may be more willing to work with the facility to resolve problems. An effective stakeholder outreach program should increase stakeholders' confidence in the company.

A company may decide to establish responsibility for all outreach activities, especially with external stakeholders, with one particular group or department. In this situation, the outreach department must be in frequent communication with other company groups to ensure that current and accurate information is available for stakeholders and that feedback from stakeholders is provided to appropriate company personnel.

Given that several departments will need to be involved in outreach anyway, at the very least providing information to the outreach group, another company may determine that the best approach is to have several groups responsible for communication with various stakeholders, with those company groups coordinating their activities according to an overall outreach plan.

The following table provides examples of possible outreach activities that can be carried out by various functional groups with identified stakeholders.

Table 12. Examples of Stakeholders & Outreach Activities

Company Group	Stakeholders	Outreach Activities
Communications	Current Employees	• general internal communications (e.g., memos) regarding activities or status of company initiatives • publication of company newsletter • publication of annual EHS or Sustainability Reports • development and maintenance of company internal website
	Prospective Employees	• facilitation of and participation in career fairs
	Investors	• ownership and maintenance of company website • arranging and hosting the Annual General Meeting • publishing the company Annual Report • publishing quarterly reports • hosting quarterly investor calls
	Community	• facilitating and assisting with facility Open Houses • advertising company information and events in appropriate media • community investment, for example: € - sponsorships € - community events € - charities € - facilitating employee volunteering
	First Nations/ Aboriginal Groups	• discuss company operations on public lands or near native lands

	Customers	• participation in industry trade shows • preparation of marketing materials • publication of company fact sheets • company website
EHS / Process	Regulators	• review company activities vs. regilatory requirements • regulatory approval applications • approval amendments
	Local Authorities	• discuss planned and existing operations with groups such as spill co-ops, air shed management groups, waste management associations
	Auditors	• coordinate and facilitate third-party audits
	Operations and Other Employees	• provide support and guidance for EHS practices • sharing information through safety meetings • monitoring and improving facility safety performance through KPIs • conducting EHS audits to identify improvement opportunities
	Land Owners and Neighbors	• discuss planned new facilities • discuss planned changes to existing facilities (size change, storage capacity) • notification of changes • obtain consents from stakeholders • face-to-face discussions re stakeholder objections
	Industry Associations	• participation on industry technical committees and contributions to safety knowledge and management
	Customers	• sharing of EHS statistics and practices
	Contractors	• discussion of EHS requirements and performance expectations • facilitating and assisting with achievement of expectations

Operations	Community	• Open House opportunities • awareness of site operations and potential off-site risks
	Industrial Neighbors	• awareness and discussions of site operations
	Regulators	• ensure operations meet regulatory approval and permit requirements • host and facilitate regulatory inspections • provide required information to regulators
	Auditors	• host and facilitate audits of facilities and processes • implement improvements based on audit results
	Employers	• provision of site-specific operations training • information sharing during safety meetings • managing and developing new employees with a short-service worker program • feedback through a safety observation process
	Emergency Response Organizations	• mutual aid agreements with neighboring industries • service arrangements with ER organizations • facility tours for emergency responders • site inspections by and response to regulatory agencies
Human Resources	Current Employees	• provision of training programs for personal or career development • publication of position agencies
	Prospective Employees	• facilitation of and participation in career fairs • publication of position postings • managing a summer student program • advertising at colleges and universities

	Health Care Professional	• establishing and managing programs relating to employee health monitoring • engaging Health Care professionals on program requirements and privacy issues for individual results • facilitating emergency health care for employees and related issues for family members (e.g., travel, accommodations, information)
	Workers Compensation Organizations	• interaction regarding management of work-related injury cases • engagement regarding return-to-work processes
	First Nations / Aboriginal Groups	• participation on Aboriginal engagement and employment organizations • postings on Aboriginal job boards • scholarships • sponsorships • celebrations
	General Public	• external branding • scholarships • sponsorships
Land Management	Land Owners, Adjacent Owners, Municipalities, Industry Groups	• discussions regarding lease agreements, land purchases, access agreements, crossing agreements

5.4.6 PROCESS KNOWLEDGE MANAGEMENT

Only through detailed process knowledge and information can the hazards and risk associated with a process or process equipment be fully understood. Without understanding those hazards and risks, it is not possible to mitigate and manage process-related risk.

Maintaining detailed process knowledge is especially important for hazardous processes and for any process equipment that, through its operation, introduces risk to people, the environment or other equipment. Examples include pressure systems, high temperature operations, chemical treatment processes, electrical equipment, rotating equipment, and so on.

US OSHA 29 CFR 1910.119 describes process knowledge as generally falling within three categories:

- information pertaining to the hazards of the chemicals within the process;
- information pertaining to the technology of the process (including safe control parameter limits; and
- information pertaining to the equipment that is used in the process.

CCPS Guidelines take this further and state that process knowledge from the following additional areas should be maintained and accessible:

- process hazard analysis;
- process equipment integrity;
- management of change;
- operating procedures;
- training;
- emergency response;
- auditing; and
- contractors.

To provide guidance, the tables in Appendix A identify minimum information that should be maintained to meet PSM requirements. However, not all information listed will be relevant at every operating location.

It is not necessary that all process knowledge and information for a facility be stored in the same location, although the number of different locations should be kept to a minimum. For example, Engineering files may be a depository for PFDs, P&IDs, electrical area classification diagrams, design bases and calculations, while the operating location may maintain information related to chemical hazards, vendor documentation, maximum intended inventory, safe operating limits and location of safety equipment. Regardless of where information is stored, it must be readily accessible to Operations.

Safe operating limits must be included in the relevant SOPs for the process or equipment, along with actions to be taken if limits are exceeded and the recovery procedure to return to operating within safe limits.

Changes to processes or equipment due to projects, MOC reviews, audits or incidents should be clearly linked to the process knowledge and process knowledge must be updated to reflect such changes. Out-of-date information must be clearly marked and should be moved to an archive file. Changes made to process knowledge must be communicated by the owner of the knowledge depository to interested parties and individuals or groups who may be impacted by the changes. MOC documentation and maintenance records must be clearly linked to the relevant process or equipment.

Personal files must not be used for retaining process knowledge; only copies can be included in personal files. Copies in personal files are uncontrolled and will not be updated when process knowledge is updated. Thus, personal files containing process knowledge may be out-of-date and should not be relied on as current.

Process knowledge and information should be maintained for the life of the process and/or equipment.

5.4.7 HAZARD IDENTIFICATION AND RISK ANALYSIS

In process safety, the term “Hazard Identification and Risk Analysis” (HIRA) includes all activities involving identification of risk and evaluation of risks. In order to manage process safety risk, a company must first identify relevant hazards. Only after this is done can the risks associated with each hazard be evaluated.

Hazard identification and risk analysis, also referred to as process hazard analysis (PHA), should be performed on all aspects of the process using an analysis technique that is appropriate to the complexity of the process. The PHA identifies, evaluates, and verifies that hazards arising from the process, and from inventories of hazardous chemicals that are connected to the process, are controlled.

HIRA activities are intended to address three key questions:

- What are hazards - what can go wrong?
- What are the potential consequences - how bad can it be?
- What is the likelihood of an event occurring - how often might it happen?

The earlier in the facility or equipment life cycle that risk analysis is conducted, the more cost effective and safe the operation of the facility is likely to be. Furthermore, because circumstances and perceptions change over time, risk analysis should be periodically repeated throughout the life of a facility. This helps ensure that appropriate safeguards are in place and remain in place to control the facility’s process safety risks.

Aspects of HIRA should be applied at various stages of a process life cycle. Hazard identification and a preliminary hazards review should occur during the planning and conceptual design phase of a project. This would normally be conducted by Operations or the project manager who may seek assistance from Engineer and/or EHS.

Following detailed planning, a Management of Change (MOC) change proposal should be submitted for review. Approval may be dependent on fulfilling additional requirements identified by the review team. These requirements may include the need for a detailed process hazards review following detailed design. The MOC may take place either before or following the detailed design phase.

Prior to startup of equipment or a process, a pre-startup safety review (PSSR) should be performed. This would typically be carried out by Operations with the support of Engineering, EHS and other key participants. Standard Operating Procedures for new or modified processes would be created or updated, respectively, prior to startup.

Finally, HIRA activities should occur prior to demolition of equipment or a process.

5.4.8 OPERATING PROCEDURES

The objective of this element is to control hazards and manage risk associated with routine operations activities, as well as non- routine activities including temporary and emergency operations, emergency shutdowns and re-starts.

In order to maintain safe operations, operators must know how and when to perform specific tasks associated with equipment operation and process control during normal operations, as well as in the event of abnormal circumstances. Safe operating procedures (SOPs) should be developed with input from personnel responsible for safely operating the equipment or process. All impacted personnel must be trained in the procedure before the SOP is implemented.

Once an SOP has been put into place, all operators must follow the steps in the SOP precisely without deviation at all times. change in procedure is identified and mitigated. The SOP must then be modified and operators trained in the change before the change is allowed to be implemented.

The following operational phases should be addressed in safe operating procedures (SOPs):

- initial startup
- normal operations
- temporary operations
- normal shutdown
- emergency shutdown
- emergency operations
- re-start - e.g., following emergency shutdown or a planned shutdown

Procedures should clearly state maximum and minimum safe operating limits for process conditions such as temperature, pressure, level, fluid flow, heater firing rate, heater stack gas composition, tank and vessel volume, and so on. Whenever an excursion outside of safe operating limits is detected, an investigation must be initiated to determine the root cause and implement appropriate corrective action to prevent the situation from reoccurring.

SOPs must be reviewed, updated and verified as accurate on a regular basis, e.g., at least every three years. SOPs for Critical Risk tasks should be reviewed and updated more frequently, e.g., annually. A review and update of an SOP may also be triggered other process safety practices, for example by a job task or safety observation, an equipment or process change, a Management of Change requirement, a process hazards review, a regulatory change or an incident investigation finding.

5.4.9 SAFE WORK PRACTICES

Safe Work Practices (SWPs) are different from Safe Operating Procedures (SOPs). SOPs are applicable to operating processing equipment. SWPs are intended to control hazards and manage risk associated with routine and non-routine work activities other than processing operations, including maintenance, throughout the entire life cycle of the operating equipment or process.

A specific SWP will typically address a procedure for conducting work safely in one of the following general areas:

- safe handling of hazardous materials – e.g., asbestos;
- use and care of personal protective equipment (PPE) – e.g., fall protection; or
- use and care of equipment or tools – e.g., hand tools;
- other specific safety procedures – e.g., hot work permits.

Table 13. Examples of Safe Work Practices

Safe Handling of Hazardous Materials	• Safe Handling of Asbestos • Safe Handling of *chemical name* • Safe Handling of *biological material name* • Hantavirus • Naturally Occurring Radioactive Materials (NORM)
Use and Care of PPE	• Respiratory Protection • Fall Protection, Restraint & Fall Arrest • Hearing Protection • Hard Hats • Footwear • Glove Selection • Fire Retardant Clothing (FRC)
Use and Care of Equipment or Tools	• Fire Protection (also part of PPE category) • Equipment Safeguards • Cranes and Hoists • Equipment Guarding • Hand Tools & Power Tools • Mobil Equipment • Vehicle Safety • Scaffolds • Monitoring & Detection Equipment

Other Specific Safety Procedures	• Electrical Safety and Grounding • Confined Space Entry • Laboratory Safety • Lockout & Tag Out • Safe Work Permits (Hot and Cold Work) • Safety Standby • Excavations & Locating Underground Utilities • Welding & Cutting • Working Alone • Waste Manifesting • Hazard Communications

For a given location, the relevant safe work practices required are dependent upon the specific hazards that must be controlled and tasks that are performed.

As with SOPs, all impacted personnel must be trained in each SWP for the location.

5.4.10 ASSET INTEGRITY AND RELIABILITY

The Asset Integrity and Reliability element of PSM is designed to prevent the sudden and catastrophic release of materials or energy by ensuring the continuous functionality of equipment and minimizing impacts of an operating failure. The element is focused on implementation of an inspection, testing and preventive maintenance (ITPM) program that also includes repair of any deficiencies found.

Perhaps the most important aspect is preventive maintenance which may be defined as scheduled proactive maintenance activities intended to prevent equipment failure by restoring equipment to fully reliable condition.

In a chemical processing facility, workers involved in purchasing, warehousing, inspection, and maintenance activities may all be impacted by the Asset Integrity and Reliability element of PSM. The activities apply generally to all types of equipment: pressure vessels, storage tanks, piping systems, relief and vent systems, emergency shutdown systems, control systems, pumps, compressors, turbine engines, turbo-generators, etc.

This may include labeling, positive materials identification, and verification that specifications are satisfied and consistent with design requirements.

As part of an effective preventive maintenance program, the location should develop a critical equipment list that includes equipment with moving or rotating parts, instrumentation and safety critical equipment. Each item on the critical equipment list should have its own detailed ITPM procedure. Where appropriate, checklists should be developed and used. In a situation where a manufacturer's maintenance manual exists, it should be supplemented as necessary with a company procedure that adds clarity to the procedure, references lockout / tag out procedures, provides a checklist with an area for sign-off, allows for a second sign-off for safety-critical systems, and so on.

Other, less critical equipment may be added to the ITPM program sometime after the program for critical equipment has been implemented.

ITPM scheduling should be based on a combination of known modes of failure and failure rates of similar equipment, knowledge of the specific item and its operability and the manufacturer's maintenance recommendations. The schedule should be incorporated into the work order system that the company uses, so that work orders are generated on the scheduled frequency for every ITPM activity.

ITPM procedures may be subject to updating as new information becomes available, e.g., results of audits, learnings from incidents, outcomes from Management of Change reviews, notifications from equipment manufacturers, etc.

5.4.11 CONTRACTOR MANAGEMENT

Historically, contract workers who are at a facility for short periods of time on an irregular basis to perform specialized services such as turnarounds have anomalously high incident rates. Some incidents involve only contractors, while others involve both contractors and facility personnel. In a chemical laboratory, a contractor may be a craft worker such as a plumber or an electrician. During a maintenance turnaround in a large facility, the contractor workforce may consist of a crew of several hundred workers.

In both cases, data has shown that contract workers who are unfamiliar with the hazards in their workplace are prone to making mistakes, which can lead to injuries and/or uncontrolled accidental releases of hazardous chemicals.

The purpose of the Contractor Management element is to ensure that contractors working on a company sites perform their work safely without introducing additional risk to other workers, the facility or the public. Considering the flammability and toxicity hazards of methanol, it is clearly very important that contractor work such as hot work or confined space entry be carefully managed in areas where methanol may be present.

Safe management of contract work starts before the contractor has been selected and continues on through to completion of the work. The appropriate steps the company take should include each of the following:

Screening / Pre-Approval

Prior to engaging a contractor to perform work, a client company should carefully screen the contractor to ensure that their safety record is acceptable, they have a safety program that meets minimum requirements of the client company and that they have an appropriate level of insurance and workers compensation should they be involved in an incident while on the client site.

The company may choose to develop its own contractor screening process or use one of several third-party contractor management systems widely available. In either case, the company must set its own acceptance criteria for hiring contractors.

Contractor Orientations and Training

Once a contractor has been screened and selected, contractor employees must undergo a site orientation and safety training. Each contract worker must have knowledge of the work that goes on at the facility and the specific hazards and chemicals present. He or she needs to understand the hazards and risks that they may face while on site and also the potential impact their work may have on others on the site.

Training should also include requirements and expectations of contractors while on site, such as conducting daily safety or tailgate meetings, recordkeeping, appropriate notifications to the client, incident reporting and investigation and emergency procedures.

A contractor orientation should be relevant for that site only. The company should establish a time frame for how frequently a specific contract worker must repeat site orientation and training.

Safe Work Permit

All contractor work should require a Safe Work Permit, regardless of whether it is hot work or cold work, in order to ensure that the contractor will not be exposed to unacceptable risk while working at the facility and that the contractor's work will not negatively impact other workers or equipment. Appropriate safeguards must be put into place for any potential risks identified through the permitting process.

All contractor Safe Work Permits should be automatically canceled at the end of the work shift for the facility employees. If the contractor's work needs to continue, a new Safe Work Permit should be authorized. This is because situations and potential hazards and risk may change with a change of shift. For example, a new work project may be scheduled for the second shift. A Safe Work Permit obtained during the first shift will not necessarily have considered any potential hazards that may be introduced by the new work project.

Work Oversight

While a contractor is working on a company site, company personnel such as Operations should continuously oversee the work of the contractor. This is done to ensure that the contractor continues to follow all of the safe work requirements of the company. It also makes it easy for a contractor to ask questions from a knowledgeable facility employee should issues arise during the work.

Work Assessment

A post-job safety review of a contractor's work should be conducted following completion of the contractor's work. This will provide valuable information to the company regarding the contractor's safe work practices which can be used for consideration of whether to hire the same contractor again in the future.

Contractor Audit

If the client company has sufficient resources, formal audits of contractor companies should be carried out. This will give the client a much better understanding of the contractor's capabilities, safety programs and safety performance. It is a good way of confirming the information revealed during the screening and pre-approval process described above. An audit can also confirm whether or not a contractor's safety programs at the company level are actually put into practice at the work site.

Through a contractor audit program, a company may develop an approved contractors list and have more confidence in the contractors that it hires.

5.4.12 TRAINING AND PERFORMANCE ASSURANCE

The objective of the Training and Performance Assurance element is to ensure that work tasks are consistently completed to minimum standards by competent personnel in accordance with accepted procedures and practices.

Training may be provided externally by third parties or in-house by knowledgeable personnel or subject matter experts. Training may be taken in a classroom setting, online, through hands-on exercises, as on-the-job training or some combination of these. Whatever format the training takes, a record of each employee's training as well as evidence of the employee's understanding of the training (e.g., a test result) should be maintained. The company should also determine the frequency at which refresher training should be taken for each type of training required.

For Operations, workers must be trained in understanding and applying written operating procedures. Whenever a Standard Operating Procedure (SOP) is created or modified, whether due to a new or updated process or as a result of changes required through a Management of Change process, workers affected by the SOP must be trained in the new or modified SOP. This training should be documented and the training records maintained.

Where an investigation of an incident indicates a deficiency in training, refresher training may be appropriate or training requirements may be modified. The appropriate action to be taken will be based on a combination of incident causes, training trends that may be identified and anticipated outcomes from actions.

A good practice is for management to develop a training matrix that identifies groups of employees (e.g., Operations, Supervisors, EHS), the training each member of each group is required to take, the date when training was completed and when repeat or refresher training is due. This will help with planning and budgeting for training as management will be able to see at glance any training that is due (or past due) for which employees.

5.4.13 MANAGEMENT OF CHANGE

An effective Management of Change (M)C) process ensures that equipment and operational changes are appropriately reviewed and authorized by safety and engineering personnel so that regulatory compliance, environmental protection and safety of plant personnel and operations are not compromised.

MOC addresses the issue of configuration management. Occasionally, it is necessary to modify the configuration of a process system in order to improve performance, reliability, or efficiency.

The MOC process should apply to changes made to any item as well as to installation of a new item including construction. For consideration within MOC, changes should include:

- modification, addition, replacement, relocation or removal of equipment, interconnections, instrumentation, materials and safety systems that is not a replacement-in-kind; and
- operational changes such as changes to a processor procedure.

The MOC process should apply to permanent, temporary and emergency changes.

Within the context of process safety management, there are two broad categories of equipment repair and replacement: replacement-in-kind and not-in-kind replacement.

Replacement-in-kind is any repair that substitutes for an existing item another part, component, or item (e.g., equipment, chemical, procedure, etc.) that meets or exceeds the design basis and fabrication specifications of the original part, component, or item. This can be an identical item or another item with the same design specification, as long as the replacement item does not adversely affect the function or safety of the item, related equipment or process. For the purposes of the MOC process, it does not constitute a "change".

Conversely, not-in-kind replacement is any repair or replacement that substitutes a part, component, or equipment item that does not meet the design basis and fabrication specifications of an original part, component, or item.

To provide some clarity, the following table shows numerous examples of not-in-kind replacements, i.e., changes that should require MOC review.

Table 14. Examples of Changes that Should Require MOC Review

Process Equipment Changes	• changing piping with new piping of a different diameter • changing carbon steel piping with stainless steel piping • temporarily replacing a centrifugal pump with a positive displacement pump • replacing a 4" pump with a 6" pump • replacing a standard 4" pump from one manufacturer with a standard 4" pump from a different manufacturer • replacing a metal wafered gasket with a Teflon gasket • building a new tank farm • adding a new storage tank • replacing a 750 bbl tank with a 1000 bbl tank

	• replacing a 750 bbl tank with a 750 bbl tank with a different design or different sizes and locations of fittings • demolishing an old tank • adding a new process • designing, building or acquiring new process equipment or a new layout for process equipment
Process Control and Process Changes	• changing the setting on a safety relief valve • raising the trip point on a high level alarm • field instrument modification that results in a change to the P&ID
Safety System Changes	• replacing a building sprinkler system with a CO2 system • changing the types of sounds on an audible alarm system • changing the color of an alarm light • relocation of a safety shower • process operation while safety systems are out of service
Infrastructure Changes	• relocating a building • building modifications that affect structural or safety features • building modifications that affect overall size • increasing the size of a chemical storage building
Operations and Technology Changes	• operating outside the safe operating limits specified in an SOP • temporarily bypassing a heat exchanger • rerouting process piping • changing the flow rate of a pump • introduction of new chemicals on site if it introduces a new hazard class, e.g., flammable, toxic, acidic, caustic • changing critical control software • changing a temporary installation or operation to a permanent one

Changes in Inspection, Testing, Preventive Maintenance or Repair Requirements	• lengthening an inspection interval • postponing a shutdown turnaround • reassigning certain maintenance tasks from maintenance personnel to operators • changing a piping thickness inspection method, e.g., ultrasonic to X-ray
Documentation Changes	• any modification that involves or results in a significant change to a controlled document (e.g., site drawing, process flow diagram, P&ID, shutdown key, operating and control philosophy, SOP, critical task procedure, emergency procedure) • substantial change to process knowledge

The general steps that an effective MOC process should include are as follows:

a. Identification of a desired or required change – Many changes, though not all, are identified by Operations.

b. Submission of a change proposal - The change proposal is submitted to the MOC Review team, which usually includes at least safety and engineering personnel.

c. MOC review and authorization - Authorization by the MOC Review team will usually include requirements that address environment, health, safety or engineering concerns identified during the review; the change is authorized pending completion of these additional requirements. Conversely, an MOC change proposal can be authorized without additional requirements if the review concludes that plans for effectively managing all relevant safety, environmental and engineering concerns are already in place. Finally, the MOC review team should have the authority to reject the change proposal if it is believed that safety, environmental or engineering concerns will not be able to be effectively managed.

d. Implementation of the change - The group that proposed the change can proceed with implementing it.

e. Filing of records – Completed MOC forms should be retained for future reference. Any drawings or other documents generated or modified during the change should also be retained.

f. Pre-Startup Safety Review (PSSR) – Whenever a piece of equipment or a process has been modified, replaced, is new or has been shut down for any reason, it is important that a PSSR is conducted to ensure that the equipment or process is safe to start up. (See section 5.4.14 below for more details.)

g. MOC Audit – An effective MOC process should include an audit process to ensure that all required steps of the process have been followed, requirements from the MOC Review team have been included with the change and documentation relevant to the MOC have been filed and are maintained. An MOC audit should also look for any changes that have been made without going through the MOC process. As with any audit process, MOC audits should be scheduled on a regular basis and include a sampling of all MOCs reviewed and changes implemented over a specific period of time.

In order to satisfy the requirements of this PSM element, the detailed MOC procedure should address the following considerations:

- The technical basis for the proposed change.
- Impact of the change on safety and health.
- Modifications to operating procedures.
- Time period during which the change will be in force (temporary or permanent).
- Authorization requirements for the proposed change.

Outcomes of the MOC process must include the following additional actions:

- Update process knowledge and safety information as required.
- Update operating, maintenance, inspection, and testing procedures as required.
- Inform and train operating, maintenance, inspection, and testing workers and contractors on the revised procedures.
- Maintain a written record of the above.

5.4.14 OPERATIONAL READINESS

An effective Operational Readiness process ensures that new, modified or shut down equipment or processes are safe to start up and that the organization is also ready. In order to determine the level of operational readiness, a pre-startup safety review (PSSR) is performed.

In the context of this PSM element, “start-up” is defined as the point when chemicals or energy are introduced into a system or processing equipment.

In addition to the overall purpose of Operational Readiness defined above, objectives of a PSSR may include, but are not limited to, verification that:

- construction tasks are complete, and construction activity has been terminated.
- construction and equipment meets design specifications;
- process control, emergency shutdown and safety systems have been tested;
- systems not yet ready for start-up remain isolated;
- equipment has been cleaned and flushed;
- safety, operating, maintenance and emergency procedures are in place;
- safety, operating, maintenance and emergency procedures are in place;
- emergency response equipment is in place;

- appropriate training for operation, maintenance and ER has been completed;
- applicable regulators are notified and permit documentation is in order;
- a process hazards review appropriate to the complexity of the process was performed and resulting recommendations completed;
- modifications followed the Management of Change (MOC) process;
- idled processes have not degraded; and
- process knowledge and safety information has been updated.

Seven situations have been identified where a PSSR should be performed prior to start-up:

a. start-up following routine maintenance;

b. start-up following a maintenance turnaround;

c. start-up following a temporary change;

d. start-up following a change to an operating facility;

e. start-up following a capital project;

f. start-up following an emergency shutdown; and

g. restart of a mothballed or idled process.

PSM regulations do not always require a PSSR for all of these situations. For example, US OSHA PSM does not require a PSSR following routine maintenance or for the restart of a mothballed process. However, it would be considered a best practice to have requirements in place to conduct some level of PSSR for these situations in addition to the other five.

The level of complexity of the PSSR will depend on the complexity of the equipment or process involved and the reasons for the shutdown that occurred. For example, a PSSR for starting up a new production process should be much more detailed than a PSSR following a simple repair of a pump.

For each start-up scenario, the company must develop an appropriate PSSR checklist to be used by the PSSR team during the review. The checklists should vary in complexity to correspond with the type of start-up. The company may find that having seven different checklists is not necessary, but that a very detailed checklist can be used for two or three situations (e.g., capital project, change to an operating facility), a medium level checklist can be used for a couple more (e.g., restart of a mothballed process) and a simplified checklist is appropriate for other scenarios (e.g., following routine maintenance, restart after an emergency shutdown). The CCPS provides examples of checklists for two different levels of complexity of a start-up.

The company must establish criteria for the situations where a PSSR is required and which checklist is to be used for each scenario.

Not only will the complexity of the PSSR process itself vary, but so should the diversity of the team that conducts the PSSR. The team for a simplified PSSR following routine maintenance may include only the maintenance worker that performed the repair and an operations supervisor responsible for the area in the process where the repair took place. However, the team conducting a PSSR following a significant change to a facility or process might include representatives from engineering, safety, operations, maintenance, instrumentation / I&E and equipment manufacturers.

A completed PSSR checklist is only one of several records that should be maintained by the facility.

At a minimum, the following records should be maintained:

- the completed PSSR checklist;
- the final report from the PSSR;
- records of action taken and work completed to address deficiencies identified during the PSSR; and
- records of any problems encountered during start-up following the PSSR (e.g., incident reports).

5.4.15 CONDUCT OF OPERATIONS

The purpose of the Conduct of Operations element is to ensure tasks are executed in a safe, disciplined and consistent manner and to describe responsibility and accountability for reliable work performance in accordance with approved procedures and work practices.

This is typically achieved through a combination of multiple aspects of facility operations and management, such as:

- consistent hiring practices (e.g., position descriptions, background checks, reference checks);
- safety orientations (for new workers, contractors and visitors);
- operator training;
- EHS and Process Safety Training;
- detailed safe operating procedures (SOPs) and safe work practices (SWPs);
- management provision of resources to facilitate operators' work;
- compliance with drug and alcohol policies;
- compliance with EHS and PSM program requirements;
- mentoring of new workers (until they are deemed competent to work without direct supervision);
- contractor management;
- incident reporting, investigation and corrective action;
- safety or job task observations;
- performance management;
- incident reporting, investigation and corrective action;
- safety or job task observations;

- performance management;
- operations progression or career development program;
- understanding the right to refuse to perform unsafe work;
- return-to-work program; and
- disciplinary program.

Most, if not all, of these issues are usually documented under other elements of the PSM system or elsewhere within the company's management systems. If that is the case, it would be a duplication of effort to have a standalone PSM document for Conduct of Operations that describes each of these issues in detail. It would be necessary to only include descriptions of those aspects not included somewhere else. However, particularly for auditing purposes and potential regulatory requirements, it may be desirable to have this element explicitly included in the PSM system as a document that points to where in the organization each issue is managed.

5.4.16 EMERGENCY MANAGEMENT

Despite our best efforts to eliminate incidents at our facilities, they do occasionally occur. Preparing for emergency situations and management of emergencies when they occur helps to minimize risk to people, the environment, equipment and facilities.

Good planning, preparation and training all help to minimize impacts when responding to an emergency situation. As part of emergency planning, the company should develop a process for identifying hazards and determining what might happen and where and how it might occur. As part of preparation, the company should install appropriate detectors and early warning devices and establish evacuation procedures, rendezvous points and headcount procedures. It is important to include mitigation measures, such as fixed fire monitors, sprinkler systems, deluge systems, automatic isolation systems, blast walls, and similar measures. These will help to contain, control, and localize damage. It is also important to inspect and test alarms, mitigation measures and safety systems on a regular schedule.

An emergency management plan should include both internal and external first responders (police, fire, emergency medical care). Internal response teams must be fully trained in emergency response procedures and have practiced through exercises and drills, so that they will be able to respond appropriately in the event of an actual emergency. External response teams can not only provide input to improve response plans, but if they are expected to respond to a facility emergency, they will need to be familiar with the facility layout and the company's emergency response plans. External response teams should be invited periodically to participate in company emergency drills.

There are a number of possible situations for which a company may need to have detailed emergency response plans, depending on facility operations. Possible scenarios from both the EHS and Process Safety perspectives include:

- Failure of critical equipment (e.g., transfer pump)
- Failure of a connection on equipment containing a hazardous material (e.g., flange)
- Failure of safety critical equipment (e.g., level measurement device)
- Over-pressure (e.g., piping rupture)
- Under-pressure (e.g., collapsed tank)
- Toxic or flammable gas release
- Chemical spill
- Fire
- Explosion
- Loss of life / serious injury / illness
- Property damage
- Vehicle accident
- Bomb threat
- Security breach
- Natural disasters (e.g., lightning strike, tornado, earthquake, flood, grass or forest fire, severe hail)

As part of emergency preparedness planning, a facility should establish its worst case scenarios for emergency situations. This would be in addition to basic scenarios involving individual situations as identified above. A worst case scenario may include multiple dependent emergency situations, e.g., a spill resulting in a fire and injuries. It may also consider broader area impacts, e.g., a blast zone beyond the facility property line or downstream / downwind impacts on neighbors.

Detailed procedures should outline step-by-step the actions to be taken in the event of a specific emergency. Documented emergency procedures not only are used as a training tool for new workers but help drive consistent and safe practices when responding to emergency situations. Emergency procedures should address all of the following:

- detailed response procedures for each potential emergency situation and worst-case scenario.
- description of who is trained and authorized to respond to each scenario.
- in case of equipment failure – safe shutdown of equipment or the process and isolation of chemicals and energy.
- in case of gas or vapor release – selection and donning of appropriate respiratory protection, control of the source of the release and air testing prior to entry into the area where the release occurred.
- in case of spill or leak – PPE required depending on the material released, control of the source of the release, spill control methods, material recovery procedures and remediation activities.
- in case of worker injury – stabilization of the injury, care of the worker, notification to external emergency responder if required, transportation to emergency services and securing of the incident area until an investigation can be completed.
- in case of fire or explosion – firefighting response, on-site assistance to third-party emergency responders, safe shutdown of equipment, energy isolation and securing of the fire or blast zone.

- notifications to external emergency responders, management, regulatory authorities, and neighbors (public and industrial, as required), including contact information and time frames for notification.

Emergency management plans should also include a section for dealing with the media. This should clearly indicate who has authority to respond to queries from and provide statements to the media. Only authorized company representatives should directly address the media. However, every person who may be involved with an emergency situation should have media training, at the very least to understand what they should or should not say if approached by a reporter on the scene of an incident.

Emergency planning and response is made easier when a company establishes a command and control center as well as communication capabilities necessary to assess the situation, coordinate responders, call for backup, and prioritize emergency medical care and first aid.

5.4.17 INCIDENT INVESTIGATION

Despite the best intentions, diligent prevention efforts, appropriate mitigation, and effective emergency response, incidents may still occur. Workers may be injured, the environment may become contaminated and equipment and facilities may be damaged or destroyed. Practices and procedures advocated by process safety can dramatically reduce the number and severity of incidents. However, it is unlikely that these practices will prevent every possible incident scenario from occurring.

Incident investigation is an essential element of an effective process safety management system. This element is designed to determine immediate and root causes of incidents, implement corrective actions to prevent recurrence of similar incidents in the future, share lessons learned and improve process and management systems across the organization.

The Incident Investigation process is applicable to all incidents and accidents that relate to:

- personal safety or health;
- the environment;

- process safety;
- equipment or property damage;
- transportation of materials or equipment;
- security;
- financial loss; or
- any other loss to the company.

The Incident Investigation process does not necessarily apply to all near misses due to limitations on resources available to conduct investigations. However, near misses with high potential should be investigated and a decision should be made to investigate a series of related near misses.

Incidents should be categorized based on severity and the response that is required. A structured incident investigation and process of root cause analysis should be implemented. Corrective actions should be developed that address the root causes and that are aimed at preventing recurrence.

Numerous sources of potential incidents are monitored on a regular basis, particularly at operating locations. Sources may include, but are not limited to, the following:

- equipment failure
- equipment damage
- unplanned equipment or process shutdown
- operating parameter excursions
- non-routine pressure relief
- leaks or spills
- emissions
- slips, trips or falls
- injuries
- illness
- wearing of PPE

- safety observations
- housekeeping
- emergency system activation
- neighbor complaints
- customer complaints
- regulatory inspections with negative findings
- compliance with regulatory requirements
- employee concerns
- SOPs or SWPs not followed
- MOC process not followed

In general terms, the incident investigation process should consist of the following steps:

- reporting of the incident;
- identification of Investigation Team members;
- conducting the investigation;
- analysis of investigation findings, the facts relating to the incident;
- determination of causation, immediate and root causes;
- preparation of an investigation report with recommendations;
- sign-off by the Investigation Team; and
- investigation report distribution.

Reporting an incident should occur as soon as practicable following discovery of the incident. Companies should develop requirements for timelines for reporting incidents and to the persons, groups or agencies that must be notified for each type and severity of incident.

An incident investigation should be initiated as soon as possible after the incident has been reported. This increases the likelihood that evidence remains undisturbed and memories of events are fresh.

Staring the investigation within 8 hours would be a best practice. The duration of an investigation should not be extended beyond a reasonable time. Many companies expect an investigation to be completed within one week, except where extenuating circumstances justify a longer time frame.

When putting together the investigation team, the following people should be considered for inclusion:

- persons knowledgeable in the process, e.g., operators
- workers involved in the incident, including contractors
- EHS and Process Safety personnel
- a manager responsible for the area where the incident occurred
- persons trained in investigation and interviewing techniques
- persons or consultants trained in air dispersion modeling, fire modeling, explosion modeling, and failure analysis

Recommended corrective actions identified in the investigation report should be addressed in a timely manner by the appropriate department or group for each recommendation. The company should develop guidelines for corrective action completion timelines.

The investigation report should be reviewed with all employees and contractors whose job tasks may be relevant to the findings, as well as managers and supervisors for the impacted areas. Lessons learned should be shared with all employees and contractors at the facility and at other facilities within the organization.

Incident investigation reports should be retained on file.

Once a company has accumulated sufficient data from incidents, the company should develop a process for incident trend analysis. While individual incident investigations can identify causes for specific incidents and develop corrective actions to prevent recurrence, trend analysis can identify systemic deficiencies that can result in a series of related incidents. Incident trend analysis is more likely to lead to broad improvements to EHS and process safety management systems.

5.4.18 MEASUREMENT AND METRICS

PSM metrics provide information regarding actual system performance, as opposed to intended performance. Metrics afford management the opportunity to investigate and correct system deficiencies that might otherwise go unnoticed for some time until a serious failure occurs.

The Measurement and Metrics element is designed to assist a company with development of performance indicators to monitor the effectiveness of the process safety management system and identify deficiencies before incidents occur.

A combination of both leading and lagging indicators may be the best way to assess system effectiveness. Lagging indicators, such as incident rates, are important but they provide information on performance-related issues that have already occurred. However, leading indicators, such as how often a safe operating procedure has been bypassed, provide information that can be used to prevent incidents from occurring.

Metrics can be created for each PSM element or a company can develop metrics that cover the entire system. The company can address metrics in a standalone element within their PSM system or it can embed metrics directly into each individual element in the system.

The following table presents some examples of basic PSM metrics for each of the elements in a process safety management system. Many more suggestions for appropriate metrics are made by the Center for Chemical Process Safety [34. 36].

Commit to Process Safety	
Process Safety Culture	• Number of meetings per year attended by senior management where process safety is discussed • Number of site visits per year made by senior management
Compliance with Standards	• Number of incidents with causes related to regulatory non-compliance (per month / quarter / year) • Number of incidents with causes related to non-compliance with codes or standards of practice (per month / quarter / annually)
Process Safety Competency	*(Because the degree of organizational competency reflects the effectiveness of individual process safety practices, metrics specific to competency may not have to be developed. A company might determine that analysis of metrics from each of the other PSM areas gains an understanding of overall competency.)* • Number of incidents where basic chemical properties that caused an incident were not known to the organization • Number of incidents where safeguards implemented following previous incidents have lapsed
Workforce Involvement	• Percent of employees trained in Workforce Involvement and their responsibilities • Results of employee surveys regarding worker acceptance of process safety responsibilities
Stakeholder Outreach	• Number of complaints or objections received by each operating location • Number of planned outreach events held
Understand Hazards and Risks	
Process Knowledge Management	• Number of corrections or updates to P&IDs and other process safety information identified during process hazard analyses or Management of Change (MOC) reviews • Number of findings from PSM audits indicating inadequate or incomplete

Hazard Identification and Risk Analysis	• Percentage of hazard review recommendations not closed by their target completion dates • Percentage of hazard review recommendations for each type of control: inherently safer alternatives, engineering control, administrative control and use of PPE
Manage Risk	
Operating Procedures	• Number of incidents with causes related to operating procedures – missing, inadequate, unavailable or unclear • Number of incidents with causes related to a worker not following procedures
Safe Work Practices	• Number of SWP-related injuries • Number of Safe Work Practices past due for review and update
Asset Integrity and Reliability	• Number of incidents with root causes related to asset integrity and reliability
Contractor Management	• Percentage of incidents and near msises that had root causes related to contractor activities (monthly / quarterly / annually) • Percentage of scheduled preventive maintenance tasks that were completed on time
Training and Performance Assurance	• *(For a company with multiple locations)* Number of operating locations without a training matrix in place • Percentage of planned training that is past due
Management of Change	• Number of MOCs received but not reviewed during the subsequent MOC Review meeting due to insufficient information provided to the review team • Number of MOCs received but not reviewed during the subsequent MOC Review meeting due to unavailability of appropriate reviewers
Operational Readiness	• Number of deficiencies found and corrected during each PSSR • Number of incidents that occurred during start-up due to causes that should have been identified by the PSSR

Conduct of Operations	• Number of incidents involving new employees • Percentage of planned site inspections completed on time
Emergency Management	• *(For a company with multiple locations)* Percentage of operating locations with up-to-date emergency response plans • Number of planned drills or exercises conducted as per requirements
Learn from Experience	
Incident Investigation	• Number of Process Safety incidents by severity level • Percentage of all incidents that are Process Safety incidents
Measurement and Metrics	• Number of PSM elements for which metrics are in place • Number of metrics for which data are being collected
Auditing	• For a given audit, the percentage of corrective actions that are not completed by their due dates
Management Review and Continuous Improvement	• Number of Management Reviews held (annually) • Number of repeat findings from Management Reviews

5.4.19 AUDITING

The purpose of PSM auditing is to evaluate the process safety management system in order to determine whether required elements are in place, requirements are actively managed and practiced and the system is effective.

Rather than try to audit the entire PSM system at one time, it may be more effective to break it down into separate audits of each PSM element. Either way, each element of the PSM system should be audited on a regular cycle, e.g., at least every three years if not more frequently.

The company should develop a multi-year audit plan that indicates when audits of the PSM elements are scheduled, when they when they are completed and when the next round of audits is due. For a company with multiple operating locations, the overall audit plan should indicate which facilities will be audited during each year.

To facilitate the audit, audit protocols (questionnaires and/or checklists) should be developed for each PSM element. The audit protocols should include references to the requirements behind each question or checklist item. Audit protocols should be modified as necessary for a specific audit, e.g., new questions added and non-relevant questions deleted.

PSM audits should be scheduled and carried out by a team of employees, contractors and consultants with the following qualifications:

- technical knowledge of the process;
- knowledge and familiarity with the facility, management organization, and functional department tasks and responsibilities; and
- training and experience in safety auditing.

Auditor training can be conducted in-house by another trained, experienced auditor. Auditors should also be trained in the PSM audit protocols and how to use them effectively. As well, auditors should be independent of the processes being audited.

The audit should follow a common auditing format which consists of the following key steps:

- hold an opening meeting with the audit team and the auditee;
- perform documentation reviews;
- conduct interviews;
- conduct facility and equipment inspections, as appropriate;
- perform information verification activities, as necessary;
- for a multi-day audit, hold a close-out meeting with the audit team and the auditee;
- at the end of the audit, hold a close-out meeting with the audit team and the auditee;

- follow-up on any missing information to confirm findings, as required; and
- finalize the audit report and send to the auditee and any other key personnel (e.g., appropriate management).

All audit findings must be able to be substantiated through interviews, observations or document reviews. Before finalizing each finding, the audit team should discuss the finding and analyze for underlying causes and systemic trends. Audit findings may not only identify deficiencies or gaps but they may also be positive observations relating to effective PSM practices or implementation of the PSM system. These should also be documented by the audit team and included in the audit report.

The written audit report provided to the auditee should assess strengths and weaknesses in the various PSM elements. Audit reports must be retained in an appropriate file. The company should promptly respond to each of the audit findings. Appropriate personnel should be assigned responsibility for developing practical corrective actions to address findings from the audit. An overall corrective action plan should be developed and monitored until all actions have been completed. Any changes necessary to the PSM system, operating procedures, process knowledge, etc., as a result of audit findings and corrective actions must be made in a timely manner. All deficiencies and corrections must be documented and retained on file for future reference.

5.4.20 MANAGEMENT REVIEW AND CONTINUOUS IMPROVEMENT

Direct involvement by management in the PSM system is critical to having a positive process safety culture, ensuring that people with the appropriate levels of authority can make knowledgeable decisions that will enable continuous improvement in safety performance and fostering buy-in and participation from employees across the organization.

Review of performance and effectiveness of each PSM element, as well as the overall system, is an essential aspect of management involvement. Several levels of management should be involved in reviews, from the supervisor directly managing someone with day-to-day responsibilities within the system to senior management of the organization.

The person with assigned responsibility for day-to-day oversight and management of the overall process safety management system should monitor and review all PSM metrics on a regular basis and analyze for trends that may indicate deficiencies in the process. He or she should also identify opportunities for improvement and work with the appropriate groups and personnel to develop corrective actions to improve practices.

The same responsible person should prepare periodic reports for review by senior management (and other levels of management) regarding the status of the overall PSM system and each of the elements. The reports should provide information on deficiencies identified, improvement actions taken and the outcomes from corrective actions. The reports should include an overall assessment of the health of the process.

Management review should be an ongoing process. The frequency of reviews will likely vary with management level. Line managers may be reviewing PSM performance on almost a daily basis, while senior management may conduct reviews of the system on an annual basis. For continual involvement and to stay up-to-date, a suggestion for senior management is to schedule a formal review of one or two PSM elements each month so that all elements of the system are reviewed annually. Management should conduct reviews with an aim to identifying opportunities for improvement of the PSM system and providing feedback to those with day-to-day responsibilities for PSM activities and management. Management review should focus on answering three key questions:

1. What is the quality of our program? (How robust is it?)
2. Are these the results we want? (Is our performance where we want it to be?)
3. Are we working on the right things? (Is our focus in the right place?)

Communication of outcomes from management reviews is critical to improvement, especially to those responsible for implementing corrective actions. A report of every management review should be prepared and shared with appropriate personnel, if not with all employees in the organization. Management review reports should be maintained on file for future reference.

5.5 IMPLEMENTING PROCESS SAFETY

A key step in managing safety is to identify the risks posed by manufacturing, transferring, transporting, and inventorying methanol. This allows safety to be designed into the process. The risk assessment can be done as part of a PHA. This section describes the major steps in conducting a PHA. Additional information for conducting a PHA for methanol is presented in the glossary and in the appendix.

As an example of a very simple risk assessment, let us compare the hazardous properties of methanol to gasoline, the most widely used fuel, which is also volatile and flammable. Methanol's physical and chemical properties provide users with several fire safety advantages compared to gasoline. Methanol has lower volatility, lower vapor density, a lower heat release rate, and a lower flammability limit than gasoline. The United States Federal EPA states that "These properties together make methanol inherently more difficult to ignite than gasoline, and less likely to cause deadly or damaging fires if it does ignite."

Other important differences should be recognized. Methanol can ignite at ambient temperatures in enclosed spaces, such as fuel tanks. This is in sharp contrast to gasoline, which produces such a large volume of vapor that the concentration can readily exceed the upper flammability limit. This particular hazard necessarily would be addressed in fuel tank design and location to ensure that tanks storing methanol are isolated from all foreseeable ignition sources. Toxicity is another consideration of methanol. The odor threshold for methanol is above the allowable exposure limit. This means that methanol's concentration may be at or above toxic levels before most people detect the odor.

5.5.1 WHAT IS A "HAZARD"?

The term “hazard” is a commonly used word. Within the context of risk assessment, the term has a specific meaning. As used in this manual, a hazard is a threat that is posed by a substance as an inherent physical or chemical characteristic of that substance. Typically, hazards are classified by type. Chemical hazards are classified by the nature of the threat posed by presence of the chemical: fire if the chemical is a flammable liquid, toxicity if the chemical is known to be poisonous, reactivity if there are other chemicals that react violently with the subject material, chemical or thermal instability if the chemical is known to decompose spontaneously under certain circumstances, and chemical incompatibility if mixing the chemical with another chemical increases a known hazard or manifests as an additional hazard. For example, methanol is classified as flammable and toxic. Persons handling, using, or storing methanol must take precautions to protect themselves and others from these hazards. It is also necessary to protect methanol from exposure to ignition sources and to wear personal protective equipment (PPE) when handling or working near inventories of methanol.

Because a hazard is a property of a substance that is characteristic of that substance, the hazard is removed when the substance is no longer present.

5.5.2 WHAT IS A "RISK"?

The term “risk” is commonly used and is subject to misinterpretation. As used in this guide, the term “risk” has a very specific meaning: the frequency, likelihood, or probability of a sequence of events that terminate in a negative or damage-inflicting consequence. A consequence is a manifestation of a chemical hazard. Mathematically, risk is calculated as the product of event frequency (or probability) multiplied by a measure of consequence severity.

The risk of a particular consequence, such as an explosion, is the probability of an explosion (for example 10% in a 10-year period, which is equal to 1% probability per calendar year), multiplied by the severity of the consequence, for instance, $20 million per occurrence. In this example the risk burden carried by the facility as an expected loss is $200,000 per year ($20 million x 0.01), less whatever amount is covered by insurance.

If management decides a risk of $200,000 per year is unacceptably high, then the risk can be lowered by implementing additional protective policies and procedures that reduce the likely frequency of that particular incident. If the facility performs PHAs and identifies additional explosion scenarios, the risk of explosion of some number of scenarios must be reduced with additional safeguards. The choice of which scenarios to safeguard against is based on cost benefit. The question is, “Which scenarios provide the greatest reduction in risk for the least expenditure?”

5.5.3 HAZARD IDENTIFICATION AND RISK ASSESSMENT METHODS

The first step in conducting a hazards review is to assemble and review information pertaining to the materials, their hazards, the technology of the process, and the design basis and condition of the equipment.

The second step is to determine which hazard review methodology to use. A variety of hazard identification and risk assessment methods are available, ranging from “What If” assessment, involving a group of persons familiar with the circumstance, to a rigorously structured quantitative Layers of Protection or Fault Tree Analysis.

The third step is to conduct the review, making recommendations to add safeguards as necessary and appropriate to satisfy management criteria. All aspects of the hazards review should be documented, including the list of recommendations.

A report is subsequently prepared and the recommendations either are implemented or discussed further; after possible further discussion, the recommendations either are revised or rejected. The risk of a particular consequence is assessed before and after implementation of the recommendation. In general, engineering safeguards are expensive and reliable. Administrative safeguards are inexpensive; however, they are subject to much lower reliability, especially over time.

Appendix B provides detailed information pertaining to the physical, chemical, and thermodynamic properties of methanol, its reactivity, and associated manifestations (thermal stability, chemical stability, incompatibility, and corrosivity). It includes a list of the types of documents that contain important information regarding the technology and equipment of the process.

Many hazard-labeling systems are used worldwide. Some of the more common systems include the United Nations system, the NFPA system, the U.S. Department of Transportation system, and others from the European Community.

5.5.4 PROCESS HAZARD ASSESSMENT DOCUMENTATION

Process hazard assessments must be documented. Documentation should be preserved throughout the life of the facility. In general terms, the documentation should indicate what information was reviewed, what questions were asked, what hazards were safeguarded against, how the scenario was developed, what the accident scenario consisted of, what corrective action was selected, and the effectiveness, reliability, maintainability, availability, and benefit/cost of the corrective action.

6 FIRE SAFETY

For safe handling of methanol, all the fire risk barriers need to be addressed with proper account to the particularities of the fuel. This chapter is initiated by a section on Methanol Fire Characteristics, focusing on flammability and burning behavior in comparison with for example gasoline and diesel. With account taken to these characteristics, sections follow on the barriers prevention, detection, and control. Important measures for Fire Prevention are discussed with focus on vapor control and removal of ignition sources, in particular for storage tanks. If preventative measures fail, it is preferred to have a methanol fire over an explosion event. The conditions affecting the potential for a methanol Fire or Explosion upon ignition are discussed separately, followed by a section on the possibilities for methanol Fire Detection. Early detection is crucial for an immediate and effective response, described in the section Fire Control. It includes recommendations for manual response and fixed fire-extinguishing installations, as well as elaborations on their effectiveness. A section is also given on Fire Ground Safety, providing fundamental recommendations for how to safely respond to a methanol spill and fire.

As for prevention, detection, and fire control, an appropriate response depends on the characteristics of the fuel. It should be noted that the physical and chemical properties of methanol and methanol-blended fuels are distinct from one another. An appropriate response to a methanol fire may for example not be an appropriate response to a methanol-gasoline fire. The focus of this chapter is fire safety of pure methanol, but a section is also dedicated to fire safety of methanol- gasoline blended fuels, at the end of this chapter.

6.1 METHANOL FIRE CHARACTERISTICS

The simplicity of the methanol molecule makes it a special fuel in many ways, not least with consideration to fire characteristics. These are discussed below, with starting point in flammability and burning behavior.

6.1.1 FLAMMABILITY

In a fire it is the vapors that burn. Methanol is liquid at normal conditions but releases vapor depending on its temperature. At 68 °F (20 °C), methanol has a true vapor pressure of about 100 mm Hg, which for example means that it releases more vapor than diesel but less than gasoline. The flammability of a fuel depends on this tendency to release vapor in combination with its flammability limits; these define the concentration range where the vapor can burn in air. Below the lower flammability limit, sustained combustion will not take place as the fuel air mixture is too lean. Above the upper flammability limit the mixture is too rich and combustion is quenched. The flammability range of methanol is 6–36 vol%, versus 1.4–7.6 vol% for gasoline and 1–6vol% for diesel. Hence, the flammability range of methanol is relatively high (associated with the oxygen in the molecule) and more fuel vapor is thereby needed to reach the concentration representing the lower flammability limit.

The lower flammability limit in combination with the tendency to release vapor can be translated to the temperature at which sufficient vapor is generated above the liquid to enable ignition. This temperature is referred to as the flashpoint. A more specific definition of flashpoint is: the lowest temperature at which the application of an ignition source causes the vapor of a test portion to ignite and the flame to propagate across the surface of the liquid under the specified conditions of the test. This is an important temperature and the UN globally harmonized system for classification and labeling of chemicals (similar to e.g. NFPA 30) therefore uses the flashpoint to classify flammable liquids. If the flashpoint in a closed-cup test is below 23 °C (73 °F) the liquid is classified as *Highly flammable* and if it also has a boiling point below 35 °C (95 °F) it is classified as *Extremely flammable*. Methanol has a flashpoint of 11 °C (52 °F) and boils at 65 °C (149 °F) and therefore falls in the category Highly flammable (corresponding to NFPA class IB), along with for example gasoline with a flashpoint of -43°F. Diesel has a flashpoint of €140 °F and is therefore not classified as flammable but as *Combustible*.

If the whole flammability range is translated to temperatures, methanol burns between 52–106 °F, versus -45–14 °F for gasoline and 140–300 °F for diesel. This means that the vapor above liquid methanol in a container is in the flammable range at normal liquid storage temperatures, while gasoline is generally too warm and diesel is generally too cold to be in the flammable range. It also means that an open pool of diesel is too cold to generate sufficient vapor for ignition at normal temperatures whilst methanol and gasoline are ignitable. Since normal temperatures can be far above the flashpoint, so much vapor can be generated for these fuels, in particular for gasoline, that the lower flammability limit is reached far from the pool surface. Ignition could hence cause a flash fire, especially when large quantities are present.

Methanol vapor is near neutral in buoyancy and prone to follow air movements. However, this depends on the temperature. Relatively warm temperatures can generate a vapor plume while low temperatures can cause accumulation in low areas. Accumulation of vapor is common also for gasoline, which is significantly heavier than air. Both gasoline and methanol are therefore considered to present explosion hazards in confined spaces.

With regards to explosion properties, gases and vapors are commonly classified in Explosion groups (IIA-IIC) and Temperature classes (T1- T6). Methanol is listed in the least hazardous group IIA, depending on the maximum safe gap (affecting the required flame arrestor) and the minimum ignition current (affecting the selection of safe electrical equipment). Methanol is also listed in the least hazardous temperature class T1, due to its high auto-ignition temperature. This describes the lowest temperature a surface must have to cause spontaneous ignition to adjacent fuel vapors, i.e. non-piloted ignition in contrast to the flashpoint. The auto-ignition temperature of methanol is about 850 °F, which is higher than of for example gasoline (~500 °F) and diesel (~600 °F).

In summary, methanol releases vapor depending on the temperature and when reaching 52 °F (its flashpoint), sufficient vapor is released to allow ignition above a methanol surface. Higher temperatures can allow ignition far from the liquid, causing a flash fire, and vapor can also be accumulated. Similar to gasoline, methanol therefore presents an explosion hazard in confined spaces, classified in the least hazardous explosion categories.

The vapor in a container with methanol is flammable at normal temperatures, which is not the case for e.g. gasoline (too rich) and diesel (too lean).

6.1.2 BURNING BEHAVIOR

All fires release heat, and most fuel fires display flames and generate a lot of heat and smoke. Fires involving pure (neat) methanol are not like most encountered fires. Methanol fires produce less heat, transfer less heat to surroundings, and are difficult to see. These particularities are associated with that methanol is combusted efficiently and produces little residual products, i.e. soot. Luminous soot particles usually give a yellow color to diffusive flames. Without soot, methanol burns with flames which are weakly light blue in color and nearly invisible to the naked eye in daylight. Furthermore, since there are no black residual soot particles present, there is no smoke.

In comparison with many liquid fuels, methanol has a low total heat of combustion of 19 kJ/g (gasoline: 38 kJ/g, diesel: 40 kJ/g, heptane: 41 kJ/g, ethanol: 25 kJ/g). How this heat is transferred is also influenced by the absence of soot production in a methanol fire. Most flammable liquid fires transfer a large amount of heat through radiation from the flames. A heptane pool fire for example transfers 36 % of the heat by radiation (and the rest by convection, i.e. heating up surrounding gases/air), but methanol only transfers 15 % of the heat by radiation. This applies also to spray fires.

The radiation has been measured from small and large methanol pool fires, up to 540 ft2. The largest pool fire showed that the radiative heat flux at a distance of 6.6 ft. was about 10 kW/m2 (40 kW/m2 results in instantaneous death, 10 kW/m2 results in pain after 3 s skin exposure, 5 kw/m2 is typically a safe exposure level). This is very low, also compared to the 20 kW/m2 measured from a corresponding M15 pool fire. In tests with a 43 ft2 methanol pool fire, the radiative heat flux at 6.6 ft. was 2.6 kW/m2 for methanol and 18.1 kW/m2 for M15.

The heat radiation is largely affected by the distance to the object and the flame temperature, but also by present smoke. Most fuels burn with smoke, which blocks radiation from the center of the flame and only allows the flame perimeter to radiate. This is often expressed as a decrease in the radiative fraction with the pool size (diameter). For most fuels the radiative fraction is constant (0.35- 0.45) for small pool sizes but decreases rapidly above pool diameters of about 7 ft. The decrease is dramatic and for pool diameters of 20 m the radiative faction is about 5-10%. However, for ethanol, which burns with luminous flames but without much smoke, radiation can be transmitted from the full thickness of the flame and the radiative fraction is almost independent of fire size. This causes a larger radiative heat flux from ethanol than from gasoline in large fires, while the opposite applies in small fires. Hence, extrapolations cannot be made for alcohols (and particularly methanol) in the same way as for other fuels.

Radiation is also important since it affects the mass loss rate of the fuel (vaporization) and thus the intensity of the fire. Another parameter affecting the mass loss rate is the ability of the liquid to absorb the heat radiation. Ethanol, which in many ways is similar to methanol, has a high absorptivity of 90 % (heptane for example absorbs 65 %). Since the radiation towards the fuel surface increases with the fire size, so does the mass loss rate (per unit area). Mass loss rates for methanol pool fires have been proposed to range between 0.013-0.029 kg/m2s but for moderately sized pools (50-500 ft2) it is relatively constant around 0.025-0.026 kg/m2s. This can compare to mass loss rates of up to 0.036 kg/m2s for diesel, 0.062 kg/m2s for gasoline, and 0.081 kg/m2s for M15. The relatively low mass loss rate of methanol in combination with the low total heat of combustion results in a theoretical heat release rate per unit area of about 475- 500 kW/m2 (measured values are generally about 425 kW/ m2). This can compare to about 1 400 kW/m2 for diesel and about 2 300 kW/ m2 for gasoline.

In summary, methanol burns efficiently without luminous flames or smoke. The low total heat of combustion and lack of luminous flames make radiation from methanol fires very low. The radiative fraction is about 15 % and likely independent of fire size (i.e. does not decrease for fires above 7 ft. as for most fuels) since radiation is not blocked from smoke. The mass loss rate (per unit area) of a methanol fire increases with the pool area but is relatively low. In combination with the low total heat of combustion it can generate a heat release rate of about 475 kW/m2, which is about 1/3 compared to diesel and 1/5 compared to gasoline.

6.2 FIRE PREVENTION

Methanol fire and explosion can fundamentally be prevented by controlling the fuel vapor and by removing ignition sources. Measures for managing these strategies are elaborated below.

6.2.1 VAPOR CONTROL

To prevent a methanol fire or explosion, the vapors can be controlled in different ways. The ultimate measure would be to remove formation of methanol fuel vapor (above the lower flammability limit) by reducing the liquid temperature below the flashpoint, 52°F. This is although generally more costly than to control the vapor inside the tank and the vapor emitted from the tank. Such measures are further described below, along with safety features to detect methanol vapor and to prevent methanol involvement in case of tank fire exposure.

6.2.1.1 STORAGE SAFETY FEATURES

Best practice for tank storage of methanol in large volumes uses internal floating roof tanks to minimize the methanol vapor space within the tank and reduce the amount of air that is available to mix with the vapor. It is also necessary to control the vapors that are emitted from the tank by equipping tank vents with flame arresters (unless the vapor space of the tank is padded with an inert gas; see below). It is important to verify that the flame arrester components are not fabricated from aluminum alloy. Methanol is corrosive to aluminum alloys and an instance has been reported where a failed flame arrester caused a tank fire after releasing excessive vapor. The flame arrester had aluminum alloy components that degraded and failed over a 13-year- period. Clearly, facility preventive maintenance was also insufficient.

Another way to control the vapors in a methanol storage tank is by inert gas blanketing or padding. It adds an additional level of protection against ignition within a tank vapor space and also avoids flammable vapors from being emitted from the tank. This measure is particularly relevant if normal temperatures of a fuel can cause the vapor concentration within the freeboard volume of the tank to be within the flammable range. For this reason padding is relevant for methanol but it is for example also used in gasoline storage tanks.

Using nitrogen as the blanketing inert gas for methanol will also add the advantage of preserving its purity. Nitrogen is free of carbon dioxide, which with methanol can cause corrosion in the presence of moist or salty air. To avoid product contamination that could increase the methanol acidity and corrosivity, dry nitrogen is therefore the preferred gas for blanketing methanol.

Furthermore, the outside of methanol tanks should be painted with heat reflecting paint, which will reduce vaporization and losses from the tanks. It is also recommended that ignition sources are strictly controlled within the proximity of methanol storage, regardless of whether the containment is in tanks or portable containers. Storage areas are furthermore recommended to be ventilated and to have clear labeling, bonding, and grounding of containers.

6.2.1.2 PRESSURE RELIEF SYSTEM

Tank internal pressure can be controlled using pressure relief/vacuum breaker valves. Vents may or may not be configured with flame arresters, depending on the specific circumstances; however, arresters are the preferred configuration.

Pressure relief valves should be sized to a fire case and, if possible, should be piped to relieve into a flare header. If configured to relieve to the atmosphere, then it is strongly recommended that Process Safety Valves (PSVs) are configured to breathe to the atmosphere through flame arresters. In addition to fire safety, it is recommended that local regulations for limiting hydrocarbon emissions are considered when configuring tank vents and pressure relief devices.

Overflow pipes are not recommended. Methanol liquid is known to collect and drip from overflow pipes when the ambient temperature is below the storage temperature. Any accumulation of condensed liquid methanol in the bermed area creates a fire hazard and may qualify as an environmental release.

Storage tanks, tanker trucks, rail cars, and portable containers are all subject to BLEVE. Safety precautions should be established that are cognizant of overpressure, radiant heat flux, and toxic exposure hazards.

6.2.1.3 GAS DETECTION

The flashpoint of methanol makes it likely that a methanol leakage in a space can vaporize sufficiently to be ignitable. A gas detection system is therefore valuable to detect such a leakage. Since the density of methanol vapor is only slightly higher than that of air (1.1 relative air) the vapor can follow the air movements. However, if the methanol is warmer than the ambient air it may rise, and if it is colder it may accumulate in low areas. This affects the positioning of gas detectors in a space. Positions close to potential leak points as well as positions in the ceiling and in the ventilation system should for example be considered, as well as positions in surrounding low points.

Detection of methanol vapor can be achieved by several different technologies. Some technologies are more suitable for toxic gases and others for flammable/explosive gases. In general, toxic gas detection needs more sensitive detectors since toxic exposure limits are often much lower than the lower flammability limit of a vapor. A gas detection system could thus be installed for several purposes.

A gas detection system can be designed to give both toxicity and flammability warning and should give alarm well before reaching toxic levels or the lower flammability limit. Appropriate actions upon methanol gas detection are increased ventilation and stopping of any methanol handling operations. A water mist fire-extinguishing system could also be activated as a precautionary measure.

6.2.2 REMOVAL OF IGNITION SOURCES

Methanol fire and explosion can be avoided by removing potential ignition sources to a safe distance from the area in which fuel vapor may be present. This is generally done by declaring areas surrounding fuel storage and handling as hazardous locations. The area is determined by how far a vapor concentration of the lower flammability limit can be expected. Some guidelines for such areas are:

- Smoking must be restricted to a designated location that is free of potential methanol vapor.
- Vehicle access must be strictly controlled and enforced.

- Use of non-sparking tools is highly recommended.
- Radios, telephones, portable instrumentation, computers, calculators, and other electronic equipment should have explosion-proof ratings for use in a methanol containment area.
- As a rule of thumb, at least 20 feet (7 meters) of “no ignition source” perimeter should be allowed around storage areas containing individual, small volume containers of methanol (e.g., cans, buckets, barrels, and totes). At least 50 feet (17 meters) of “no ignition source” perimeter should be allowed around storage and logistics areas containing and/or handling larger volumes of methanol (e.g., individual tanker trucks, rail cars, and small storage tanks). A minimum of 200 feet (70 meters) of “no ignition source” perimeter should be allowed for logistics terminals that simultaneously load or unload multiple trucks, multiple rail cars, barges, ships, and large-volume storage tanks. The adequacy of hazard zone perimeters should be verified.
- In the event that a tanker truck, rail car, or storage tank is involved in a fire, evacuation should proceed to a distance of at least one-half mile (850 meters) in all directions. Methanol is toxic; it should be noted that the odor threshold of methanol is well above the toxic exposure limit and that structural fire fighters’ protective clothing does not offer effective protection in responding to methanol spills and fires[6].

6.3 FIRE OR EXPLOSION

If ignition of methanol occurs, then combustion will ensue as either a fire or an explosion. The route by which ignition is manifested depends on ambient temperature, the energy of the ignition source, whether the vapor has traveled as a near-neutrally buoyant dense gas, and whether accumulated vapor is confined or unconfined. If the ambient temperature is above the flash point, and if there is a large amount of vapor space in a container, tank, room, building, or enclosure, then flashback and explosion are likely. If the ambient temperature is below the flashpoint, if potential ignition sources are low energy, and if vapor can readily dissipate to the atmosphere, then explosion is less likely.

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[6] Refer to 2008 Emergency Response Guidebook for additional guidance.

6.4 FIRE DETECTION

Combustion of a substance generates carbon dioxide, water, soot, and heat. Something that distinguishes methanol from most solid and petroleum-based fuels is the amount of soot produced at combustion. Soot particles are a result of incomplete combustion and make the smoke black and the flames luminously yellow. From a detection point of view, soot thereby provides easily recognizable fire signatures for automatic and manual (human) detection. Methanol gives a very "clean" combustion and detection advantages of soot do not apply. For early detection of a methanol fire, measures can instead monitor signatures such as heat, electromagnetic radiation, or gases. Different measures for fire detection are discussed below from a methanol fire perspective, divided into automatic and manual measures.

6.4.1 AUTOMATIC FIRE DETECTION

Smoke, heat, and flame detection are the most common means for fire detection. The possibilities for detection of a methanol fire are discussed subsequently, along with other means for detection.

6.4.1.1 SMOKE DETECTION

A commonly used fire detector is the optical smoke detector which is triggered by an increase of particles in the air. The smoke detector is generally claimed to give earlier detection than e.g. the heat detector, which is valid for many fuels producing much soot when burning, e.g. solids and petroleum-based products. Smoke production is for these fuels namely high in comparison with the released heat at the early stages of a fire. However, methanol gives a very "clean" combustion, and detection advantages of soot do not apply. Without soot, the smoke (combustion gases) is almost invisible. A smoke detector will therefore most likely not trigger until later in a methanol fire, when it has spread to involve adjacent materials.

6.4.1.2 HEAT DETECTION

Heat is another signature which is generated and can be detected from a fire. However, a methanol fire releases significantly less heat than most other fuels, which could give delayed detection. Nevertheless, heat detection could still be a good alternative in small enclosures and spaces with low ceiling. Heat detection is generally considered to be slower than other detection technologies, but there are also new detection systems which are more advanced and more sensitive heat, e.g. systems based on fiber optics.

6.4.1.3 FLAME DETECTION

A good alternative for quick fire detection is flame detectors. They commonly detect in the ultraviolet (UV) or infrared (IR) region, where the latter is preferred for methanol flames. This is because the electromagnetic radiation emitted when carbon dioxide is generated is more significant than for most flames Radiation from carbon dioxide can be absorbed from soot particles but since almost no soot is produced in a methanol fire it becomes an easily detectable flame signature. Most common is to detect this radiation in a narrow spectral band around 4.3 Qm, which is in the IR region. Detectors can be set for different parts of the IR spectrum and it is hence important that this region is covered (which it is for most IR-detectors). Furthermore, to avoid faulty alarms, some detectors are programmed to only give alarm if detecting radiation in several parts of the IR region (or in both the IR and UV regions), which should be avoided for methanol fires.

6.4.1.4 OTHER MEANS FOR DETECTION

Another alternative to detect a non-sooty fire is by the different gases produced. Contamination of the air can for example be detected by monitoring oxygen and carbon dioxide. Such a system could advantageously be combined or programmed from a vapor detection system used to detect leakage before fire. An increase of carbon dioxide then causes fire alarm.

CCTV cameras are often used for security purposes and can also be used for fire detection. Regular cameras can be used with image analysis software to identify possible fires and give alarm but for methanol fires the cameras must register infrared radiation. Thermal imaging cameras are thus needed, which may be an expensive investment. Benefits of such systems are the combination of surveillance and fire detection and that localization and spread of a fire is easily monitored in case of an alarm. There are also solutions on the market which combine CCTV in the visual spectrum with conventional flame detectors. With software-based communication the CCTV can monitor the fire in case of alarm from the flame detector.

6.4.2 MANUAL FIRE DETECTION

Fire is manually detected visually by seeing flames or smoke. As described above, a methanol fire generates no visible flames and significantly less smoke than conventional fuels. If methanol ignition occurs in daylight hours it is therefore unlikely that the fire will be detected until it spreads to adjacent materials that emit luminous flames or a visible plume of smoke. To ensure that a fire outbreak involving methanol can be promptly detected there are particularly two instrumentation technologies available. The first is vapor detection, i.e. detection before ignition takes place. If a methanol source is emitting large quantities of vapor, it is only a matter of time before ignition and flashback occurs. With carried vapor detectors there is a possibility to detect a leakage and also to isolate and mitigate the source of vapor before the vapors ignite. The second technology is thermal imaging, which has been used for many years to identify hot spots and loose connections in electrical systems. It works equally well on methanol fires and can be used to swiftly scan for temperature changes in an area and to localize fire.

6.5 FIRE CONTROL

The key elements of fire protection are immediate and appropriate response as well as maintaining control of the fire. Fires can be brought under control using several combinations of strategies and tactics, for example:

1. Allowing the fire to consume all the available fuel and burn out.
2. Limiting the fire from exposing surroundings and spreading by spraying it with water (slowing the fire intensity and reducing heat radiation).
3. Quenching the fire by limiting the contact with air, (e.g. by gas fire extinguishment or use of foam).
4. Interrupting the combustion chain reactions (e.g. by water-mist or foam).

Controlling a methanol fire requires suitable installations and deliberate actions with consideration to the particularities of methanol. For example that methanol has a low flashpoint, bound oxygen, lack of radiation, that it is 100% miscible in water, and ignitable up to 75 vol% water content. These particularities and associated risks are discussed below to provide recommendations for fixed fire-extinguishing systems and manual response. The effectiveness of the most common fixed systems is also discussed in further detail.

6.5.1 FIXED FIRE EXTINGUISHMENT

For confined spaces with permanent methanol installations, an automated local or total compartment fixed fire-extinguishing system should be considered. Dry powder or carbon dioxide fire-extinguishing systems are most likely to provide quick extinguishment. If this is not practical, then automated application of foam, water-mist (fog), or water-spray (traditional sprinkler) should be considered. The foam fire-extinguishing system can be traditionally designed with alcohol resistant high or medium expansion foam; foam concentrate can also be used as an additive to water-mist or water-spray to increase the possibilities for extinguishment. Water-spray and water-mist (fog) systems will otherwise not extinguish a methanol fire until the fuel is sufficiently diluted. This is achieved faster with a water-spray (large drops/more water), whilst a water-mist (small droplets/less water) is more effective as a suppressant. The significant reduction of heat radiation (e.g. from a spray fire) can protect surroundings until extinguishment or allow fire fighters a close approach (and a more likely successful operation). Water-based systems are particularly useful for local protection of equipment since they generally allow quick activation, continued surrounding operations, harmless environment, and no contamination. Protection of adjacent equipment can also be made manually by cooling it with water if a portion of a facility is involved in fire.

Regardless of whether an automated water-based system is installed, a permanent freeboard or drainage solution should be considered. This will limit the size of a potential leakage and allows using foam or water to neutralize the spill. If only water is used as suppressant, there must be sufficient space to increase the volume of the methanol-water solution by at least a factor of four. Otherwise, the volume of firewater may cause the fire to spread. If permanent drainage or freeboard is not practical, provisions should at least be made to prevent the resulting methanol-water solution from (1) entering drains and manholes and (2) spreading and carrying the fire into other parts of the facility. To provide more efficient extinguishment it is preferred to use water with alcohol-resistant foam.

The effectiveness of the most common fire-extinguishing systems is elaborated subsequently.

6.5.1.1 GAS FIRE-EXTINGUISHMENT

The capacity of a fixed gas fire extinguishing systems is generally based on the minimum extinguishing concentration (MEC) of the agent to extinguish the present fuels. With a certain safety margin, a minimum design concentration can be determined for the system. The MEC of an agent to extinguish a fuel is determined by a cup burner test (e.g. Annex B in ISO 14520-1), which for methanol is affected by the oxygen bound to the molecule. For the common IG-combination gases (IG-541/Inergen, IG-100/Nitrogen, IG-01/Argon, IG-55/Argonite), methanol is the liquid fuel which requires the highest concentration for extinguishment, i.e. it is the most difficult liquid fuel to extinguish. The same trend applies also to other physical agents (e.g. CF4, CO2) as well as to the chemical catalytic halon 1301-CF3Br and chemically scavenging 1, 1, 1, 2, 3, 3, 3-hepta fluoropropane. The suppression differential between methanol and heptane is for example very large for halon 1301; more than twice as much agent is required for methanol compared to n-heptane. For physical agents it is required to increase the amount of agent by 25-40 % to extinguish methanol compared to n-heptane. Measured MEC values for some common agents extinguishing methanol are: CO2 (27.2 %), N2 (88.7 %), IG-55 (45.4 %), and IG-541 (44.2 %). This data can also be used to theoretically estimate the MEC of other physical agents, with the knowledge that the MEC is inversely proportional to the heat capacity of the gas.

6.5.1.2 WATER FIRE-EXTINGUISHMENT

The low flashpoint, bound oxygen, low radiation, and wide flammability range of methanol give reduced possibilities for extinguishment with water. Water extinguishes fire mainly by physical means: cooling the flame, dispersing oxygen and fuel vapor, cooling the fuel, and attenuating radiant heat. The dominating mechanism depends on the fuel type, characteristics of the applied water (droplet size, water spray flux, etc.), and the fire scenario (shielding of the fuel, fire size, ventilation conditions, etc.).

Oxygen dispersion is often an important mechanism of a water-mist system, caused by expanding steam. As for gas fire-extinguishing systems, dispersion is not as effective on methanol compared to many fuels. It has oxygen bound to the molecule and consequently a relatively low oxygen index.

For a high flashpoint fuel, such as diesel, the dominating mechanism when using water-mist is generally cooling of the fuel surface. At the same time as fuel is directly cooled down by water, the water-mist reduces the fire size by minimizing heat transfer from the flame to the fuel. In total, the rate of supply of fuel vapor for combustion is reduced; eventually so much that combustion is not supported in the flame. For the low-flashpoint fuel gasoline, fire is instead primarily extinguished by cooling of the flame. Sufficient flame cooling results in termination of combustion reactions in the fuel-air mixture and thus extinguishment (but easy re-ignition). For gasoline, this mechanism is dominant over surface cooling, which is generally the case for fuels with a boiling point lower than that of water. However, the lack of soot in methanol flames minimizes radiation heat losses and reduces the effectiveness of flame cooling, requiring energy abstraction in other ways.

Application of water to a methanol fire provides some oxygen dispersion, some flame cooling, and some cooling of the fuel, but also dilution by accumulation of droplets at the fuel surface. This results in a reduced vaporization rate, which is the primary extinction mechanism for alcohols. With diesel this reduction occurs by cooling of the liquid to the flashpoint, but with an alcohol the flashpoint is also increased when the fuel is diluted in the surface layers. Hence, extinguishment of methanol by water primarily consists in reducing the fuel vapor available for combustion by affecting the fuel temperature to flashpoint relation in different ways.

Combustion is in principal terminated when the flashpoint surpasses the temperature of the fuel surface layer.

The flashpoint depends on the water-content of the methanol, as presented in Figure 2. It shows that methanol water solutions are flammable to about 40 % weight (35 vol%) composition of water at normal room temperature. A warmer fuel generates more vapor and as a general rule it is stated that methanol is ignitable to 75 vol% dilution by water. This corresponds to a fuel temperature of about 39 °C (102 °F) according to Figure 2. A fuel on fire obviously has a significantly higher temperature and measurements after tests with water-spray have shown a water content of up to 87.6 vol% at extinguishment. It should furthermore be noted that increasing water content also reduces radiation, which makes the flames of a methanol fire increasingly invisible (also in an enclosure without daylight the flames eventually become totally invisible).

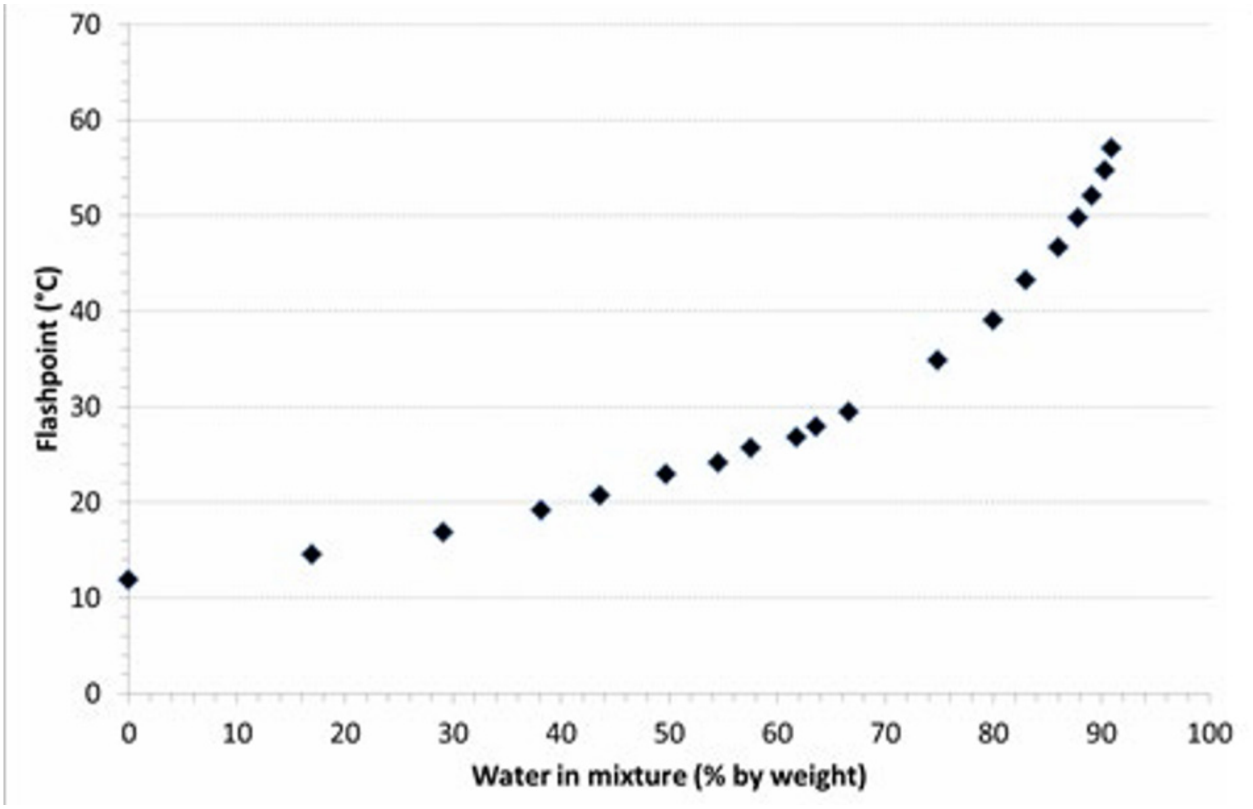

Figure 2 Flashpoint of methanol (°C) on the y-axis versus water dilution (%) on the x-axis.

Fuel by obstructions is the most demanding to extinguish. Obstructions reduce dilution and cooling effects and may also heat the fuel (if hot obstructions are in contact with the fuel). In case of a pool fire, re-ignition may occur until the flashpoint has surpassed the fuel temperature in the whole pool.

Portable foam or water-based fire-extinguishing equipment may be necessary to extinguish some obstructed fires.

It should be noted that extinguishment by dilution implies that a combustible fuel-water solution may be carried away and spread fire with the drainage until sufficient water has been supplied.

6.5.1.3 FOAM FIRE-EXTINGUISHMENT

Application of fire-extinguishing foam creates a film which hinders release of fuel vapor from the surface and thus suppresses combustion. However, conventional fire-extinguishing foam will be decomposed if used for a fire in methanol and other polar fuels. It is therefore necessary to use alcohol resistant foam for fixed fire-extinguishing systems covering methanol installations. Alcohol resistant foams have generally been tested for acetone and isopropyl alcohol (IPA), which are the most challenging of polar solvents to extinguish.

Foam can be used in many different applications, from hand-held fire-extinguishers to cannons. Furthermore, mixing a small concentration of alcohol resistant foam as an additive in a water-spraying or water-mist systems can improve their effectiveness against methanol significantly.

6.5.2 MANUAL RESPONSE

Methanol burns with a low total heat of combustion and a low radiative fraction, implying that the radiative heat flux from a methanol fire is significantly lower than from many other fuels (e.g. diesel, heptane, or ethanol). This means that a methanol fire of the same size be less harmful for the surrounding building, equipment, and personnel. It also means that it will be possible to approach the fire more closely than would be possible with for example a gasoline or diesel fire. A small fire should be immediately approached, e.g. with a handheld foam or powder fire-extinguisher. The foam should be of alcohol resistant (AR) type and the dry powder should be suitable for Class B (flammable liquids) and Class C (flammable gases) fuels to be effective for extinguishment of methanol. It is recommendable that all fire-extinguishers in the vicinity are of suitable kind, to ensure that the retrieved extinguishers are functional.

The low radiative heat flux and non-luminous flames also mean that a methanol fire is difficult to see, in particular in daylight and when the fuel is diluted with water. This makes it difficult to determine the location and intensity of the fire. To make a reasonable determination, it is necessary to use a thermal imaging device (IR- camera). Such devices should be available at the entrance to a space with methanol installations and also to fire fighters and first responders.

If fire causes high temperatures in a space with volatile fuel, large amounts of non-combusted fuel vapor may be produced. The auto- ignition temperature of methanol is high but when fuel vapors reach an ignition source (local fire) there is potential for an energetic re-flash/deflagration if sufficient oxygen is available. This risk also applies in case oxygen is let into a previously closed space, e.g. at ingress by fire-fighters.

6.6 FIRE GROUND SAFETY

When fighting methanol fires, the responders must be trained and equipped with consideration to the particular risks associated with the fuel. Some fundamental fire ground safety recommendations for fighting methanol fires are given in the subsections below. Although the composition and capabilities of a fire brigade are outside the scope of this manual, this section also touches on some of the key issues that should be kept in mind when relying on outside responders.

6.6.1 PERSONAL PROTECTION EQUIPMENT

Methanol is a toxic poison, which must not be ingested, inhaled, or contacted with skin. Methanol is such a strong polar solvent that it rapidly degrades many plastics and synthetic fabrics and absorbs through skin. Furthermore, SCBA breathing equipment worn with conventional turnouts does not provide sufficient protection against the toxicity of methanol, methanol-water solutions, or methanol vapor. Hence, conventional fire fighters' protective clothing does not offer sufficient protection in responding to methanol spills and fires[7]. SCBA with a level "B" chemical resistant suit to prevent skin absorption is required in such cases.

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[7] Refer to 2008 Emergency Response Guidebook for additional guidance.

For a safe response to methanol spills and fires, fire responders must thus wear the following minimum Personal Protection Equipment (PPE):

- methanol compatible turnouts (fire-resistant uniform) with helmet, gloves, and anti-static boots;
- full face, positive-pressure SCBA; and
- communication equipment.

6.6.2 LOCALIZATION AND ASSESSMENT OF FIRE

In order to effectively fight a liquid fire, it is necessary to identify the location of the fire. Hand held thermal-imaging (IR) equipment is available to assist fire fighters responding to methanol fires. Such equipment should be available for use on the fire ground and in the air over the fire ground. Responders must be trained in using the instrumentation, and incident command must be trained to take advantage of thermal-imaging capabilities.

When the location of the fire cannot be determined with a high degree of confidence, it is possible to position the first line of defense too close to the fuel source. Uncertainties associated with locating and characterizing methanol and methanol-gasoline blend fires require a cautious and deliberate approach. This is particularly true if there is any possibility of a BLEVE, or thermally induced rollover of the contents of a storage tank, pressure vessel, or transport container (bulk and non-bulk). It is highly desirable to determine a plan of attack using a bird's eye view of the fire as seen with a thermal imaging device[8]. This capability can save lives when fighting methanol and methanol-gasoline fires.

6.6.3 USE OF WATER

In order to combat a methanol fire, it is essential that water is used wisely. If too much water is used, for example to cool surrounding equipment, and if water runoff mixes with burning methanol, then the solution can create a so-called "running fire". With methanol this is a particularly hazardous since such propagation of fire may not be immediately noticed by responders.

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[8] A video of a methanol tanker truck fire and boiling liquid expanding vapor explosion (BLEVE) provides an excellent demonstration of the usefulness of the thermal imaging technique in protecting life safety of fire ground personnel. (http://www.firefighternation.com/videos/methanol-tank-truck- fire)

Methanol does not produce a visible flame in daylight and the flames become increasingly invisible with water-content.

Burning and non-burning methanol-water solutions must be kept away from other fuel sources and degradable materials, such as vehicles. Non-burning solutions must be prevented from contacting ignition sources and hot equipment that could cause these solutions to ignite. Flammable methanol-water solutions must also be prevented from entering confined spaces, such as sewers and drains. Furthermore, fire ground command must be vigilant to prevent fire teams from becoming surrounded by or partially immersed in flammable methanol-water solutions. This is a hazard that can potentially become a life safety issue.

To provide more efficient extinguishment of a methanol fire, it is preferred to use water with alcohol-resistant foam. However, methanol fires are known to restart if foam suppression is discontinued too soon. Therefore foam should be applied for a substantial period of time, also after the fire is out. Foam hinders vaporization and can also be used as a preventative measure, to hinder ignition of a methanol spill. It is good practice to verify that fire suppression foam is of the correct type and that its suppression capability does not degrade as a result of time in storage, storage temperature variability, or by exposure to freezing or temperatures over 100 °F, if the facility is in a hot or cold climate.

Application of water within the interior of a tank will not suppress a methanol fire and more likely exposes responders to a tank explosion resulting from thermally induced rollover and expansion of tank contents.

6.6.4 OUTSIDE RESPONDERS

Most facilities relying on this manual will not have their own fire brigade and must rely on outside sources for firefighting. This in no way compromises response effectiveness, provided there is provision for early detection, alarm, rapid callout, and instrumented, as well as visual fire assessment. Offsite responders must be aware that they are responding to a methanol fire and be trained and equipped in the same way as an in-house fire brigade. It is recommended that facility operators contact their local first responders and set up site visits and fire drills to increase familiarity with the site. Good practice is to periodically perform response exercises for various scenarios; also table-top exercises are useful. Special provisions may be necessary to accommodate a response by an outside party. For example, responders must either bring their own or be provided access to sufficient amounts of alcohol resistance fire suppression foam. The same applies to equipment for aerial and fire ground thermal imaging capability, which is a major benefit for responders. Special provisions should be determined and accommodated prior to introducing methanol into the facility.

6.7 METHANOL-GASOLINE BLENDED FUELS FIRE SAFETY

Alcohol (ethanol and methanol) have replaced MTBE as the oxygenated compound in motor fuels in large metropolitan centers in the United States that are subject to air-quality restrictions. The state of California is blending between 7 and 10 vol% ethanol. In Europe, the Renewable Energy Directive calls for B7, E5, and E10 blending requirements for bio-fuels. Most metropolitan fuel terminals will use inline-blending technology to add methanol to gasoline. Smaller operations in suburban and rural areas may use splash blending. In view of this, tanker transport trucks of 10,000-gallon capacity (38,000 liters) are likely the largest amounts of blended fuel encountered by responders in the United States and Europe at this time. This is expected to change during the next three to five years if subsidies of ethanol bio- fuel production are removed.

The following discussion of fire safety of methanol-blended fuels should be reviewed within this context as it applies primarily to 10,000 gallon batches, and also to larger splash-blended fuels in tank inventory in rural environments.

6.7.1 PROPERTIES OF METHANOL-GASOLINE BLENDED FUELS

Methanol is miscible in both gasoline and water; however, its affinity for water is greater than that for gasoline. A solution of methanol and water is not miscible in gasoline. Methanol-water solutions form a separate phase that sinks to the floor of tanks, tanker trailers, and secondary spill containment. This has specific implications for how first responders deploy to an emergency involving methanol-gasoline blended fuels.

Methanol-gasoline fuel blends have two worst-case scenarios. The first is thermally induced rollover of contents of a tank due to uneven heating of stratified layers. The other is a BLEVE. Both can manifest pressure waves and may be accompanied by large fireballs that have a high rate of radiant heat flux.

If fires involving methanol-gasoline blended fuels are suppressed with water (even small fires with fog, mist, or fine droplet spray), then firewater in contact with the fuel blend will immediately begin forming a separate phase that extracts methanol from the blended fuel and concentrates it in a methanol-water phase that sinks to the bottom of the blended fuel enclosure. The result is stratification of two flammable liquids: gasoline floating on a methanol-water phase. Stratification can cause unexpected and unwanted results if the containment is a metal tank subject to heat flux from a fire outside the tank and/or heat from a gasoline fire within the tank.

The heat capacities of gasoline and a solution of water and methanol are very different. Therefore, the rate at which temperature rises in each of the stratified layers will be different. The temperature of the gasoline layer will increase more rapidly than that of the water- methanol layer because water has a very large heat capacity compared to gasoline. If convection currents within the tank caused by unequal heating of the layers become sufficiently vigorous, and if water in the lower layer flashes to steam, then the tank essentially experiences a steam explosion accompanied with a giant fireball consisting of most of the flammable liquid contained within the tank. Because of the very large amount of water, which must be added to dilute methanol beyond its flammability range, it is unlikely that this amount of water will be added prior to rollover. In fact, the addition of water may increase the likelihood of rollover. Therefore, the entire contents of the tank are flammable liquid. In a worst-case scenario, the fireball will abruptly release the heat of combustion of the tank's contents.

The second worst-case scenario, a BLEVE, would more likely occur in the event of a tanker truck transportation accident. In this case, the overpressure and the heat flux from the fireball depend on the amount of fuel remaining in the tanker at the time of BLEVE.

6.7.2 METHANOL-GASOLINE BLENDED-FUEL FIRES

A more typical blended-fuel scenario may involve overfilling a 15M/85G fuel into a bermed area. The severity of the consequences depends on how much fuel is spilled, whether the hot work hazard zone for the tank is rigorously enforced, the speed of the response, and whether the responders are properly equipped and trained to use thermal imaging and to apply alcohol-compatible, heat-resistant foam.

Gasoline burns with a luminous flame; therefore, the gasoline portion of the fire is easily recognized. The 15/85 fuel blend burns with a slightly luminous flame. The methanol-water phase may be under the gasoline, where it is prevented from burning, or it may begin burning when the floating gasoline layer is consumed. The methanol-water phase will burn with an invisible, non-luminous flame. Responders may believe that the application of foam has suppressed the fire; however, methanol fires are persistent. It is in fact necessary to apply foam for an extended time after the fire is out. Two to three times as much AR-AFFF foam is required to maintain fire suppression as is required to initially extinguish the flames. This means that foam inventory needs to be sufficient to cover a spill to considerable depth. It is important to remember that a gasoline fire requires conventional AFFF for effective fire suppression. On the other hand, a methanol or methanol-water fire requires AR-AFFF or film- forming fluoroprotein (FFFP) foam for effective suppression. A 15M/85G blend requires FFFP to combat the higher temperature of a gasoline fire and resist solvent attack of methanol.

AFFF foams have no alcohol resistance. They immediately break down when exposed to alcohol. The AR-AFFF foam has low heat and temperature resistance. The AR-AFFF degrades when exposed to high temperatures associated with a gasoline fire. If AFFF foam is applied to a methanol fire, and if AR-AFFF foam is applied to a gasoline fire, then both foams are ineffective, and responders will have to rely on water spray and/or let the fire burn itself out.

Application of the wrong foam in the wrong place at the wrong time may cause fire intensity to increase, with the result that tank roll over and/or BLEVE become very real possibilities.

6.7.3 RESPONSE TO METHANOL-GASOLINE BLENDED-FUEL FIRES

Responding to methanol-gasoline blended-fuel fires is complex. The first thing to understand is the composition of the fuel. The second is to determine the size of the fire and its likelihood of spreading. The third criteria is to have a well-trained and practiced team with equipment suitable to fight both methanol and gasoline fires.

The following is a short list of questions that may be useful in staging practice responses.

- How does the incident commander decide which monitors and which hose crews get which foam at what times?
- What types of foams are needed, and are foam inventories sufficient?
- How is the incident commander going to track fire propagation?
- How are hot spots identified?
- How will the commander know if a BLEVE or tank rollover is imminent?
- How long should the incident commander continue applying foam after the fire is initially extinguished?
- What is the best strategy: fight the fire, or withdraw and allow the fire to burn itself out?
- At what point in the response must the decision to withdraw be made, what information is necessary to make it, and who is going to make it?

7 EMERGENCY RESPONSE

Accidental releases represent one of the major environmental, health, and safety hazards associated with the use, storage, and distribution of methanol. This chapter addresses the six major stages of emergency response (ER) to methanol releases: (1) spill prevention, (2) spill response, (3) release containment, (4) cleanup and remediation, (5) notification and reporting, and (6) incident investigation recordkeeping.

Effective ER starts by developing an Emergency Response Plan (ERP) that identifies potential hazards from operations, natural and man-made disasters, sabotage, and vandalism, which can impact operations, human life, or the environment. Appropriate response measures are then developed for each scenario, identifying the internal resources, personnel, equipment, and training needed, as well as the coordination with outside response agencies, such as the fire department, regulatory agencies, and private contractors.

A good ERP includes regular drills (both planned and surprise) and annual reviews to ensure that the plan is fully implemented and kept current. In ER, time is an enemy. Time to alarm, time to respond, time to deploy, and time to control an incident are important benchmarks in assessing ER effectiveness and efficiency. Within this context, "effectiveness" is taking the correct action in the correct place at the correct (earliest possible) time. Efficiency is performing repeatedly and effectively in a variety of situations and circumstances.

7.1 SPILL PREVENTION

Spill prevention is an integral part of ER planning. The best spill prevention strategy is incorporated into process safety management at the design stage. Effective spill prevention programs involve process engineering controls, standard operating procedures, standard maintenance procedures, spill response planning, and periodic training geared to each employee's degree of involvement in the response actions.

Engineering controls associated with methanol storage tanks include: overfill protection by means of visible and audible high-level alarms; automatic instrumented trips to terminate flow prior to overfill; vents equipped with flame arresters; secondary containment systems, such as dikes, bunds, or berms; vapor detectors and alarms; and explosive gas detectors to detect and warn of fire and explosion hazards in the event of a release.

Methanol must be stored in an area that is well ventilated and is bermed, diked, or bunded. If designed in accordance with NFPA 30, the storage area shall be capable of containing at least 110% of the volume of the largest storage tank in the contained area. Additional volume is recommended if substantial amounts of fire water are used. In the event of a leak inside the containment area, pooled liquid methanol should ideally be completely covered with alcohol-resistant foam. If the containment area is adequately sized, the methanol spill can be diluted with at least four parts water to one part methanol to reduce the risk of fire. These precautions are to be taken regardless of whether the methanol is on fire. The objective is to prevent vapor migration and flashback by reducing the vapor release rate from the liquid surface.

Operation and maintenance procedures for preventing and detecting leaks and spills should include periodic visual inspections (at least once per shift). Nondestructive testing of the condition (fitness for continual service) of tanks, valves, pipes, hoses, and dikes should be conducted on a regular basis, as well as preventative maintenance of mechanical, electrical, and structural components. This includes detection and alarm systems. Consideration should be given to specifying level control and vapor detection as unclassified or as an SIL 1 instrumentation loop.

Methanol handling, containment, and control systems must be maintained to be “fit for continual service.” Written procedures for loading and transferring methanol, as well as steps necessary for emergency shut off, should be developed and reinforced through periodic training of operating personnel.

Workers must be trained to handle methanol in a safe manner. Systems and procedures that protect the employees, the plant, and the environment should be implemented. Spill kits must be available in all areas where methanol is handled, stored, or used.

A complete spill kit must include:

- Various types and sizes of sorbent materials (vermiculite or activated carbon, sorbent pads).
- Plastic (non-sparking) shovel to disperse the sorbent materials.
- Yellow caution tape or other barrier devices to isolate the area.
- Drum or container to hold the collected waste material.
- Emergency communication devices, such as explosion-proof mobile phones or two-way radios.

Personal protection equipment for the responders should, at a minimum, include:

- Chemical splash goggles and face shields.
- Butyl or nitrile gloves.
- Anti-static rubber boots.
- Chemical-resistant coveralls.
- Provision for supplied fresh breathing air (air-purifying respirators with organic vapor cartridges should never be used for protection against methanol vapors).
- Multiple fire extinguishers.
- Industrial first aid kits.
- Full body water showers and eye wash stations capable of supplying 15 minutes of water should be positioned nearby to decontaminate exposed personnel.
- Ample supply of potable water for washing and drinking.
- Vehicle suitable for emergency transport.

7.2 SPILL RESPONSE

Facilities that use, store, or distribute methanol need to be prepared in case of a spill by developing and implementing spill response plans and conducting scheduled and surprise drills at least once a year, or more often if possible.

STEPS IF A SPILL OCCURS

1. Stop or reduce methanol release rate at the point of release, if it can be done safely.
2. If there are noxious vapors, evacuate, sound a vapor release alarm, and notify supervisor or emergency coordinator.
3. Eliminate all sources of ignition to a safe standoff distance from the point of release and nearby methanol pooling.
4. Evacuate all persons not wearing protective equipment from the area of the spill or leak until cleanup is complete (this requires that cleanup levels be pre-determined).
5. Do not walk through spilled product. Avoid skin contact and inhalation.
6. Stay upwind and keep out of low-lying areas that might accumulate vapor.
7. For large spills and fires, immediately call the fire department.

7.3 RELEASE CONTAINMENT

Methanol releases can range from large volumes in shipping vessels, tanker trucks, and rail cars, to large spills from storage tank and pipeline failures, to medium spills during transfer operations, to small drum, tote, or hose leaks. The spill response plan should take into account the anticipated location and conditions of the release. Most frequently, methanol spills are likely to result from tote, drum, or transfer hose-associated accidents.

Whenever possible, spilled methanol should be kept from entering sewers or drains, which comprise confined spaces subject to explosion, and where liquid can flow to streams, rivers, lakes, or the ocean. If possible, remove leaking containers to the outdoors or to an isolated, well-ventilated area, where the spill can be contained and the liquid can be safely transferred to an appropriate container.

Free liquid should only be collected or transferred using explosion- proof pumps, grounded and bonded containers, and spark-resistant tools.

Spills onto pavement or bare ground should be contained by surrounding the liquid with mechanical or chemical barriers, such as sand, vermiculite, zeolite, or absorbent dikes. For small spills, cat litter can be used as an effective absorbent. The spill surface should be covered with the absorbent materials or activated carbon to capture the pooled methanol. After use, the saturated sorbent materials or soil-containing methanol should be removed and packed for recovery, recycling, or disposal.

Methanol vapor is slightly denser than air and should be kept from flowing into confined spaces, such as sumps, manholes, and utility tunnels, where the vapors may settle and reach flammable concentrations. These spaces should be checked for explosive atmospheres prior to re-occupancy.

Fine droplet water spray, mist or fog can knock down airborne methanol vapors but may not prevent ignition in closed spaces. AR-AFFF fire suppressing foam may be applied to the spill for vapor suppression and to diminish the fire hazard. Methanol fires can be difficult to extinguish. Best practice is to continue spraying AR-AFFF foam for a period of time after the fire is thought to be extinguished.

In order to prevent fires or explosions, vapor releases inside buildings or in confined spaces should be ventilated to achieve less than 10% of the LEL for methanol, which is equivalent to 0.6% or 6000 ppm. However, at that level, methanol vapors are still considered “Immediately Dangerous to Life and Health.” The building must be evacuated until response personnel determine that it is safe to re-enter and methanol concentrations in air are less than 200 ppm. All ignition sources in the immediate area, such as smoking, flares, sparks, or flames, should be shut off or removed from a radius of 328 to 656 ft (100 to 200 meters) from the spill area.

Outdoor releases of methanol vapors will likely disperse relatively quickly. Isolating the area 328 to 656 ft (100 to 200 meters) from the spill source in all directions and staying upwind of the release plume are the appropriate response measures. If a tank truck or rail car is involved, expand the isolation area to one half mile (800 meters) from the release source.

The purpose in expanding the radius of the exclusion limit is to protect personnel against overpressure, radiant heat flux, and shrapnel in the event of a BLEVE.

Pipeline spills may require setting up diversion channels or pathways to direct methanol toward natural or engineered collection basins and away from sensitive ecological areas or waterways. This may be necessary even after closing upstream and downstream valves or bypassing the flow until the residual content is drained.

It is not practical to recover methanol from spills into natural bodies of water, such as rivers, lakes, and oceans.

7.3.1 SITE CONTROL ZONES

Site control is an essential component in ERP implementation. To control the spread of contamination and employee exposure to chemical and physical hazards, the spill area should be divided in three concentric circles centered on the Exclusion Zone (EZ) or “hot zone” where the spill is contained. This is surrounded by a Contaminant Reduction Zone (CRZ), which includes a single point of ingress and egress of response personnel and equipment, as well as the decontamination corridor for cleaning personnel and equipment exiting the hot zone. The Support Zone (SZ) located in the outermost perimeter is used for staging response equipment, and for locating the command post and communications center. Access to the EZ and CRZ will be restricted to authorized personnel only. The

Emergency Response Coordinator (ERC) will identify work areas that personnel are authorized to enter and will enforce site control measures.

7.4 SPILL CLEANUP AND REMEDIATION

Only properly trained and equipped employees should be allowed to participate in methanol spill control and cleanup operations. In the United States, emergency responders must have training according to the OSHA Hazardous Waste Operations and Emergency Response (HAZWOPER) rules contained in section 1910.120 of Title 29 of the Code of Federal Regulations [59]. For methanol spills where explosive concentrations are suspected or possible, Level "A" fully encapsulating, vapor-protective clothing with supplied air-respiratory protection must be worn. Smaller spills may require Level "B" vapor protective clothing and gloves and supplied-air respiratory protection. Due to the quick saturation of activated charcoal to methanol vapors, air-purifying respirators with organic vapor cartridges should never be used.

Once the fire, explosion, and health hazards have been controlled, the goal of a methanol spill cleanup operation is to recover as much pure material or methanol-water mixture as possible before it undergoes complete dilution to maximize its recycling or reclamation potential. Methanol-saturated absorbent materials can also have caloric value as secondary fuel blending or incineration. Possible treatment processes for recovered methanol mixtures include reverse osmosis, carbon adsorption, steam stripping, and air stripping. However, cost-benefit considerations will need to be evaluated on a case-by-case basis.

Contaminated absorbent material and affected soil may need to be treated as a hazardous waste. Treatment and disposal options will depend on the applicable regulations. Depending on the location and affected medium, it may be necessary to remediate the methanol spill site. Methanol is not persistent in the environment, and when released onto surface waters, soil, and groundwater, it will readily dilute to low concentrations, allowing native soil or aquatic bacteria to biodegrade it in a relatively short period of time. The relative speed of methanol's biodegradation is expected to result in natural cleanup times that are faster than the active cleanup times. However, regulatory requirements and potential liability may require an active remediation process.

7.5 SPILL NOTIFICATION AND REPORTING

The United States Emergency Planning and Community Right-To-Know Act (EPCRA) requires immediate notification to the Federal National Response Center, the State Emergency Response Commissions, and the Local Emergency Planning Committees for chemical releases above certain thresholds. In addition, state and local government agencies may also have notification and reporting requirements following a hazardous materials spill. Methanol's Reportable Quantity in the United States Comprehensive Emergency Response and Liability Act (CERCLA) Hazardous Substances List is 5000 pounds (2.2 tonnes), which is equivalent to 755 gallons (2858 liters). In Canada, reporting requirements are triggered for spilled amounts as low as 53 U.S. gallons (200 liters). In the European Union (EU), the public will be able to access an electronic database on pollutant releases through Regulation Number 166/2006 (European Pollutant Release and Transfer Register). Spill notification may trigger requirements to remediate the spill area and restore any damage to the environment, in addition to penalties and fines.

7.6 INCIDENT INVESTIGATION AND RECORDKEEPING

A key component of ER planning is to conduct an incident investigation to identify the causes of the release and correct any deficiencies in process safety systems and operating procedures, as well as to improve on the response effort itself.

The facility should have a written incident investigation and follow-up procedure to ensure that appropriate corrective measures are implemented and that all relevant records and documentation of the investigation are maintained.

7.7 INCIDENT COMMAND STRUCTURE

During a small spill that can be handled within the facility, the onsite Emergency Response Commander (ERC) has primary responsibility for responding to and correcting emergency situations and for taking appropriate measures to ensure the safety of site personnel and the public.

The ERC is also responsible for ensuring that corrective measures have been implemented, appropriate authorities have been notified, and follow-up reports have been completed. Possible actions may include evacuation of personnel from the release area. Facility personnel are required to report all spills, fires, injuries, illnesses, and property damage to the ERC.

In a larger incident that requires outside responders, such as the fire department and/or Hazardous Materials Response Unit to be called in for assistance, the ERC will pass command responsibilities to the lead agency's Incident Command (IC), who will direct the response efforts.

Depending on the size and magnitude of the event, an IC may involve one person or a team. The IC may be supported by information, safety, and liaison officers, and may also require support personnel to coordinate operations, logistics, planning, and finance.

7.7.1 COMMUNICATIONS

Successful communication between field teams in the EZ and personnel in the support zone is essential in an emergency situation. To ensure proper communication and safety, the buddy system (or two-person team) should always be used during field investigation and cleanup activities in the EZ. Intrinsically safe (explosive-proof) cellular telephones or two-way radios (for areas with no cellular phone service) should be available to all ER personnel. Different response agencies use different radios and call codes. It should be verified that radios are compatible with those of the responders that a facility may be forced to rely upon.

8 METHANOL INCIDENTS AND SAFEGUARDS

This chapter presents a review of the major types and causes of methanol-related incidents and accidents and describes the most common hazards experienced by various methanol users. Also discussed are effective safeguards that can help reduce the occurrence and severity of hazardous incidents.

8.1 OVERVIEW OF METHANOL INCIDENTS

Although there have been many reported significant incidents of spills involving methanol, including, fires, and explosions in the international media, there is no comprehensive list of incidents and accidents available. The widespread uses of methanol from chemical intermediates and solvents to alternative fuels make this a complex task.

The table below presents incident data compiled from research on the Internet dating from 1998 to 2011 and includes incidents reported in the United States, Canada, Brazil, France, Italy, Germany, Sweden, China, India, Malaysia, South Africa, and Australia. The complete list of incidents on which this table is based is included in Appendix D of this manual.

Table 16. Types of Methanol-related Incidents by User Sector (1998-2011)

Sector	No. of Incidents	% of Incidents	Fire and/or Explosion	Spill	Other
Biodiesel	23	28%	23		
Industrial	23	28%	21	2	
Transportation	22	27%	12	6	4
Home	4	5%	4		
Pipelines	4	5%	1	3	
Schools	3	4%	3		
Commercial	1	1%	1		
Water Treatment	1	1%	1		
Total	81		66	11	4
Percentage	100%	100%	81%	14%	5%

This table is not intended to be a complete or representative statistic of the relative frequency or magnitude of such incidents. However, it can serve as a point of departure to evaluate the common types of incidents involving methanol and to assist users in identifying the risks and developing safety measures to prevent potential disasters.

The industrial sector, which includes biodiesel production, was the top category responsible for most methanol incidents, accounting for 56% of all cases. Biodiesel manufacturing itself represents half of the 46 industrial incidents, with 23 fires and/or explosions. Most of the other industrial cases also involved fires or explosions, plus two reported spills.

Of the 22 incidents in the transportation sector, which accounted for 27% of all cases, almost one half involved road transport of methanol, and another 36% were railway related. There were four shipping incidents reported, as well. Twelve of the 22 incidents resulted in a fire or explosion, six caused spills, and the remaining four resulted in collisions, turnovers, derailments, and ships running aground with no significant loss of material.

A review of 81 separate incidents involving methanol from 1998 to 2011 indicates that **fires or explosions account for 81% of all incidents**, and **spills represent 14%.**

Table 17 below shows the rates of injuries and fatalities caused by the methanol-related accidents reported.

Table 17. Methanol Incident Fatalities and Injuries by User Sector (1998-2011)

Sector	No. of Incidents	Fatalities	Injuries	% all Fatalities	% all Injuries
Transportation	22	14	9	54%	18%
Industrial	23	5	15	19%	31%
Biodiesel	23	4	6	15%	12%
Water Treatment	1	2	1	8%	2%
Commercial	1	1	1	4%	2%
Schools	3	0	12	0%	24%
Home	4	0	5	0%	10%
Pipelines	4	0	0	0%	0%
Total	81	26	49	100%	100%

Transportation-related accidents accounted for the highest number of casualties, with 54% of all fatalities and 18% of all injuries. Industrial accidents other than biodiesel had the highest number of non-fatal injuries involving 15 people, as well as five fatalities. The biodiesel industry accounted for four deaths and six injured workers. Injuries reported for homes and school incidents were due to burns. No fatalities were reported in home, school, or pipeline incidents. The single incident reported in a wastewater treatment plant (due to a welding incident) represents the highest severity rate with two deaths and one injured worker.

Fatalities due to poisonings from the illegal use of methanol in alcoholic beverages are not included in this analysis. Nonetheless, 61 homeless people died from drinking methanol-laced beverages in just one incident reported in Khartoum, Sudan, on June 24, 2011. This was more than twice the total fatalities from all of the incidents reported in these tables over a 13-year period.

> Industrial methanol users (including biodiesel manufacturers) and the transportation sector together account for more than four out of every five incidents reported, and 88% of all fatalities.

8.1.1 COMMON CAUSES OF INCIDENTS

It is not always possible to determine the root cause of the incidents reported by the media or in the compiled reports. Almost one- third of the incidents reported have an unknown cause. Another 10%, or eight cases, can be categorized as “non-intended” uses involving children and adults playing with methanol and fire, or school science class experiments gone awry.

8.1.2 ROUTINE OPERATIONS AND MAINTENANCE

In the industrial and biodiesel sector, maintenance-related issues appear to account for over half of the incidents with known causes. “Hot work” involving welding or grinding on methanol storage tanks or containers represents half of the maintenance incidents, and faulty electrical installations and equipment, transfer lines, pumps, or safety valves account for the rest.

Routine operations like mixing materials, reactions involving high temperatures or pressures, and material transfer operations seem to account for 45% of fire or explosion incidents in the industrial sector, although it is not possible to identify the specific sources of ignition in these cases.

Biodiesel manufacturing accounts for two-thirds of all industrial incidents reported with known causes.

8.1.3 TRANSPORTATION ACTIVITIES

In the transportation sector, collisions by auto transport, railcars, or ships and barges account for more than three-quarters of all of the incidents with known causes. Spills make up the rest of the incident types.

Transportation accidents by and large appear to have occurred during routine operations while the vehicles or vessels carrying methanol were on the road, on rail, or underway in marine waters. Only two incidents could be directly attributed to maintenance issues, although the proximate causes of the other accidents are not known. Interestingly, there are no reported cases of spills during material transfer operations. All transportation spills reported are due to collisions or turnovers, with one incident of a minor spill in a storage rail yard.

8.1.4 PIPELINE INCIDENTS

Of the four reported pipeline incidents (three spills and one fire), all were process-related, and three occurred during routine maintenance activities.

8.2 KEY FINDINGS

The incident statistics above point out that, while fire and explosion – often resulting from a spill or other release – are the most common outcomes of methanol incidents, their causes can vary depending on the activity being conducted. Transportation incidents, whether on road, rail, or water, seem to occur during routine activities. Pipeline and industrial incidents are associated with equipment maintenance and, in biodiesel production in particular, with routine operations.

One thing that they all share is the human element, which is of key importance in evaluating the consequences of these incidents. This underlines the critical importance of understanding the hazards of methanol and of learning and practicing the procedures for safe handling and responding to emergency situations.

While it is not possible to identify the relative contributions of place, people, and process that resulted in each event, we can benefit from lessons learned in incident analysis and process safety management of similar industries and processes. Common factors that contributed to these incidents include the following:

- Insufficient understanding of the physical, chemical, and flammable properties of methanol.
- Methanol container, hose, or pipeline integrity not preserved.
- Methanol vapors allowed to accumulate or released in flammable concentrations.
- Inadequate spill containment capability.
- Obvious ignition sources, such as hot work, not recognized or controlled.
- Ignition sources such as static electricity, electric arc from non-explosion-proof equipment or installations, friction and mechanical sparks, or exothermic chemical reactions not identified or difficult to control.
- Inadequate equipment maintenance.

- Standard Operating Procedures for routine operations not followed or inadequate.
- Process safety measures not in place or not followed.
- Fire prevention systems not in place, inadequate, or not operational.
- Inadequate Emergency Response planning, training, equipment, and/or supervision.
- Failure to recognize the magnitude of the hazard or developing event and to take appropriate and timely life safety protection measures.

8.3 CONCLUSIONS

As the analysis of historical incidents above suggests, the hazards inherent in the use, storage, and transportation of methanol can result in serious and catastrophic events. Loss of life, serious injury, and/or significant material losses can occur when this chemical is not handled properly and with adequate safeguards. The following conclusions are based on information gathered from these incidents:

- Conditions conducive to serious or catastrophic events exist in all phases of the methanol value chain, including the manufacture, transportation, distribution, storage, and processing sectors, as well as in educational, recreational, and residential settings.
- Serious incidents from the use, transportation, or storage of methanol can and do occur in large and small operations with widely differing levels of technical capability.
- Emergency Response and Spill Prevention capabilities, training, and equipment are essential elements of safe methanol handling, as many spills have resulted in fires and explosions.
- The majority of incidents, and many fatalities, could have been prevented by implementing proper Hot Work Permit procedures prior to welding or grinding activities.
- Mechanical integrity and proper preventive maintenance of equipment for methanol service is of key importance for all methanol users.

- Understanding the importance of corrosion causes and prevention in methanol service conveyance systems, pipelines, and storage tanks is essential. This is of particular importance in marine terminals, tank farms, chemical plants, loading racks, and for all industrial users.

- Recognition, identification, and control of potential ignition sources must be emphasized in all situations where methanol is present and releases are possible. This should include sources of heat, fire, friction, electrical arc, static electricity, sparks, chemical reactions, and physical process conditions, among others.

- Industrial methanol users, and the biodiesel manufacturing industry in particular, will benefit from implementing process safety management practices and procedures for routine and special operations, as well as emergency conditions.

- Operator training in the physical, chemical, and flammable properties of methanol is an essential element in safe handling, in particular for industrial and transportation workers.

8.4 SAFEGUARDS

To reduce the probability and consequences of a serious or catastrophic incident, methanol users must have the right tools to help them recognize the particular hazards of the type of operation or activity they are involved in and to identify the appropriate safeguards to control those hazards.

Below are some of the key elements that must form part of an effective safety management system for methanol users. These elements may be scaled to the appropriate level depending on the type of operation, storage or throughput volume, and conditions in which methanol is handled.

8.4.1 PROCESS SAFETY MANAGEMENT

Process Safety Management (PSM) is a safety management system that has been in effect in the chemical industry for more than 20 years. The methanol specific PSM process is described in detail in Chapter 5 of this manual.

8.4.2 CORROSION PREVENTION

Liquid methanol is electrically conductive compared to natural gas and distilled fuels. Because of its high conductivity, containers holding methanol are more susceptible to galvanic corrosion than containers holding hydrocarbons like gasoline. Conductivity increases corrosion of alloys commonly used to handle natural gas and distillate fuel. This is particularly true for aluminum, brass, copper, titanium and zinc metals and alloys. Additionally, methanol is a solvent and is compatible with only selected plastics and rubbers. Plastic containers commonly used for gasoline may lose structural integrity when used to hold methanol and must be replaced with more corrosion- and solvent-resistant materials. Storage containers and pipeline conveyance systems should not be used in methanol or methanol vapor service without a rigorous mechanical integrity program. Corrosion protection is discussed in Appendix B of this Manual.

8.4.3 HOT WORK PERMIT PROGRAM

The hazards associated with hot work can be reduced by implementing an effective hot work permit program. This should include prior work authorization, safe welding practices, and a fire watch. See Section 4.3, Safety Precautions, in this manual for additional information.

8.4.4 FIRE PREVENTION AND RESPONSE

The three key aspects of fire response are early detection, immediate response, and appropriate action. While the particular application of these principles may vary, a well-planned and developed system depends on training, equipment, and practice. See Chapter 6 for more information.

8.4.5 EMPLOYEE TRAINING

It is the employer's responsibility to inform all employees of the hazards and risks associated with methanol and to inform them on how to effectively control those risks. As the incidents above show, accidents usually occur because the individuals handling methanol or performing work near methanol storage and handling areas are unaware of the risks. Accidents are a sign that management has not assigned the appropriate priority to properly training and supervising employees.

Operating personnel need to be trained in interpreting and applying the written operating procedures, as well as those for upset conditions and emergency response. As a practical matter, training includes both classroom and one-on-one, on-the-job training, supplemented by drills and simulations, which may include complete mock events or simple table-top exercises.

Training is a dynamic process that must be refreshed on a regular basis. Effective training involves:

1. Initial training upon assignment.
2. Periodic refresher training.
3. Update training. This is the most important and should be done whenever a change is made in the process or when an incident or near-miss occurs.

Effective training and skills development must be conducted in a manner and at a level that is clearly understood by all workers, and must include evaluation tools that demonstrate a minimum level of understanding and skills proficiency. A thorough understanding of how the physical and chemical properties of methanol affect flammability hazards and severity is an essential training topic for all methanol workers. Consult the Methanol Institute's Technical Bulletins on Using Physical and Chemical Properties to Manage Flammable Liquid Hazards for additional information.

9 ENVIRONMENTAL PROTECTION

This chapter discusses the environmental impacts of methanol.

The most important properties of methanol that define its effects on the environment are its solubility, volatility, and toxicity. These determine the fate and transport of methanol releases into air, water, and ground and its effects on living organisms.

Methanol is found naturally in plants, animals, and humans. Environmental methanol can come from both natural sources and human activities. Based on releases reported in the United States Toxics Release Inventory (TRI), more methanol is released into the air than to any other environmental medium, though some methanol is also distributed into water.

Atmospheric methanol comes primarily from industrial sources. Methanol degrades by photo-oxidation and undergoes aerobic and anaerobic degradation through biological mechanisms. It has low toxicity to most aquatic organisms and is not known to bio-accumulate significantly in fish. The Organization for Economic Cooperation and Development's (OECD's) Screening Information Data Set (SIDS) Program [54] has determined that methanol is a low-priority chemical, whose properties are not considered harmful to the environment under normal circumstances. The US EPA has determined that methanol has a limited persistence in the environment.

The US has an environmental regulation related to process safety management that directly corresponds with the US OSHA regulation for PSM. The regulation, administered by the EPA, is 40 CFR 68 Chemical Accident Prevention Provisions, in particular subparts D and G. Subpart D explicitly describes requirements for a process safety management system, while subpart G describes requirements for a risk management plan and refers back to the requirements in subpart D. Detailed information regarding PSM is described in chapter 5 of this manual.

9.1 ENVIRONMENTAL FATE AND TRANSPORT

The main physical and chemical properties of methanol that affect its fate, transport, distribution, and persistence in surface water and groundwater are its miscibility, its affinity for other materials (partition coefficients), and biodegradation.

Methanol is 100% miscible in water and has a low water-octanol partition coefficient, meaning that the two liquids will mix completely in all proportions. Therefore, if spilled onto surface water, methanol will dissolve and dilute to very low concentrations relatively quickly. Although pure methanol is highly volatile in air, once it dissolves in water, it becomes very stable and will not readily come out of solution. This makes it difficult to remediate methanol spills in water. In an open ocean methanol spill, naturally occurring wave action, quick dissolution within the water column, and the near-infinite availability of water results in rapid dilution to nontoxic concentrations.

Dissolved methanol does not have much affinity for mineral surfaces or organic carbon in soil. However, once methanol reaches low concentrations in soil, it readily biodegrades under a wide range of geochemical conditions.

Biodegradation, the breakdown of methanol into carbon dioxide and water through the action of bacteria, is the primary mechanism for removing methanol from the environment. Methanol spills to surface waters can quickly biodegrade under aerobic conditions in a matter of days or weeks. However, for releases where fine soil, low hydraulic conductivity, low nutrient, and anaerobic conditions prevail, methanol degradation in soil or groundwater can be very slow and can take approximately one year or longer to reach non-measurable levels.

An active microbial community of methanol degraders can become established within a few days after a surface water release. Dissolved oxygen concentration in water is the limiting factor for the biodegradation rate. In surface water, a typical degradation rate is 10 mg/l per day. At concentrations less than 3,000 mg/l, methanol is readily degraded in a wide range of subsurface conditions. However, methanol concentrations above 10,000 mg/l can inhibit the microbial population and lower the degradation rate.

9.2 AIR EMISSIONS

The relatively high vapor pressure of pure methanol causes it to volatilize readily into the air. If released below ground, it will concentrate in soil gas within pore spaces, though it is easily biodegradable. In the atmosphere, methanol vapor reacts with nitrogen oxides (NOx) to generate methyl nitrate. As a volatile organic compound (VOC), methanol can contribute to the formation of photochemical smog. Methanol is broken down by sunlight and has a half-life of 17 to 18 days. After five days, the estimated removal from the environment is 75%-82%; that rate increases to 95% in 20 days.

According to the United States Toxics Release Inventory (TRI), 100 million pounds (45458 metric tons) of methanol were released on- and off-site from facilities in all industries in the U.S. in 2017. Approximately 82% of the emissions were released into the air, and less than 2.7% into surface waters. The largest emitter in 2017 was the pulp and paper industry.

Methanol is included in the EPA's list of 188 Air Toxics, pursuant to the United States Clean Air Act amendments of 1999, as well as in the Integrated Risk Information System (IRIS) database for pollutants with potential adverse health effects.

9.3 GROUNDWATER EFFECTS

The potential for mixing, dispersion, and dilution is a key factor in determining the rate of degradation of the methanol plume. If the infiltration area is large, biodegradation can result in concentrations of less than 3 mg/l in one to two years, even for high volume releases. This period can extend to five or ten years in the case of smaller but continuous releases such as from a leaking underground pipeline, where the methanol plume reaches stability with a high concentration core, especially where the water table is shallow (reference – Smith, Molson, Maloney).

This is of particular importance in facilities and fuel transfer terminals with an aging infrastructure of underground piping. Accelerated corrosion rates can occur in methanol piping in the presence of even small amounts of water.

Fuel transfer terminals or pipelines that transfer 85/15 gasoline-methanol blends face potentially greater environmental impacts than those transferring pure methanol. This is because methanol acts as a solvent, aiding the dispersion of the gasoline in groundwater, and competes with benzene for aerobic bacteria, causing the release to take considerably longer to biodegrade. The problem of ensuring underground piping integrity can be sufficiently severe in fuel transfer terminals that piping is being relocated to above-ground installations in concrete channels.

9.4 IMPACTS TO DRINKING WATER

Methanol is not currently listed as a contaminant on the United States EPA's National Primary Drinking Water Regulation (NPDWR), the National Secondary Drinking Water Regulation (NSDWR), or the Drinking Water Health advisories. Methanol is listed as a candidate on the Contaminant Candidate List 4 (CCL-4) released by EPA in 2016.

9.5 BIOLOGICAL EFFECTS

The EPA Office of Pollution Prevention and Toxics found that methanol is essentially nontoxic to four aquatic fish species that were tested based on the reported values of median lethal and effective concentrations. However, biodegradation of methanol from a surface water release can cause oxygen depletion in the water, which in turn could harm local fish species.

Methanol is toxic to aquatic organisms, such as fish, daphnids, and algae, at levels well above 1,000 mg/l and especially above 10,000 mg/l. According to the EPA, these values indicate a low acute toxicity of methanol to freshwater fish. Methanol's toxicity to aquatic plants is variable. It is highly toxic to eel grass and algal mats and has low toxicity to green algae.

Methanol toxicity for estuarine and marine fish is similar to that for freshwater species. Methanol is low to moderately toxic to freshwater invertebrates (water fleas, aquatic sow bugs) and estuarine and marine invertebrates (mussels, brine shrimp). Methanol's toxic effects of short-term exposure to marine life are temporary and reversible. Methanol does not bio-accumulate significantly in animals higher up in the food chain.

Knowledge of methanol's effects on mammals comes primarily from research on laboratory animals, including mice, rats, cats, dogs, and monkeys. In the wild, the distinctive odor of methanol would likely warn animals to avoid a release area and prevent exposure. However, methanol is a component of antifreeze, which can be highly toxic when consumed by household pets.

Inhalation, oral, and skin exposure studies in laboratories show that rodents, rabbits, and dogs suffer from loss of muscle coordination, unconsciousness, and coma after high methanol doses. However, these animals do not exhibit the acidosis and eye changes typically seen in humans at high lethal and sub-lethal doses. The lethal air concentrations for animals tends to be lower than for humans, while the oral lethal doses are much higher for animals than for humans.

9.6 CLIMATE EFFECTS

More Methanol is produced from natural gas than from any other feedstock. A well-operated, existing methanol production plant using natural gas has an efficiency of approximately 68%. The upper limit of efficiency of methanol production from this fossil feedstock, consisting of up to 80% of methane and 20% of a higher hydrocarbon like ethane, propane, butane, and others, is estimated at 75%. Methanol can also be generated from biomass, coal or by using electrical energy via hydroelectric or wind power with energy efficiencies of only 55%-60%, compared to the conventional natural gas manufacturing process.

In the 1990s, a typical methanol manufacturing plant would emit approximately 0.9-1.0 tonnes of carbon dioxide (CO2) for every tonne of methanol produced. In addition to the environmental concerns, large CO2 emissions represent operational inefficiencies in a methanol plant because the carbon emitted as CO2 is not available for making methanol molecules. For these reasons, methanol plants began and continue to focus on efficiency improvements that reduce CO2 emissions.

Over the last decade, methanol plants have been able to reduce CO2 emissions by up to 40%. This has been accomplished through the implementation of efficiency improvements and through replacement of older facilities with newer plants that use more efficient technology. Some facilities report emissions as low as 0.54 tonnes of CO2 per tonne of methanol produced. This is equivalent to emitting 3.6 lb of CO2 per gallon (0.43 kg of CO2 per liter) of methanol.

According to the Intergovernmental Panel on Climate Change (IPCC), methanol produced from biomass for use in motor vehicles would reduce the overall greenhouse gas emissions compared to fossil fuels because CO2 from biomass-derived fuels originates from the air, and the emissions are not counted in an emission inventory or a life cycle analysis.

9.7 WASTE TREATMENT AND DISPOSAL

Waste methanol in concentrations equal to or greater than 24% by weight meets the EPA's definition of an ignitable hazardous waste.

Product-grade methanol, when disposed, is a listed hazardous waste. Waste methanol, or water contaminated with methanol, is considered a hazardous waste and must never be discharged directly into sewers or surface waters. It may only be disposed of at a licensed facility permitted to handle Hazardous Waste as defined in the United States Resource Conservation and Recovery Act (RCRA). Contaminated products, soil, or water with methanol must be moved only by registered transporters in approved containers. The recommended disposal method for methanol is incineration for heating value recovery. Concentrated liquid methanol can be used as secondary fuel in systems compatible with water-soluble waste. Waste methanol is also amenable to reclaiming by filtration and distillation.

10 PRODUCT STEWARDSHIP AND SUSTAINABILITY

10.1 PRODUCT STEWARDSHIP AND RESPONSIBLE CARE

For the global methanol industry, product stewardship is the central focus from the input of raw materials during methanol production to the consumer and ultimately the disposal of methanol. The Methanol Institute plays an essential role in promoting product stewardship for the global methanol industry.

Within the global chemical-producing industry, product stewardship is commonly understood to be the development and management of chemical products throughout their entire life cycle, from "cradle to grave." The goal of product stewardship is to ensure that parties up and down the product supply chain have active management systems to ensure the safe, environmentally sound, and socially responsible handling of the product.

Each party needs to assess on an ongoing basis how issues involving research, raw materials, product handling, use, and final disposition are being addressed. This involves a shared and sustained commitment of responsibility so that issues are identified and corrective actions are implemented at any point in the product chain. The ultimate goal of product stewardship is to improve the responsible management of chemical products throughout their life cycles – from the input of raw materials to ultimate product end-use and disposal.

The Methanol Institute plays its role in product stewardship by communicating safe handling guidelines for methanol across the global distribution chain and to the downstream customers.

With the increase in global demand for methanol, especially in recent years, it has been essential for the methanol industry to maintain and observe the highest standards involving safety, health, and the environment. The Methanol Institute is responsible for methanol health and safety initiatives, such as product risk evaluation, evaluation of exposure risks throughout the supply chain, and education and training on proper methanol handling, storage, and use. In addition, the Methanol Institute has been serving as the voice for the international methanol industry, especially pertaining to the health effects, safety precautions, and environmental impacts of methanol. The Methanol Institute also maintains the world's most comprehensive database of methanol health effects and environmental impacts.

10.2 PRODUCT STEWARDSHIP MANAGEMENT SYSTEM

Similar to safety and environmental management systems, such as International Organization for Standardization (ISO) 14001 and Occupational Health and Safety Advisory Services (OHSAS) 18001, product stewardship requires a management system approach that follows the "plan – do – check – act" cycle. This management system should document the right way to do things, assign responsibilities for implementation, and outline the process to do the following:

- Train, correct, and reward people.
- Constantly seek a better way.
- Audit to make sure the system is working.
- Track and report on performance, and use this feedback to drive improvement.

The expectation is that companies will incorporate the product stewardship culture and practices into their existing management systems used to manage all aspects of the company's operations and businesses. A product stewardship culture is a shared belief that no product bought or sold by the company should cause harm to people or the environment.

10.3 PRODUCT STEWARDSHIP PRACTICES

As with all aspects of Responsible Care, companies are expected to instill a culture of product stewardship through the organization and to integrate the practices of product stewardship into the management systems that are used to develop, manufacture, market, and further improve the state of profitable, high-quality, and sustainable products.

Ten Product Stewardship Practices (PSPs) need to be implemented across the company by all levels of management and employees. These ten practices address the fundamental activities that are necessary to ensure the stewardship of a product over its life cycle, from product concept to product end of life, and to instill a product stewardship culture within a company.

10.3.1 PSP #1: LEADERSHIP AND ACCOUNTABILITY

Clearly state the long-term commitment of senior leadership to product stewardship in written policies. Specifically, leaders should:

- Encourage employees across the organization to understand product stewardship concepts and incorporate these in their own roles and responsibilities.
- Ensure that adequate resources are available to establish, review, and attain product stewardship performance goals for each product.
- Demonstrate and reinforce the company commitment to product stewardship by taking action to address poor product stewardship performance, resolve difficult issues, modify support resources, or change a product management/commercialization strategy.

10.3.2 PSP #2: ENVIRONMENTAL, HEALTH, AND SAFETY INFORMATION

It is important to establish a database to store, update, and access product Environmental, Health, and Safety (EH&S) information. This information includes product testing data, regulatory registrations, and workplace exposure/plant emission data. There are many available sources from which to collect information, including internal research and development, industry partners, academia, and government sources. It is important to ensure that information is updated as new information becomes available and on a regular basis. The Methanol Institute's web site at www.methanol.org can be a useful tool for developing an EH&S information database.

10.3.3 PSP #3: SELLING

Promote two-way communication with downstream second parties, which will enable companies to understand market expectations for Methanol, as well as social, EH&S, and ethical concerns. It is especially important to provide balanced and accurate information on EH&S issues to second parties transporting or handling Methanol. This helps to ensure that customers and downstream users are aware of the new developments and insights into EH&S information on the products. Actively seek feedback from downstream second parties on their product end-use applications and risk management experiences with the product to help develop further awareness. Involve Research and Development (R&D) early with customers and their customers to assist in product design, and minimize potential difficulties in the use, handling, recycling, and disposal of products. Sharing this Methanol Safe Handling Manual with downstream distributors and customers is a good way to promote product stewardship. If additional copies are needed, you can contact the Methanol Institute at: mi@methanol.org.

10.3.4 PSP #4: PUBLIC CONCERNS AND ISSUES

Ensure consideration of the relevant concerns of individuals or groups not in the direct flow of Methanol use. An early discussion of concerns within these groups will help reduce both real and perceived hazards.

10.3.5 PSP #5: PERFORMANCE INDICATORS

Integrate product stewardship performance metrics and goals into employee assessment, recognition, and reward processes. All employees need to demonstrate commitment to product stewardship in their daily work activities.

10.4 SUSTAINABILITY

Methanol users participating in Responsible Care and Responsible Distribution are also developing and implementing sustainability strategies. One of the biggest drivers for change in supply and demand chain operations is the pressure to be more environmentally responsible and sustainable in their product sourcing, logistics, transportation, distribution, and operational practices.

10.4.1 A PRIMER ON SUSTAINABILITY

The 1987 United Nations Sustainable Development Conference in Johannesburg, South Africa defined sustainable developments as those that “meet present needs without compromising the ability of future generations to meet their needs.” A key concept that places sustainability in more familiar business terms is the “three Es” or “triple bottom line” concept of economics, environment, and (social) equity. The central point is that most business and government decisions need to integrate these three dimensions in order to evaluate their full impacts to the planet and reach the most desirable approach. The term “green” is often used as a synonym for sustainability, although its meaning is more broadly applied. These concepts can be very useful tools in planning a sustainability strategy and setting performance benchmarks.

Most leading global enterprises have accepted the business case for sustainability. Companies with extensive supply and demand networks, such as the chemical industry, are looking for standardized metrics and indicators of sustainability performance that can be applied across the supply chain.

Many organizations following Responsible Care and Responsible Distribution are also implementing "Lean" production methods to improve manufacturing processes, increase efficiency and reduce costs throughout the value chain. Lean manufacturing seeks to eliminate all waste from a production system.

Methanol value chain companies can benefit from leveraging their lean production implementation plans to support their sustainability efforts. The "lean to green" movement capitalizes on the similarities between sustainability and lean management. The lean goals of improving quality, eliminating waste, reducing time to complete a task, and lowering total costs are compatible with the sustainability goals of eliminating waste and pollution, improving energy efficiency, increasing utilization of renewable resources, and lowering the costs to the planet of conventional material sourcing, production, and distribution practices. In addition, both lean and sustainability emphasize the importance of stakeholder education, employee teamwork, and application of analytical tools and metrics to drive performance. Sustainability and lean management are both process-oriented activities. The core principle of lean production is continual improvement. Not surprisingly, the best Responsible Care, Responsible Distribution, and Sustainability systems also reflect this principle.

10.4.2 ALTERNATIVE ENERGY

The global recognition of the environmental and social impacts of energy derived from fossil fuels is also raising concerns that new and alternative energy supplies should meet recognized standards of sustainability. The acceptance and future success of biofuels as fossil fuel substitutes will greatly depend on their overall social, economic, and environmental impacts, the three pillars of sustainability. In that respect, not all renewable fuel sources are the same. Producing biofuels from food crops, or as part of the process of deforestation undertaken to grow biofuel crops, will affect their relative carbon footprints and is likely to meet growing societal resistance.

Methanol's use as an alternative fuel source in gasoline blends, in biodiesel production, and as a key component in hydrogen fuel cells helps to reduce the direct consumption of fossil fuels. However, 98% of today's commercial methanol is produced in large chemical manufacturing plants using non-renewable natural gas. Production of methanol from renewable resources using waste materials as feedstock is a promising alternative.

Currently, several biomethanol production technologies are in development from demonstration projects to limited production facilities in Europe. One such technology developed by Chemrec AB, a Swedish company, utilizes black liquor produced as a waste in paper mills in a gasification process to produce bio-based methanol.

BioMCN, one of the world's largest biodiesel manufacturers based in the Netherlands, is using renewably produced glycerin to make biomethanol. Crude glycerine, a byproduct of biodiesel production, is purified, evaporated, and cracked to obtain synthesis gas (syngas), which is used to synthesize biomethanol. The biomethanol is purified by distillation and used with vegetable oils and fats in the standard process to produce biodiesel, again generating glycerin as a byproduct, thus closing the production cycle in what is termed "cradle to cradle." Syngas can also be obtained from other forms of biomass such as wood or algae derived from organic waste materials and from crops other than those used for food consumption. BioMCN operates a biomethanol plant producing 200,000 metric tons per year.

Iceland-based Carbon Recycling International (CRI) is manufacturing "renewable methanol" by first using geothermal energy to produce hydrogen from water, then combining it with captured carbon dioxide emissions from geothermal electricity generation to produce methanol. CRI has operated a demonstration facility in Iceland since 2007 and expanded the George Olah production plant in Svartsengi, Iceland to 5 million liters per year capacity in 2015.

At the research and development stage, researchers at the University of Southern California are working on a technology to strip carbon dioxide from the atmosphere to produce methanol. A definitive evaluation of the carbon footprints of various alternative fuels is beyond the scope of this manual. However, the major renewable fuel source, ethanol, faces a number of challenges as a sustainable alternative. These include a negative energy balance where the inputs exceed the outputs, environmental impacts on water and soil from being produced from corn and sugar cane, and the social impacts from competition with food crops and agricultural land. By contrast, on a number of sustainability criteria, methanol from renewable sources compares favorably to ethanol. It can be produced from a wide variety of sources, exclusive of crops intended for human consumption and high commercial value biomass. Methanol allows re-use of by-products in "cradle-to-cradle" loops and can utilize carbon dioxide as an input. [(References 9.5.2-1 to 9.5.2-5) Pimentel, Chemrec, BioMCN, CRI]

11 RISK COMMUNICATION

11.1 WHAT IS RISK COMMUNICATION?

When we first consider risk communication, it is generally as a means of communicating information in an emergency response or crisis situation, as the following definition suggests [15]:

Risk communication is a science-based approach for communicating effectively in situations that may be characterized as:

- high concern, high stress
- emotionally charged, or
- controversial.

This is certainly true, and there are situations in the global methanol industry where this definition applies, such as large methanol spills, fires, and disruptions in the supply, to name a few. It is also likely safe to presume that when we talk about the risks of methanol, we are talking about a topic of high concern to many people.

Risk communication also has applications at home, at work, and in the community as the following definition suggests: Risk communication is the art of putting science in the hands of people, in a way they can use (USEPA [64]).

The focus of this chapter is on the use of risk (and hazard) communication in non-crisis situations. The fundamentals of risk and hazard communication are the same, no matter the situation, whether it be a routine communication or a high-stress situation. This chapter introduces the tools and principles for effectively communicating information about risks, as well as hazards, about the industry in non-crisis situations.

In this context, it is important to keep in mind two other key definitions – the concepts of "Hazard" and "Risk." When we are considering the global use of methanol, hazard and risk may be considered as follows:

- The "hazard" associated with methanol is its intrinsic ability to cause adverse effects.

- The "risk" is the probability that such effects will occur in the various applications in which methanol will be used and discharged (or the exposure scenarios for use of methanol).

This entire manual focuses on the hazards of methanol and the means used to limit those hazards and thereby the risk of exposure of methanol to workers, the community, and the environment.

This chapter emphasizes the application of risk (and hazard) communication pertaining to the distribution and use of methanol in the context of the second definition above: putting science in the hands of people in a way they can use.

The need may arise for a more detailed look at risk communication in crisis situations. The Methanol Institute has a Crisis Communication Guidebook that includes a more detailed review of risk communication principles for use during crisis situations, including dealing with the media.

11.2 WHY IS RISK COMMUNICATION IMPORTANT?

Effective and thoughtful risk and hazard communication can build trust and confidence in the employee population and the community at large. This is crucial in order to prevent inaccurate or potentially damaging public response in the event of a crisis.

Also, recall in the Product Stewardship chapter, the concepts of the Responsible Care Ethic and Responsible Distribution. A key principle of each is sharing information with affected parties, whether they are employees, nearby communities, political interest groups, sub- distributors, or suppliers. Planning your message to be consistent with the principles of Responsible Care and/or Responsible Distribution, as well as achieving the basic tenets of risk communication, go hand in hand.

While we are not focused on crisis situations in this chapter, the risks and hazards of methanol are real. When we are addressing issues of people’s health and safety, it is important to realize that these are matters of high concern to people.

11.3 RISK COMMUNICATION BASICS

The first definition of risk communication above stated that risk communication is a “science-based” approach of communication. Indeed it is. Effective risk communication requires planning and preparation. There are four basic steps to effective risk communication:

1. Determine the communication goal.

   Communication goals about a particular methanol business, work location, new technology, or other situation are numerous in non-crisis situations, such as sharing a new procedure with a supplier, training new employees in a manufacturing process, informing a neighborhood community about a new alarm procedure at a plant, etc. Is the goal to inform your audience and/or to persuade them to act? Write down the purpose of the communication and any desired outcome prior to constructing the message.

2. Know the audience.

   For example, if information is planned to be shared with a neighboring community or a work crew within a plant, request input from a representative(s) of the community or work crew, rather than assuming what their concerns may be. This is applicable for all communications, whether routine (such as information bulletins, training classes, etc.) or high-stress situations. Getting input from the audience, particularly with regard to concerns about health and safety, will not only be enlightening for the entity preparing the message, it can also help build credibility with the audience, which is crucial in risk communication.

3. Develop the components of the communication - the message and the medium.

   Select a medium for communicating that will reach the most people, and take care not to inadvertently leave groups out. For example, communicating important information (such as what to do when a shelter-in-place alarm is activated) via a web bulletin to an economically disadvantaged community is likely not an effective means of communicating such an important message. Make sure that language barriers are considered and planned for in order to reach the most people.

4. Make sure the information provided is accurate and timely.

This is particularly important when communicating in a crisis situation, but applies to all risk and hazard communication. Ensuring that the person delivering the message is competent is critical to building and maintaining credibility with the audience.

11.4 COMMUNICATING COMPLEX TECHNICAL AND SCIENTIFIC INFORMATION

Scientific information will be more useful to the audience, and greater communication success will be achieved, if the information provided is relevant and easily understood. To help audiences understand the issues, create well-targeted messages. Also be sure to use clear, non-technical language to discuss risks and other specific information indicating the nature, form, severity, or magnitude of the risk.

The following are some ways to clearly communicate complex scientific or technical information:

- Always use consistent names and terms (e.g., switching from parts per million to parts per billion can result in alarm because the higher numbers may be noticed, but not the unit of measure).
- Avoid acronyms and jargon, and provide careful definitions in advance. Never assume an audience “knows what you are talking about.”
- Use familiar frames of reference to explain how much, how big, or how small, and try to create a mental picture of such measures as “parts per billion” or “tons per day.” Numeric analogies, such as “the United States produces enough garbage in a day to fill 100 American football fields 14 feet (4.25 m) deep,” are more meaningful to average listeners than talking about 250,000 tons or tonnes of garbage per day. However, examples should not be trite or condescending or overly dramatic. Take the time to develop meaningful examples and calculations.

- Acknowledge uncertainty. Recognizing and admitting uncertainty is simply the reality of most risk communication situations, but especially in a crisis situation. Saying "I do not know" is an acceptable response and can build credibility. If an audience demands 100% certainty, they are more than likely questioning the underlying values and process, not the science. Try to identify the real concerns behind the demand for certainty and address them. For example, the statement, "If you're not certain, how can we know we're being protected?" is not a question about data but rather about personal and family safety. That is the issue to be addressed.

11.5 UNDERSTANDING THE PUBLIC'S PERCEPTION OF RISK

A key barrier is the term "risk" itself – how it's measured, described, and ultimately perceived. Interested parties perceive risk differently, and people do not believe that all risks are of the same type, size, or importance.

Perceptions of the magnitude of risk are influenced by factors other than numerical data (see table below from the U.S. Department of Health and Human Services (USDHHS) [61]). Understanding these factors will help determine the degree of risk with which a message may be perceived and assist in crafting an appropriate communications strategy.

Risk Perceived To...	Are More Accepted Than...
Be Voluntary	Risks perceived as being imposed
Be Under an Individual's Control	Risks perceived to be controlled by others
Have Clear Benefits	Risks perceived to have little or no benefit
Be Distributed Fairly	Risks perceived to be unfairly distributed
Be Natural	Risks perceived to be man-made
Be Generate by a Trusted Source	Risks perceived to be generated by a less credible source
Be Familiar	Risks perceived to be exotic
Affect Adults	Risks perceived to affect children

11.6 EARNING TRUST AND BUILDING CREDIBILITY

The ability to establish constructive communication will be determined, in large part, by whether an audience perceives the person delivering the message to be trustworthy and believable. Consider how people form their judgments and perceptions.

Key elements in trust and credibility, and their relative importance, are depicted as follows:

(Courtesy of the Center for Risk Communication, with permission)

Do not underestimate the absolute requirement that people need to know that you care before they care what you know!

11.7 LOOKING FOR OPPORTUNITIES TO GET YOUR MESSAGE OUT

Do not wait for a crisis situation to begin the process of risk communication. In fact, the more thorough and thoughtful an industry, company, government body, etc., can be about the issues they deal with and how the public may perceive the risks, the better prepared that entity will be in any crisis situation. Some opportunities to reach out may include, but are not limited to, the following actions:

- Submit letters to the editors of local newspapers.

- Contact your local newspaper to find out how to submit an opinion article.

- Call in to local talk radio programs when pertinent topics are being discussed.

- Contact local talk radio producers to solicit an invitation to appear on their programs.

- Contact local civic groups to solicit speaking opportunities.

- If you give a speech, contact local news outlets and ask them to cover your presentation.

- Contact local television news producers to explore ways they can cover your issues.

The creation and use of a stakeholder registry to plan and manage communications would be highly beneficial. A stakeholder registry lists all identified stakeholders with which the company may wish to communicate, as well as the method or style of communication for each stakeholder (e.g., e-mail, written report, community meeting), the frequency of communications (e.g., weekly update, monthly, during a crisis) and perhaps a brief summary of content.

For additional discussion about stakeholder outreach as it relates to Process Safety Management requirements, examples of stakeholders and potential areas of communication, refer to section 5.4.5 in this manual.

12 GLOSSARY

12.1 TERMS, ABBREVIATIONS, AND ACRONYMS

-A-

accident An unfortunate incident that happens unexpectedly and unintentionally, typically resulting in property damage or personal injury.

ACGIH American Conference of Governmental Industrial Hygienists. ACGIH publishes recommended upper limits (Threshold Limit Values – TLVs) for worker exposure to chemicals within the workplace.

acute effect(s) An adverse effect with severe symptoms developing rapidly and coming quickly to a crisis as a result of exposure to heat, overpressure, or toxic material.

adiabatic flame temperature (see also Peak Flame Temperature) The highest possible flame temperature presuming there is no loss of heat 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 a portion of the heat of combustion is transferred to the surroundings via convective and radiant heat transfer.

AFFF Aqueous Film-forming Foam.

AFNOR Association Française de Normalisation.

alcohol(s) Any of a class of organic compounds characterized by the presence of a hydroxyl group covalently bonded to a saturated carbon atom.

alkali metal(s) Group 1A elements in the periodic table.

alkanes Any of a class of hydrocarbons in which one carbon atom is bonded to four other atoms. Alkanes are said to be "saturated."

API American Petroleum Institute.

AR-AFFF Alcohol-resistant Aqueous Film-forming Foam.

ASME American Society of Mechanical Engineers.

atmosphere(s) A measure of atmospheric pressure at mean sea level equal to 14.7 pounds per square inch (psi) of pressure.

autoignition point/autoignition temperature The minimum temperature required to initiate or cause self-sustained combustion independently of the heating source or heated element. As the temperature of a flammable liquid is increased above the fire point, a minimum temperature is attained at which self-sustained combustion occurs in the absence of an ignition source. This temperature is called the autoignition point or autoignition temperature.

-B-

BEI Biological Exposure Indices.

bermed Having a mound or bank of earth, used specifically as a barrier or to provide insulation.

bioaccumulation The increase in concentration of a substance in an individual's tissues due to uptake from food. It occurs when an organism absorbs a toxic substance at a rate greater than that at which the substance is metabolized.

biodegradable An organic substance that can decompose or be degraded to its constituents by the action of living organisms, such as bacteria and fungi.

biodiesel A vegetable oil- or animal fat-based diesel fuel consisting of long-chain alkyl esters. Biodiesel is typically made by chemically reacting lipids (e.g., vegetable oil, animal fat) with an alcohol such as methanol.

BLEVE An acronym for a Boiling Liquid Expanding Vapor Explosion. A hazardous situation exists when a storage tank containing highly flammable gases and liquids (e.g., methanol) under pressure is exposed to direct flames of a fire. Fire making contact with the shell of the tank causes simultaneous loss of strength in the metal and a rapid development of internal pressure in the vapor space above the liquid. If the venting mechanism (pressure relief valve) built into the structure is only sized for normal vapor expansion and not for "fire case," then the inability to vent fumes causes pressure to rapidly accumulate within the tank. The combination of a weakened shell structure and high internal pressure results in an instantaneous tank failure and catastrophic release and ignition of vapor. Use of unmanned firewater monitors is typically recommended in potential BLEVE incidents. BLEVE may occur within 10 to 30 minutes of initial flame contact unless the tank is cooled. A firewater application rate of at least 500 U.S. gallons (approximately 1,900 liters) per minute is required to cool the tank. BLEVEs can cause containers to "rocket" away from the site of the explosion due the force of the explosion.

boiling point or boiling point temperature (B.P.) The temperature at which a liquid phase material changes to a vapor phase. Boiling point is usually expressed in degrees of temperature (centigrade, Celsius, Fahrenheit, Kelvin, or Rankine).

BTU A commonly used abbreviation for British Thermal Unit, a measure of heat. One BTU is equivalent to the heat that is necessary to raise 1 pound of water 1 degree Fahrenheit, specified at the temperature of water's maximum density (39°F or 4°C). One BTU contains 252 calories or 1,055 Joules.

bunded An enclosure to contain either a reclaimed area, a chemical, or other hazardous substance if it spills.

-C-

C or ceiling The concentration value of an airborne substance that is not to be exceeded during any part of the working exposure.

CABA Compressed Air Breathing Apparatus.

calorie (cal) The amount of heat required to increase the temperature of 1 gram of water 1 degree Celsius from 14.5°C to 15.5°C.

CANUTEC Canadian Transportation Emergency Center. A national center in Ottawa that is operated by the Department of Transportation. On request, CANUTEC relays pertinent emergency information concerning specific chemicals. CANUTEC has a 24/7 telephone number (613-996-6666).

carcinogen A substance that causes cancer; a substance or agent capable of producing cancer in mammals.

CAS Number Chemical Abstract Service Number. A number assigned by the Chemical Abstracts Service that identifies a specific chemical. The CAS number provides indexing to access information about particular substances.

cc (cubic centimeter) A metric measure of volume equal to one milliliter (ml).

CCL-4 United States EPA's Contaminant Candidate List43, released in February 2016. See Contaminant Candidate List.

CERCLA Comprehensive Emergency Response and Liability Act.

CFR An acronym for the United States Code of Federal Regulations.

chemical family A group of single elements or compounds with a common general name (for example, gasoline, naphtha, kerosene, diesel, etc., and blended cuts of the "hydrocarbon" family).

chemical feedstock A chemical that is used as the starting point for the manufacture of other, more complex chemical substances.

chronic effect An adverse effect on a human or animal body with symptoms that develop slowly over a long period of time.

Class IA The National Fire Protection Agency (NFPA) designation for flammable liquids having flash points temperatures below 73°F (22.78°C) and boiling point temperatures below 100°F (37.78°C). An example of a class IA flammable liquid is n-pentane.

Class IB The National Fire Protection Agency (NFPA) designation for flammable liquids with flash point temperatures below 73°F (22.78°C) and boiling point temperatures greater than or equal to 100°F (37.78°C). Examples of Class IB flammable liquids are methanol, benzene, propane gasoline, and acetone.

Class IC The National Fire Protection Agency (NFPA) designation for flammable liquids with flash point temperature(s) greater than or equal to 73°F (22.78°C) and less than 100°F (37.78°C). Examples of Class IC flammable liquids are turpentine and n-butyl acetate.

Class II The National Fire Protection Agency (NFPA) designation for combustible liquids having flash point temperatures equal to or greater than 100°F (37.78°C), but less than 140°F (60°C). An example of a Class II combustible liquid is kerosene.

Class IIIA The National Fire Protection Agency (NFPA) designation for combustible liquids that have flash point temperatures equal to or greater than 140°F (60°C) and less than 200°F (93.33°C). Examples of Class IIIA combustible liquids are creosote oils and phenol.

Class IIIB The National Fire Protection Agency (NFPA) designation for combustible liquids with flash point temperature equal to or greater than 200°F (93.33°C). Ethylene glycol is an example of a Class IIIB combustible liquid.

CNG Compressed Natural Gas.

coefficient of volumetric thermal expansion The change in the volume of a liquid per degree of change in temperature.

coma A profound state of unconsciousness from which the subject cannot be awakened.

combustible (adj) A substance, solid, liquid, or gas that will burn; a description of flammability of a liquid based on flash point; generally refers to liquids with a flash point greater than or equal to 100°F (37.78°C)

combustible liquid(s) A National Fire Protection Agency (NFPA) designation for liquids having flash point temperatures at or above 100°F (37.78°C). Combustible liquids are subdivided into three classes as above based on flash point temperature.

combustion A chemical reaction that releases energy as heat and usually light. In everyday usage, it generally indicates something is burning or on fire. Combustion and burning are essentially equivalent terms.

confined space A term used in labor safety that refers to an area with enclosed conditions and limited access.

Contaminant Candidate List (CCL) The primary source of priority contaminants for which the United States EPA conducts research to make decisions about whether regulations are needed. The contaminants on the list are known or anticipated to occur in public water systems; however, they are currently unregulated by existing national primary drinking water regulations. Listing in the CCL is based on a contaminant's potential to occur in public water systems and the potential for public health concern.

Contaminant Reduction Zone (CRZ) The site control zone surrounding the Exclusion Zone. The CRZ holds the only access point for entry of response personnel and equipment, as well as the decontamination corridor for cleaning personnel and equipment exiting the Exclusion Zone.

corrosive (adj) A gas, liquid, or solid that causes irreversible damage to human tissue or containers; defined by the United States Department of Transportation (DOT) as a liquid or solid that causes visible destruction or irreversible alterations in human skin tissue at the site of contact.

Cradle-to-Grave An environmental assessment of the impact of a product or chemical through its entire life cycle, from manufacture to eventual disposal.

-D-

decomposition The breakdown of a material or substance (by heat, chemical reaction, electrolysis, decay, or other processes) into parts or elements or simpler compounds.

deflagration (explosive deflagration) A low-velocity (less than the speed of sound) explosion that burns furiously and persistently. Vapor cloud explosions are typically deflagrations, not detonations. Strictly speaking, most deflagrations are not explosions, but are fire balls with very fast flame fronts that approach 343 meters/second at 20°C. An explosive deflagration produces an appreciable blast wave, which has the potential of damaging equipment and injuring people. Many substances that deflagrate when weakly ignited will detonate under sufficiently strong ignition. A deflagration wave can, in some circumstances, accelerate spontaneously to a detonation.

density The property of a substance that measures its compactness; the mass of a substance divided by the volume it occupies.

dermal toxicity The adverse effects resulting from skin exposure to a substance; toxicity associated with a substance of chemical that enters the body by absorption of the chemical through the skin.

detonation (explosive detonation) A detonation is caused by a very rapid chemical reaction that passes through the exploding material at speeds of 0.6 to 6.2 miles per second (1 to 10 km/s), well in excess of sonic velocity. High pressures are developed, and the products of combustion move in the same direction as the pressure wave. A detonation is a shock wave accompanied by the chemical reaction that sustains it. Explosives that normally detonate are termed "high explosives" and have high shattering power, even when unconfined. Trinitrotoluene (TNT) is an example of a detonating high explosive.

detonation velocity The velocity at which the shockwave front travels through a detonated explosive.

dilution The process of making a substance less concentrated by adding a solvent, such as water.

DIN Deutsches Institut für Normung E.V.

DMDC Dimethyl dicarbonate.

DME Dimethyl Ether.

DMFC Direct Methanol Fuel Cell.

DMT Dimethyl Teraphthalate.

dose The amount of a poisonous substance that causes adverse health effects.

DOT (USDOT) An acronym for The United States Department of Transportation, a Federal agency that regulates the transportation of chemicals and hazardous materials.

DOT Guide Number (see also UN and UA Numbers) The four-digit hazard code assigned by the U.S. DOT. 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.

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.

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.

Drinking Water Advisory A non-regulatory document that analyses the currently available cancer and non-cancer data on a contaminant, as well as studies on its organoleptic (taste and odor) effects.

-E-

EH&S Environmental Health and Safety.

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 (QS/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 x 1012 pico Siemens. A unit micro Siemen is equivalent to 1 x 106 pico Siemens.

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

EPA (USEPA) The United States Environmental Protection Agency, a Federal agency that regulates environmental hazards.

EPCRA Emergency Planning and Community Right-to-Know Act.

ER Emergency Response.

ERC Emergency Response Coordinator.

ERP Emergency Response Plan.

EU European Union.

explosion A rapid increase in volume and release of energy in an extreme manner, usually with the generation of high temperatures and the release of gases. An explosion creates a shock wave.

extinguishing materials A substance that prevents the spread of fire and arrests the chemical reaction that allows sustained fire. Ideal extinguishing materials for methanol fires include alcohol-resistant foam, dry powder, carbon dioxide (released from automatically triggered sources), or water in at least a three- to four-fold excess of methanol by volume.

EZ Exclusion Zone; also known as "hot zone."

-F-

FFFP Film-forming fluoroprotein.

fire monitor (firewater monitor) A stationary, typically unmanned firewater nozzle that can be aimed and left unattended to disperse a stream of water into a predetermined area.

fire point The minimum temperature at which self-sustained combustion occurs.

Fischer-Tropsch process (water gas process) An industrial method of making hydrocarbon fuels from carbon monoxide and hydrogen. Hydrogen and carbon monoxide are mixed in the ratio 2:1 (water gas is used with added hydrogen) and passed at 392°F (200°C) over a nickel or cobalt catalyst. The resulting hydrocarbon mixture can be separated into a higher boiling fraction for diesel engines and a lower boiling fraction gasoline fraction. The process is also used in the manufacture of SNG (Synthetic Natural Gas) from coal.

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

flammable A solid, liquid, or gaseous substance that will ignite easily and burn rapidly, as opposed to a combustible substance that will not ignite as easily or burn as rapidly.

flammable limits Pertaining to ignition of liquids, gases, and vapors in air. Also called the explosive limits. The lower and upper flammable limits define the concentrations outside of which ignition will not occur due to the mixture being too concentrated (rich) or too diluted (lean), respectively. (See flammable range, LEL, UEL.)

flammable liquid(s) Generally, liquids do not actually burn in the liquid state. Liquids release vapors that ignite when a flammable mixture with air is attained in the presence of an ignition source.

flammable material(s) Any solid, liquid, vapor, or gaseous materials that ignite easily and burn rapidly when exposed to an ignition source. Examples of flammable materials within this broad definition include certain solvents such as methanol, dusts like flour, certain finely dispersed powders like aluminum, and gases like hydrogen and methane.

flammable range The numerical difference between the upper and lower explosive limits measured as the experimentally determined volumetric concentration of a substance in air above which and below which ignition does not occur.

flash point/flash point temperature The minimum temperature at which a liquid (or solid) gives off a sufficient volume of vapor at atmospheric or near atmospheric pressure to first form an ignitable mixture with air near the surface of the liquid or within the test apparatus. The United States Department of Transportation defines the flash point temperature as the "minimum temperature at which a substance gives off flammable vapor(s) which, in contact with sparks or flame, will ignite." The term does not ordinarily have meaning or significance when applied to flammable gases or solids.

freezing point temperature The temperature at which the liquid and solid states of a substance coexist at one atmosphere (atm) of pressure.

fuel cell An electrochemical cell that converts chemical energy from a fuel (such as methanol) into electric energy. Electricity is generated from the reaction between the fuel supply and an oxidizing agent. The reactants flow into the cell, and the reaction products flow out of it, while the electrolyte remains within it. Fuel cells can operate continuously as long as the necessary reactant and oxidant flows are maintained.

fuel in vaporized stoichiometric mixture The volume percent of vaporized fuel available to a combustion reaction which occurs at stoichiometric concentration.

functional groups Structural molecular fragments of organic compounds that are found in all members of a given class of compounds and that are centrally involved in the chemical reaction of a chemical class.

-G-

g/cm³ Grams per cubic centimeter. A metric unit of concentration measure (weight/volume) expressed in units of grams of weight per cubic centimeter of volume.

g/m³ Grams per cubic meter. A metric unit of concentration measure (weight/volume) expressed in units of grams of weight per cubic meter volume.

gal Gallon. A commonly used abbreviation for both a U.S. and an English (Imperial) unit of volume. A U.S. gallon contains 231 cubic inches (3.8 liters). An Imperial gallon is defined as the volume that contains exactly 10.0 pounds of water at standard temperature and pressure (which is 277.4 cubic inches or 4.56 liters).

gas(es) The phase of matter in which a substance has no definite shape and a volume that is defined only by the size of the container in which the gaseous matter resides.

ground (electrical) A common return path for electric current, or a direct physical connection to the Earth.

GWBB-8 h Grenswaarde beroepsmatige blootstelling (Belgium 1998). A measure of exposure concentration for an eight-hour workplace exposure.

GWK-15 min Grenswaarde kortstondige blootstelling (Belgium 1998). A measure of exposure concentration within the workplace for a time duration of 15 minutes.

-H-

hazard A hazard is a situation that poses a level of threat to life, health, property, or environment. Most hazards are dormant or potential, with only a theoretical risk of harm; however, once a hazard becomes "active," it can create an emergency situation. Hazard and vulnerability interact together to create risk.

HAZCHEM Code Also known as Emergency Action Code (EAC), a code designed to be displayed when hazardous chemicals are transported or stored in bulk. It is used to help the emergency services take action quickly in any accident. The code consists of a number followed by one or two letters. The number indicates the type of substance to be used in treating the accident (e.g., stream of water, fine spray, foam, dry agent). The first letter indicates the type of protective clothing needed, along with information about the possibility of violent reaction on whether the substance should be contained or diluted. The second letter, where it exists, is E, indicating that people have to be evacuated from the proximity of the incident. In the UK, the code is usually displayed as part of a panel, which includes an international UN number for the substance, a telephone number for specialist advice, the company name, and a symbol indicating the danger or hazard posed by the material (e.g., skull and crossbones for toxic substances).

HAZOP (HAZOPS, HAZOP Analysis) An acronym for HAZard and OPerability Study. A safety procedure by which various engineering and administrative safeguards are assessed to identify accidental release scenarios for hazardous materials.

HAZWOPER An acronym for Hazardous Waste Operations and Emergency Response. It refers to five types of hazardous waste operations conducted in the United States under OSHA Standard 1910.120 "Hazardous Waste Operations and Emergency Response." The standard contains the safety requirements employers must meet in order to conduct these operations.

heat capacity (see also Specific Heat or Specific Heat Capacity) The amount of heat needed to raise either 1 gram of a substance 1 degree Celsius or 1 pound of substance 1 degree Fahrenheit.

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.

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.

hot work Any process that can be a source of ignition when flammable material is present or can be a fire hazard regardless of the presence of flammable material in the workplace. Common hot work processes are welding, soldering, cutting, and brazing. When flammable materials are present, processes such as grinding and drilling become hot work processes.

–I–

IARC The International Agency for Research on Cancer. A scientific group that classifies chemicals according to their cancer-causing potential.

IC Incident Command.

ICC International Code Council.

IDLH Immediately Dangerous to Life and Health. Pertaining to measurement of toxicity, the maximum concentration from which one could escape within 30 minutes without experiencing any escape-impairing symptoms or any irreversible adverse health effect. IDLH levels are published for many substances by NIOSH/ OSHA Pocket Guide to Chemical Hazards, United States Department of Health and Human Services/United States Department of Labor.

IEC International Electrotechnical Commission.

IEEE Institute of Electrical and Electronics Engineers. ignition The initiation of combustion.

IMPCA International Methanol Producers and Consumers Association. incident A hazardous situation that has come to pass.

IPCC Intergovernmental Panel on Climate change, a scientific intergovernmental body set up by the World Meteorological Organization (WMO) and by the United Nations Environment Programme (UNEP). It assesses the scientific, technical, and socioeconomic information relevant for the understanding of the risk of human-induced climate change.

IRIS Integrated Risk Information System.

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

ISO International Organization for Standardization

-J-

joule(s) Symbol j. The SI unit of measure for energy.

-K-

K Kelvin The degrees of temperature relative to thermodynamic absolute zero.

kg(s) kilogram(s) A commonly used abbreviation for a unit of metric measure for the weight (mass) of a substance: 1,000 g = 1 kg.

kJ kilojoule(s) SI abbreviation for common unit of energy.

kPa kilopascal(s) SI abbreviation of commonly used measure of pressure.

-L-

latent heat of vaporization The energy to transform a given quantity of a material into a gas.

LEL Lower Explosive Limit Also lower flammability limit. The volumetric concentration of a flammable material in air at 1 atmosphere of pressure, below which the mixture of fuel and air is too lean or dispersed to ignite in the presence of an ignition source with a standard and relative high amount of energy, such as a spark.

Level A Protection Protection used for hazardous work conditions with a high potential for exposure to very high concentrations of chemical splash, immersion, or exposure to chemical vapors. It consists of a fully encapsulated chemical suit with supplied air- breathing apparatus for the highest available level of respiratory protection. It is required for chemical hazards with a high vapor pressure and toxicity through skin absorption or which are carcinogenic.

Level B Protection Level B has the same level of respiratory protection required as in Level A protection; however, it allows for certain areas of exposed skin on the wearer and encapsulating garments that are not "vapor tight." Used in exposure situations at chemical concentrations below established exposure limits and chemicals that are not vapors or gases that are toxic by skin absorption or are carcinogenic.

Liquid Flammability Class A system of classification used by NFPA and ICC that 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 to lean, there is insufficient fuel to support sustained combustion.

LPG Liquefied Petroleum Gas.

-M-

M.P. Melting point. A commonly used abbreviation for the melting point temperature of a solid material.

M85 A fuel mixture consisting of 85% methanol and 15% gasoline.

MAC Maximale aanvaarde concentratie (the Netherlands 2002). Maximum Occupational Exposure Concentration Limits.

MAC-TGG 8 h Maximale aanvaarde concentratie. Maximum Occupational Exposure Concentration Limits for an eight-hour exposure.

MAK Maximal Arbeitsplatzkonzentrationen (Germany 2001). Maximum Concentrations of Chemical Substances in the Workplace: Occupational exposure concentration limits.

mass burning rate The loss in mass per unit time by materials burning under specified conditions.

methanol (methyl alcohol, wood alcohol) Methanol (CH3OH) is a colorless, poisonous liquid with essentially no odor and very little taste. Chemically, it is the simplest alcohol and is derived by replacing a hydrogen atom of the methyl group with a hydroxide atom. Methanol is a liquid at room temperature and pressure that is miscible in all proportions with water and with gasoline. Methanol is a polar solvent that disperses readily within the surface environment and is quickly rendered nontoxic by the combined processes of dilution and degradation. Because of its solubility, methanol can be difficult to remove from potable ground water.

mg/m3 A metric unit of concentration measure (weight/volume) expressed in units of milligrams of weight per cubic meter of volume.

MI Methanol Institute.

Minimum Ignition Energy (MIE) The smallest amount of energy of a piloted ignition source that 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, and (4) nuclear.

miscible A liquid that will evenly dissolve in another liquid; 100% miscibility is when two liquids will mix completely in all proportions. mm Hg Millimeters of mercury. A measure of pressure.

mol(s) A commonly used abbreviation for mole, as in a mole weight of a particular element, chemical, compound, or substance.

MSHA Mine Safety and Health Agency (see OSHA).

MTBE Methyl Tertiary Butyl Ether.

mutagen A substance that causes mutations within humans or animals. A mutation is a change in the genetic material in a body cell. Mutations can lead to birth defects, miscarriages, and cancer in humans.

-N-

NACE National Association of Corrosion Engineers.

NAERG The North American Emergency Response Guidebook, a paperback publication developed jointly by Transport Canada, the United States Department of Transportation, and the Secretariat of Communications and Transportation of Mexico. A free electronic version can be downloaded from the Transport Canada web site at http://www.tc.gc.ca/eng/canutec/guide-ergo-221.htm. The ER Guidebook is a guide for first responders to quickly identify the specific or generic hazards of material involved in a transportation incident. The information assists first responders in protecting themselves and the public from chemical exposure during the initial response phase of the incident.

NEC Acronym for National Electrical Code of the United States (NFPA 70).

NFPA An acronym for the National Fire Protections Association. This group classifies substances according to their fire and explosion hazard.

NFPA #30 A National Fire Protection Association code called the Flammable and Combustible Liquid Code.

NFPA #30A A National Fire Protection Association called the Code for Motor Fuel Dispensing Facilities and Repair Garages.

NIOSH National Institute for Occupational Safety and Health. This United States government agency tests equipment, evaluates and approves respirators, and conducts studies of workplace hazards. NIOSH also proposes workplace exposure standards to OSHA.

NPDWRs National Primary Drinking Water Regulations. Also called primary standards. Legally enforceable standards that apply to public water systems in the United States. Primary standards protect public health by limiting the levels of contaminants in drinking water.

NSDWR National Secondary Drinking Water Regulation.

NTP National Toxicology Program. An entity that tests chemicals and reviews evidence for cancer in the United States.

-O-

OECD Organization for Economic Cooperation and Development.

OES The Occupational Exposure Standards (United Kingdom 2001).

OHSAS Occupational Health and Safety Advisory Services.

organic Of, relating to, or denoting compounds containing carbon (other than simple binary compounds and salts) and chiefly or ultimately of biological origin.

OSHA The Occupational Safety and Health Administration, a United States Federal agency that adopts and enforces health and safety standards within industrial workplaces other than mines and mills (e.g., chemical manufacturing plants, petroleum refineries, oil production fields, merchant liquid air plants, etc.). MSHA (the Mine Safety and Health Agency) is responsible for health and safety standards in mines and mills.

OVA Organic Vapor Analyzer.

-P-

partition coefficient The ratio of concentrations of a compound in the two phases of a mixture of two immiscible solvents at equilibrium. Partition coefficients are a measure of differential solubility of the compound between these two solvents.

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

PEL The Permissible Exposure Limit for a chemical within the workplace. PELs are enforced by OSHA in the United States.

PHA Process Hazard Analysis.

PLC Programmable Logic Controller

PPE Personal Protection Equipment. An ensemble worn by a worker to protect against physical and chemical hazards. It can include head, eye, and hearing protection equipment, gloves, safety shoes, and additional specialized equipment for specific hazardous conditions.

ppm Parts per million. A volumetric unit of measure for the concentration of a substance in air or in a solution.

process safety Refers to the prevention of unintentional releases of chemicals, energy, or other potentially dangerous materials during the course of chemical processes that can have a serious effect to the plant and environment. Process safety involves the prevention of leaks, spills, equipment malfunction, over pressures, over temperatures, corrosion, metal fatigue, and other similar conditions. Process safety management systems programs focus on design and engineering of facilities, maintenance of equipment, effective alarms, effective control points, procedures and training. It is sometimes useful to consider process safety as the outcome or result of a wide range of technical, management, and operational disciplines coming together in an organized way.

producer gas (air gas) A mixture of carbon monoxide (CO) and nitrogen (N2) made by passing air over very hot carbon. Usually some steam is added to the air, and the mixture contains hydrogen (H2). Producer gas is used as a fuel in some industrial processes.

Product Stewardship A principle where environmental protection centers around the product itself, and everyone involved in the lifespan of the product is called upon to take responsibility to reduce its environmental impact. For manufacturers, this includes planning for, and if necessary, paying for the recycling or disposal of the product at the end of its useful life. This may be achieved by redesigning products to use fewer harmful substances; to be more durable, re-useable, and recyclable; and to make products from recycled materials. For retailers and consumers, this means taking an active role in ensuring the proper disposal or recycling of an end-of-life product.

psi (also psig) Pounds per square inch. A measure of pressure; the pounds of force per square inch of surface area, or pounds per square inch of gauge.

psia Pounds per square inch absolute. A measure of pressure in pounds of force exerted per square inch of surface area that includes 14.7 psi of atmospheric pressure experienced at mean sea level; psia = (psi + 14.7).

PSM Process Safety Management.

PSP Product Stewardship Practice.

PSV Process Safety Valve.

-R-

R&D Research and Development.

RCRA Resource Conservation and Recovery Act, a United States Federal law that regulates hazardous waste from generation to final disposal, also referred to as “cradle to grave.”

reactive A solid, liquid, or gas substance that releases energy under certain conditions.

Reid Vapor Pressure (RVP) A commonly used measure of vapor pressure for gasoline and other liquid fuels, defined as the pressure exerted by a liquid at 100°F as determined by the test method ASTM D-323. The test method does not apply to liquefied petroleum gases such as propane.

Responsible Care Ethic An initiative under which companies work together to continuously improve their health, safety, and environmental performance and to communicate with their stakeholders about their products and processes.

Responsible Distribution Ethic An initiative where the principles of the Responsible Care Ethic are extended to all aspects of the distribution of chemicals, chemical products, and chemical services.

risk A situation involving exposure to danger (i.e., when a vulnerability is exposed to a hazard).

Risk Assessment The determination of quantitative or qualitative value of risk related to a concrete situation and a recognized hazard.

Risk Communication The interactive exchange of information and opinions throughout the risk-analysis process concerning hazards and risks, risk-related factors, and risk perceptions among risk assessors, risk managers, consumers, industry, the academic community and other interested parties, including the explanation of risk-assessment findings and the basis of risk-management decisions.

running fire (running liquid fire) A burning liquid that flows away from the point of release and ignition. Running fires are particularly hazardous if allowed to enter sewers, drains, man-ways, or sub-grade structures, such as electrical or pipeline vaults where the burning material can pool and block evacuation routes.

-S-

SCBA Self-Contained Breathing Apparatus. A supplied air tank with a pressure-demand regulator used in high-hazard environments as part of Level A and B protection.

SCC Stress Corrosion Cracking.

SDS Safety Data Sheet.

SDWR Secondary Drinking Water Regulations. Non-enforceable United States Federal guidelines regarding cosmetic effects (such as tooth or skin discoloration) or aesthetic effects (such as taste, odor, or color) of drinking water.

SIDS Screening Information Data Set.

SNG Synthetic Natural Gas.

solubility The maximum amount of material that will dissolve in a given amount of solvent at a specified temperature to produce a stable solution.

solvent A liquid capable of dissolving other substances. In industrial use, commonly used to mean a chemical capable of dissolving petroleum-based products.

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.

specific heat (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.

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

STEL Short-Term Exposure Limit. Pertains to inhalation exposure of a toxic aerosol.

stewardship See Product Stewardship.

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. Oxygen-to-fuel ratio: oxygen/Fuel = $(1 + x/4)$ where x = H/C of the fuel

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.

Support Zone The outermost of the site control zones, the SZ is the perimeter used for staging response equipment and the location of the command post and communications center.

Sustainability Practices and processes developed with the intent of improving the quality of human life while living within the carrying capacity of supporting ecosystems. A commonly used definition is to "meet present needs without compromising the ability of future generations to meet their needs." A key concept that places sustainability in more familiar business terms is the "three Es" or "triple bottom line" concept of economic, environmental, and (social) equity sustainability.

-T-

TDG Transportation of Dangerous Goods. Canadian regulations with equivalency to the United States 49 Code of Federal Regulations (CFR).

teratogen A substance that causes birth defects by damaging the fetus.

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.

TLV Threshold Limit Value. Airborne concentrations of chemical substances that represent conditions under which it is believed that nearly all workers may be repeatedly exposed, day after day, over a working lifetime, without adverse health effects. In the United States, values of the TLV are set by the American Conference of Governmental Industrial Hygienists (ACGIH). TLV is usually expressed as parts per million (ppm) or milligrams per cubic meter (mg/m3). TLVs are published annually in Threshold Limit Values for Chemical Substances and Physical Agents.

TLV-STEL Threshold Limit Value-Short Term Exposure Limit. A 15 minute, time-weighted average exposure that should not be exceeded at any time during a workday, even if the eight-hour TWA is within the TLV-TWA. It is the concentration to which it is believed that workers can be exposed continuously for a short period of time without suffering from (1) irritation, (2) chronic or irreversible tissue damage, (3) dose-rate dependent toxic effects, or (4) narcosis of sufficient degree to increase the likelihood of accidental injury, impaired self-rescue, or materially reduced work efficiency.

TLV-TWA Threshold Limit Value-Time Weighted Average. The TWA concentration for a conventional eight-hour workday and a 40-hour workweek, to which it is believed that nearly all workers may be repeatedly exposed, day after day, over a working lifetime, without adverse health effects

ton In the United States and Canada, a unit of weight (mass) equal to 2,000 pounds.

tonne The metric unit of weight (mass) equal to 1,000 kilograms (2,204.62 pounds).

tote A portable vessel widely used for containment during shipping and storage of relatively small amounts of bulk liquid chemicals. The so-called JumboBin Tote is a sealed metal box fabricated of 304 stainless steel. The tote is fitted with lifting lugs on the four top corners and short legs on the four bottom corners.

toxic/toxicity The degree to which a substance can damage an organism. Toxicity can refer to the effect on a whole organism, as well as the effect on a substructure of the organism. A central concept of toxicology is that effects are dose-dependent.

TPA Terephthalic acid.

TRI Toxics Release Inventory. A publicly available EPA database that contains information on toxic chemical releases and waste management activities reported annually by certain industries, as well as federal facilities, in the United States.

turnout Also called turnout gear or bunker gear, it is a firefighter's uniform consisting of overall pants, boots, gloves, a hat or helmet, and often a jacket. The components of turnout gear may vary with agency and geographic zone.

TWA Time Weighted Average

-U-

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.

UEL Upper Explosive Limit (see also upper flammability limit, flammable range, LEL). The maximum molar or volumetric concentration of a vapor in air above which ignition does not occur. Fuel concentrations above the upper explosive limit are said to be too rich to burn.

UFC An acronym for Uniform Fire Code of the United States (NFPA 1).

UFL Upper Flammability Limit (see also upper explosive limit). The maximum molar or volumetric concentration of a vapor in air above which ignition does not occur. Fuel concentrations above the upper explosive limit are said to be too rich to burn.

UN Number or UN IDs Four-digit numbers that identify hazardous substances and articles such as explosives, flammable liquids, and toxic substances for the purpose of international transport.

UNEP United Nations Environment Programme.

USDHHS U.S. Department of Health and Human Services.

-V-

vapor The gaseous form of a substance that is normally a liquid or solid at ordinary temperature and pressures.

vapor pressure The pressure exerted by a vapor that is in equilibrium with the liquid at a given temperature. A measure of how readily a liquid or solid releases a vapor that mixes with air at the surface of the liquid or solid. A higher vapor pressure indicates a higher concentration of vaporized substance in air and, therefore, increases the likelihood of a person's breathing the vapor into his or her lungs while breathing toxic-laden air.

viscosity The quality of resistance to flow.

VLE-15 min Valeurs limites d'Exposition a court terme. (France 1999). Limit value for a short-term exposure of 15-minute duration.

VME-8 h Valeurs limites de Moyenne d'Exposition. Limit value of average exposure for an eight-hour workplace exposure.

VOC Volatile Organic Compound.

vol% or v/v% Volume percent. A measure of concentration that relies on relative volume rather than relative weight (mass).

volatility The tendency of the molecules of a substance to escape from the liquid phase and enter the gas phase. Liquids that have high volatility have high vapor pressure.

-W-

waste stream The complete flow of waste from domestic or industrial areas through to final disposal.

WMO World Meteorological Organization.

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APPENDIX A - PROCESS SAFETY INFORMATION

As discussed in section 5.4.6 Process Knowledge Management, process safety information must be retained that relates to chemical hazards, process technology and process equipment, as well as from several additional areas recommended by the CCPS. These tables identify minimum information that should be maintained to meet PSM requirements. As noted in 5.4.6, not all information listed will be relevant at every operating location.

A.1 CHEMICAL HAZARDS

Table A-1: Chemical Hazards Information
• Toxicity information • Permissible exposure limits • Physical data • Reactivity data • Corrosivity data • Chemical stability data • Calorimetric data • Lower explosive limit (based on sample testing) • Upper explosive limit (based on sample testing) • Flash point (based on sample testing)

A.2 PROCESS TECHNOLOGY

Table A-2: Process Technology Information
• Process flow diagram (PFD) • Process chemistry • Reactants / catalysts • Potential runaway reactions • Chemical treatment information • Material and energy balances • Utility requirements (steam, natural gas, merchant gases, special heat transfer media, etc.) • Maximum intended inventory • Control system logic • Normal operating parameters (temperature, pressure, flow, composition) • Special circumstances (very high pressure, very high temperature, cryogenic temperatures, etc.) • Safe operating limits (e.g., upper and lower limits for temperature, pressure, flow, composition) • Maximum permissible time at upper and lower operating limits • Zones of concern for over-pressurization, explosion, fire or toxic exposure • Evaluations of the consequences of deviations

A.3 PROCESS EQUIPMENT

Table A-3: Process Equipment Information
• Unit names with tag number, nameplate, date in service and anticipated life • Materials of construction • Design specifications • Vendor documentation (e.g., invoices, specifications, operation manuals, maintenance manuals, warranties) • Piping & instrumentation diagrams (P&IDs) • Electrical area classification diagrams • Isometric drawings • Electrical line drawings • Plot plans (including underground utilities and piping) • Relief system design basis and calculations • Ventilation system design basis and calculations • Listing of relevant design codes and standards • Safety systems • Shutdown keys • Shop fabrication drawings • Piping specifications • Control system logic diagrams • Instrument data • Design and basis for fixed fire protection systems • Structural analysis and drawings • Design basis for fixed / dedicated hoists • Location of safety equipment (safety showers, eyewash)

A.4 ADDITIONAL INFORMATION REQUIRED

Table A-4: Additional Information

- Process Hazard Analysis (e.g., HAZOP)
  - € - records of participation
  - € - final reports
  - € - action trackers
  - € - other related information
- Process Equipment Integrity
  - € - equipment lists
  - € - equipment specifications
  - € - reference to codes and standards used for equipment design and
  - € selection
  - € - manufacturer operating and maintenance manuals
  - € - instrumentation index
  - € - instrumentation specifications
  - € - control systems records
  - € - maintenance procedures
  - € - preventive maintenance (PM) plan
  - € - maintenance and PM records
  - € - deficiency correction records
  - € - inspection and test plan
  - € - inspection and test records
  - € - records of inspections and tests of safety and emergency
  - € equipment
- Management of Change (MOC) Documentation
  - € - MOC change proposal forms (for approved and rejected MOCs)
  - € - records of completion of MOC Review requirements
  - € - records of MOC closure
  - € - MOC audit reports
  - € - MOC audit corrective action trackers
- Operating Procedures
  - € - records of initial start-up
  - € - operator logs
  - € - procedures for normal operation
  - € - shutdown procedures
  - € - emergency procedures
  - € - strategy for recycling & processing off-spec material
- Training
  - € - site / employee training matrices (i.e., training plan)
  - € - records of training including verification (competency tests, JTOs,
  - € etc.)
- Emergency Response (ER)
  - € - ER plans
  - € - emergency escape procedures and routes
  - € - identification of muster points

- € - site plan showing locations of safety and emergency equipment
- € - records of inspections, testing and maintenance of safety equipment, alarms and emergency lighting
- € - ER exercise / drill plan
- € - worst case scenario descriptions and supporting documentation
- € - records of ER exercises and drills including lessons learned and deficiency corrections

- Inspection and Audtis
  - € - facility inspection and audit plan
  - € - records of inspections and audits including names of inspectors /
  - € auditors, reports and deficiencies found
  - € - deficiency correction records
- Contractors
  - € - contractor assessment procedures and plans
  - € - records of contractor assessments
  - € - records of contractor post-work reviews

APPENDIX B - PROPERTIES OF METHANOL/METHYL ALCOHOL

B.1 PHYSICAL PROPERTIES

CH_3OH	
• Color	Colorless
• Opacity	Clear
• Odor	Faintly sweet, pungent odor like ethyl alcohol
• Odor Threshold	Odor threshold is highly variable in air and ranges over several orders of magnitude; 10 ppm to 20000 ppm. [12] 100 ppm to 1500 ppm reported [3] 141 ppm [56] 160 ppm - The range of accepted odor threshold values is quite broad. Caution should be used in relying on odor alone as a warning of potentially hazardous exposures. [48]
• Conversion Factors	1 ppm = 1.33 mg/m3; 1 mg/m3 = 0.76 ppm

B.1.1 SOLID

CH_3OH *(solid)*	T < -98°C (-144°F); P = 1 atm (14.7 psia)

B.1.2 LIQUID

CH_3OH *(liquid)*	-98°C (-144°F) < T < 65°C (149F); P = 1 atm (14.7 psia)
• Specific Gravity of Liquid Relative to Water (water = 1.0)	0.7866 @ 25/4°C 0.7915 @ 20/4° C 0.7960 @ 15/4° C 0.8 @ 20° C
• Density	6.63 lb/ U.S. gal @ 60° F
• Viscosity [37], [16]	1.258 mPa s @ -25°C (-13°F) 0.793 mPa s @ 0°C (32°F) 0.808 mPa s @ 0°C (32°F) 0.690 mPa s @ 10°C (50°F) 0.593 mPa s @ 20°C (68°F) 0.544 mPa s @ 25°C (77°F) 0.449 mPa s @ 40°C (104°F) 0.349 mPa s @ 60°C (140°F) Note: 1 mPa s = 1 cP (Centipoise)

• Coefficient of Cubic Thermal Expansion	0.00149 per °C @ 20°C 0.00159 per °C @ 40°C
• Thermal Conductivity	207 mW/m K @ 0°C (32°F) 200 mW/m K @ 25°C (77°F)
• Saturation Concentration (vapor in the air)	166 g/m^3
• Vapor Pressure @ PTotal=(14.7 psia)	12.3 kPa (96 mm Hg) 1.86 psia @ 20°C (68°F)
• Vapor Pressure @ PTotal=(760 mm Hg)	4.63 psi @ 38°C (100°F)
• Reid Vapor Pressure	32 kPa (4.6 psi) @ 15.6°C (60°F)
• Volatility	100 vol% 99.9 wt%
• Evaporation Rate (Butyl Acetate = 1)	4.6
• Evaporation Rate (Ether = 1)	5.2
• Surface Tension	22.5 dyn/cm
• Electrical Conductivity	4.4×10^7 pS/m

Vapor Pressure of Liquid:

P in mmHg	T in °C (°F)	P in mmHg	T in °C (°F)
1	-44.0 (-47)	1520	84.0 (183)
70	-16.2 (3)	3800	112.5 (234)
40	5.0 (41)	7600	138.0 (280)
100	21.2 (70)	15200	167.8 (334)
400	49.9 (122)	30400	203.5 (398)
760	64.7 (148)	45600	224.0 (435)

B.1.3 VAPOR

CH_3OH *(vapor)*	65°C (140°F) < T; P = 1 atm (14.7 psia)
• Relative Density of Vapor Saturated Air (air = 1)	1.01 @ 20°C (68°F) 1.02 @ 30°C (86°F)
• Density	1.1
• Viscosity	9.68 QPa s @ 25°C (77°F) 13.2 QPa s @ 127°C (261°F)
• Thermal Conductivity	14.07 mW/m K @ 100°C (212°F) 26.2 mW/m K @ 127°C (261°F)
• Critical Temperature	240°C (464°F) 512.5° K
• Critical Pressure	1,142 psia (8.084 MPa) 78.5 atm
• Critical Volume	0.117 m^3/kg-mol
• Critical Density	0.2715 g/cm^3
• Critical Compressibility Fctor	0.224
• Acentric Factor	0.556
• Henry's Law Constant	4.55 x 10^{-6} atm-m^3/g-mol
• Airborne Saturation Concentration	166 gm/^{3}
• Airborne Concentration Conversion	1 mg/ml = 764 ppm @ 25°c (77°f) at 1 atm, 14.7 psia, 760 mm Hg 1ppm = 1.31 mg/m^3 @ 25°C (77°F) at 1 atm, 14.7 psia, 760 mm Hg

B.2 CHEMICAL PROPERTIES

• Chemical Name	Methanol
• Chemical Family	Aliphatic Alcohol
• Chemical Formula	CH_3OH
• Molecular Weight	32.04 grams/mole
• Elemental Composition by Weight	Oxygen - 50 wt% Carbon - 37.5 wt% Hydrogen - 12.5 wt%
• Solubility CH_3OH (liquid) in Water	100%; miscible in all proportions
• Solvents	Ethanol, ether, benzene, acetone, alcohol, chloroform
• pH	7.2
• Biological Oxygen Demand	0.6 to 1.12 lbs/lb in 5 days

B.2.1 REACTIVITY

• Flammable	May explode when exposed to flame
• Stability	Stable material
• Hazardous Polymerization	Will not occur

B.2.2 DECOMPOSITION

Excessive heating and/or incomplete combustion will generate carbon dioxide, carbon monoxide, formaldehyde, and possibly unburned methanol.

B.2.3 INCOMPATIBILITIES

- Methanol-water solutions at 40:60 concentration and methanol-water, 30:70 mixtures can be ignited by a static discharge. [93].
- Air, methanol-air mixtures at 1.81 bar (26.25 psia) and 120°C (248°F) may explode with or without the addition oxygen and water. [8]
- Explosive reaction with chloroform + sodium methoxide and diethyl zinc.
- Reacts violently and uncontrollably with strong reducing agents and dilute solutions of alkyl aluminum salts, diethyl zinc, acetyl bromide, cyanuric chloride. Incompatible with beryllium dihydride. Reaction with the ether-containing hydride is violent, even at -196°C (-321°F). [8].
- Reaction with alkali metals (sodium, potassium, magnesium) is vigorous, and often subject to a lengthy induction period. Mixtures with powdered MG or Al are capable of powerful detonation. Reaction with K may lead to an explosion.
- Methanol reacts violently with strong oxidizers (calcium hypochlorite, barium, perchlorates, peroxides, permanganates, chlorates); strong acids (nitric, hydrochloric, sulfuric); and halogen gases (bromine, chlorine, fluorine, and iodine).
- Reacts vigorously and dangerously with oxidizing materials.
- Methylene chloride may become flammable in the presence of small amounts of methanol.
- Reacts violently with liquid phosphorus (III) oxide above 24°C (75°F).
- Reaction of liquid methanol with solid potassium tert-Butoxide causes ignition after 2 minutes.

B.3 CORROSIVITY TO METALS, ALLOYS, GASKETS, AND PLASTIC

Corrosivity points immediately to the issue of materials selection, which in turn points directly to application. What type of equipment is in question: pumps, piping, vessels, heat exchangers distillation towers, accumulators, reformer furnaces, strippers, etc.? What are the normal, abnormal, and emergency process conditions? What are maximum, minimum, and typical control parameters: flow, temperature, pressure, composition, impurities, etc.?

Is it a batch process or a continuous process? What is the anticipated inspection and testing schedule, the anticipated maintenance program, the intended service life? Given a particular selection, what are the anticipated failure modes and mechanisms?

All of these considerations enter into materials selection. The process is technically complex and organizationally difficult. The vast array of conditions and circumstances that fall within the purview of materials selection for methanol service means that the most appropriate material is based on the particular details of the specific application.

While issues pertaining to materials selection are fundamental and likely among the most often asked questions, there are no standard or universal answers. Recognizing this, the following guidance is provided as very general in nature. It is the responsibility of those asking the questions to search out the best answers for their particular circumstance.

- Pure anhydrous methanol is mildly corrosive to lead and aluminum alloys and more so to magnesium, and platinum. That is not to say that aluminum alloys are unfit for methanol service, but rather to alert users to the necessity of periodic inspection and nondestructive testing. Positive materials identification, inspection, and nondestructive testing are essential for fitness for continued service. This applies to all pressure boundary materials in all chemical services, including methanol. Rate of attack on aluminum alloys is typically a slow pitting form of corrosion; however, it can be accelerated to the point of compromising integrity of structural components if not anticipated and monitored.

- Methanol-water solutions can be corrosive to some non-ferrous alloys depending on application and environmental circumstances. This caution applies to equipment built with copper alloy, galvanized steel, titanium, aluminum alloy components, and some plastics and composites. Coatings of copper (and copper alloys), zinc (including galvanized steel), and aluminum exhibit corrosive degradation of various types and at various rates depending on circumstances accompanying application. In general, corrosive attack of structural components such as aluminum alloy floating roofs on storage tanks is slow; it requires periodic visual inspection and nondestructive testing to verify "fitness for continued service." The same can be said for heat exchanger tube materials, pump components, valve trim, and sensing elements in direct contact with methanol.

- Mild steel is usually selected as the construction material, provided moisture is excluded from the system. If moisture and trace amounts of inorganic salts are expected to exist within the system from time to time, then one should consider upgrading from carbon steel to 316 L stainless steel or a titanium or molybdenum stabilized grade of 316 L stainless steel. The issue in the presence of moisture and inorganic salts is corrosion within weld-heat-affected zones. Weld integrity can become an issue.

- Best practice uses molybdenum-stabilized low carbon 300 series stainless steel. Though expensive, this material protects against generalized corrosion, pitting corrosion, stress corrosion cracking, hydrogen induced cracking, and product contamination. Mild steel is widely used for piping. Piping connections are made with welded flanges and methanol compatible gaskets. Threaded connections are not considered suitable in methanol service. Non-ferrous materials should not be used for the construction of permanent pipework. It is recommended that underground storage, buried pipelines, and underground piping be protected with a cathodic protection system and be inspected on a regular basis.

- Many resins, nylons, and rubbers, such as neoprene, nitrile (Buna-N), and ethylene propylene (EPDM), are suitable, though some are more suitable in flowing applications than others. Buna-N is NOT recommended by its manufacturers for dynamic applications (i.e., service in flowing methanol). Buna-N is satisfactory for fluid-static applications; however, it is not considered to be a superior material for methanol service.

- Fluorinated materials such as Teflon are used satisfactorily as equipment components in methanol service. Of these, Teflon offers good dimensional stability and is resistant to attack and degradation.

- Rubber hoses should have an internal wire coil for strength and electrical continuity. Use of hoses should be restricted to temporary applications, such as loading and unloading. Hose material must be compatible with methanol service. All hoses should be clearly labeled for methanol service only. Hose ends must be capped or otherwise protected to avoid contamination during storage. Hoses should be periodically replaced with new hoses, rather than kept in service to the point of failure.

- First-time hose and piping must be washed with water and then methanol to ensure that contaminants are removed before being placed in service.

- Methanex ranks compatibility of gasket and O-ring materials in methanol-fueled truck service in the following table:

Compatibility of Gasket and O-ring Materials with Methanol[9]

Gasket/O-Ring Material	Rating[10] (Compatibility with Methanol Fuel in Truck Service)	Recommended[11,12]
Natural Rubber	Good	No Recommendation Given
EPDM (Ethylene-Propylene)	Good	Yes, Recommended
Neoprene	Good	Yes, Recommended
Silicone	Good	Yes, Recommended
Kalrez	Good	Yes, Recommended
Teflon	Good	No Recommendation Given
Fluorosilicone	Good	No Recommendation Given
Buna-N	Fair	Not Recommended
Nitrile	Fair	Not Recommended
Polyurethane	Sometimes OK	No Recommendation Given
Butyl Rubber	Poor	No Recommendation Given
Butadiene	No Data	No Recommendation Given
Fluorocarbon	No Data	No Recommendation Given
VITCON (most types)	No Ranking Given	Not Recommended

[8] REFERENCE: efunda - engineering fundamentals; efunda.com; O-Ring Compatibility Guide

[10] Cautionary note regarding Buna-N & Nitrile: These materials may be adequate for static situations such as gloves to protect against methanol contact. These materials are generally not recommended for dynamic situations involving flowing methanol, such as gaskets on pumps and fittings.

[11] Note regarding VITON F: Most VITON types are not recommended for methanol service due to swelling of the material when exposed to methanol. However, VITON F shows only small changes when exposed to methanol. Manufacturers recommend use of VITON F for methanol service.

[12] REFERENCE: Daemar Inc. (daemar.com); Chemical Compatibility Chart

Methanol is one of the few specialized environments that may cause stress corrosion cracking (SCC) in titanium alloys. SCC failures have occurred in dry methanol, methanol/acid, and methanol/halide mixtures.

Water is an effective inhibitor and will maintain the passivity of titanium in many environments if present in weight % concentrations. General guidance is provided in the following table.

Titanium Alloy Grade	wt% Water Intermittent Exposure[a]	wt% Water Sustained Exposure[b]
1, 2, 7, 11, 16, 17	1.5	2.0
9, 12	2.0	2.0
28	2.5	3.0
5, 23	3.0	3.0
19, 29, 6-2-4-6	5.0	10.0

[a] intermittent exposure = short-term, noncontinuous exposure

[b] sustained exposure = long-term, continous exposure

B.4 STRUCTURE AND PROPERTIES

• Index of Refraction, nD	1.328 @ 20°C (68°F)
• Dielectric Constant, εr	32.66 @ 20°C (68°F)
• Bond Angle	all 109.5o
• Magnetic Susceptibility	5.3 x 10^{-7} cm^3g
• Surface Tension	22.5 dyn/cm @ 20°C (68°F)
• Viscosity	0.808 mPa's @ 0°C (32°F) 0.690 mPa's @ 10°C (50°F) 0.593 mPa's @ 20°C (68°F) 0.449 mPa's @ 40°C (104°F) 0.349 mPa's @ 60°C (140°F)

B.5 COMBUSTION AND IGNITION PROPERTIES

• Flash Point T at P = 1 atm (14.7 psia)	12°C (54°F) closed cup TCC method 15.6 (60.1 F) open cup TOC method
• Auto-ignition T at P = 1 atm (14.7 psia)	385°C (725°C)[13]
• Explosive Limits in Air at Ambient T and P	6-36VOL%[14],[15]
• Magnetic Susceptibility	5.3 x 10^{-7} cm^3g
• Surface Tension	22.5 dyn/cm @ 20°C (68°F)

[13] Methanex Corporation & Terra Industries among others indicate auto-ignition temperature as 464°C (867oF).

[14] The Lower Explosive Limit (LEL) of 6 vol% and the flash point for methanol (12°C, 54°F) are closely linked. Equilibrium vapor pressure at the flash point temperature is 46 mm Hg.

[15] The Upper Explosive Limit (UEL) of 36 vol% corresponds to a temperature of 41°C (106°F) and a vapor pressure of 274 mm Hg. The explosive range extends over a relatively wide range of temperatures and to a vapor pressure that is over a third of an atmosphere of pressure. Methanol produces an explosive mixture of vapor in air within the explosive range of 6 to 36 vol%. Precautions must be taken to insure that methanol vapors do not come in contact with a potential ignition source at vapor concentrations between 6 and 36 vol %.

• Explosive Range	30 vol%
• Flame	Non-luminous blue flame Not visible to naked eye in daylight
• Flammable Methanol-Water Mixtures: (mixtures below 25 vol% are classified as combustible)	Down to 25 vol% (21 wt%) methanol
• Stoichiometric Air/Fuel Weight Ratio	6.45
• CH^3OH (vapor) in Stoichiometric Air/ Vapor Mixture	12.3 vol%

B.5.1 FIRE EXTINGUISHING MEDIA

- Carbon dioxide
- Dry chemical
- Alcohol-resistant foam – AR-AFFF with 6% proportioning with water
- Water mist or fog[16]

B.6 THERMODYNAMIC PROPERTIES[17]

• Latent Heat of Vaporization (L→G)	37.43 kJ/mol (279.0 cal/g @ 25°C, 298.15 K, (77°F)) 35.21 kJ/mol (262.5 cal/g @ 64.6°C, 337.3 K, (48°F))
• Standard Enthalpy of Formation Vapor ($\Delta_f H^\circ_{gas}$)	-205. ±10. kJ/mol
• Standard Enthalpy of Combustion Vapor ($\Delta_c H^\circ_{gas}$)	-763.68 ±0.20 kJ/mol
• Standard Enthalpy of Formation Liquid ($\Delta_f H^\circ_{liquid}$)	-238.4 kJ/mol
• Standard Enthalpy of Combustion Liquid ($\Delta_c H^\circ_{liquid}$)	-725.7 ±0.1 kJ/mol
• Standard Entropy of Liquid Phase (S°_{liquid})	127.19 J/mol K
• Standard Entropy of Liquid Phase ($S^\circ_{solid\ 1\ bar}$)	1.117 J/mol K
• Heat Capacity of Gas at Constant Pressure ($C_{p\ gas}$)	44.06 J/mol K @ 298.15 K
• Heat Capacity of Liquid at Constant Pressure ($C_{p\ liquid}$)	79.5 J/mol K @ 298.15 K
• Heat Capacity of Solid at Constant Pressure ($C_{p\ solid}$)	68.39 J/mol K @ 120 K 5.40 J.mol K @ 20.5 K 105.00 J/mol K @ 173 K

• Enthalpy of Fusion ($\Delta_{fus}H$)	2.196 kJ/mol @ 176 K
• Entropy of Fusion ($\Delta_{fus}S$)	12.5 J/mol K @ 176 K
• Enthalpy of Phase Transition ($\Delta H_{trs\ Xtline \rightarrow L}$)	3.159 kJ/mol @ 175.4 K
• Specific Heat	2.51 kJ/kg K; 0.6 Btu/lb-°F
• Heat Capacity Ratio, γ = Cp/Cv	1.203 @ 77°C (171°F)
• High Heating Value (HHV)	22.7 MJ/kg, 9800 Btu/lb, 726 kJ/mole
• Low Heating Value (LHV)	19.937 MJ/kg @ 25 °C

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[16] Because methanol is miscible in water, application of water will spread the fire until the dilution ratio reaches at least 3/1. Water-methanol solutions are flammable to a composition of 76 vol% water.

[17] Methanex Corporation Web site: www.methanex.com/methanol/techsafetydata.htm; Lange's Handbook of Chemistry, 10th Edition, CRC Handbook of Chemistry and Physics, 44th Edition; CRC Handbook of Chemistry and Physics, 68th Edition; Perry's Chemical Engineers' Handbook, 6th Edition; James A. Plambeck, University Chemistry: Molar Thermodynamic Properties of Pure Substances, © 1995; Robert D. Goodwin, "Methanol Thermodynamic Properties from 176 to 673 K at Pressures to 700 bar," Journal of Physical and Chemical Reference Data, October 1987, Vol. 16, Issue 4, pp. 799-892.

APPENDIX C - REGULATORY, HEALTH, AND SAFETY INFORMATION FOR METHANOL

C.1 U.S. REGULATIONS AND CODES

This table lists the primary United States Federal OSHA, EPA, and DOT regulations that affect the production, storage, packaging, distribution, or use of methanol. This listing is not necessarily inclusive of all relevant regulations and codes. Relevant and applicable state and local codes and regulations for the particular facility should also be consulted.

Regulation/Code	Relevant Section or Part
Occupational Safety and Health, Code of Federal Regulations – 29 CFR	Part 1904 – Recordkeeping
	Section 1910.20 – Access to Exposure and Medical Records
	Section 1910.38 – Employee Emergency Plans and Fire Protection Plans
	Section 1910.119 – Process Safety Management of Highly Hazardous Chemicals
	Section 1910.120 – Hazardous Waste Operations and Emergency Response
	Section 1910.132 to 139 – Personal Protective Equipment
	Section 1910.146 – Confined Space Entry
	Section 1910.147 – Control of Hazardous Energy (Lockout/Tagout)
	Section 1910.151 – First Aid/Medical Service
	Section 1910.331 to 335 – Electrical Safety
	Section 1910.1000 – Air Contaminants (exposure limits)
	Section 1910.1200 – Hazard Communication

Regulation/Code	Relevant Section or Part
Environmental Regulations – 40 CFR	Part 61 – National Emissions Standards for Hazardous Air Pollutants
	Part 68 – Chemical Accident Prevention Provisions (Clean Air Act/Accidental Releases)
	Part 68 Subpart D – Program 3 Prevention Program (Process Safety Management requirements)
	Part 68 Subpart G – Risk Management Plan
	Part 141 – Safe Drinking Water
	Part 260 to 269 – Hazardous Waste Management System
	Parts 302 and 355 – Release of Hazardous Substances, Emergency Planning and Notification
	Parts 370 and 372 – Hazardous Chemicals Reporting: Community Right to Know
	Part 373 – SARA Title III Reporting
	Subchapter R, Parts 700 to 799 – Toxic Substances Control Act

Regulation/Code	Relevant Section or Part
Transportation Regulations – 49 CFR	Part 106 – Rulemaking Procedures
	Part 107 – Hazardous Materials Program Procedures
	Part 171 – General Information, Regulations, Definition
	Part 172 – Hazardous Materials Table, Special Provisions, Hazardous Materials Communications, Emergency Response Information, and Training Requirements
	Part 173 – Shippers, General Requirements for Shipments and Packaging
	Part 174 – Carriage by Rail
	Part 176 – Carriage by Vessel
	Part 177 – Carriage by Public Highway
	Part 178 – Specifications for Packaging

Regulation/Code	Relevant Section or Part
Transportation Regulations – 49 CFR	Part 179 – Specifications for Tank Cars
	Part 180 – Continuing Qualifications and Maintenance of Packaging
	Part 190 – Pipeline Safety Program Procedures
	Part 191 – Transportation of Natural and Other Gas by Pipeline: Annual Reports, Incident Reports and Safety Related Condition Reports
	Part 192 – Transportation of Natural and Other Gas by Pipeline: Minimum Federal Safety Standards
	Part 195 – Transportation of Hazardous Liquids by Pipeline
Regulation/Code	**Relevant Section or Part**
Navigable and Navigable Water Regulations - 33 CFR	Part 1 to 26, Subchapter A – General delegation of authority, rulemaking procedures and enforcement regulations
	Part 126 – Handling Explosives or Other Dangerous Cargoes within or Contiguous to Waterfront Facilities
	Part 130 – Financial Responsibility for Water Pollution
	Part 153 – Control of Pollution by Oil and Hazardous Substances; Discharge Removal
	Part 154 – Facilities Transferring Oil or Hazardous Materials in Bulk
	Part 155 – Oil or Hazardous Material Pollution Prevention Regulations for Vessels
	Part 156 – Oil and Hazardous Material Transfer Operations
	Parts 160 to 167, Subchapter P – Ports and Waterways Safety
Regulation/Code	**Relevant Section or Part**
Shipping Regulations – 46 CFR (Water Transportation)	Part 2 – Vessel Inspections
	Part 10 to 12 – Licensing and Certification of Maritime Personnel
	Part 15 – Manning Requirements
	Part 30 to 40, Subchapter D – Tank Vessels
	Part 151 – Barges Carrying Bulk Liquid Hazardous Materials Cargoes

C.2 INTERNATIONAL REGULATIONS, STANDARDS, AND GUIDELINES

This table lists the international regulations, standards, and guidance that affect the production, storage, packaging, distribution, or use of methanol. This listing is not necessarily inclusive of all relevant international regulations, standards, and guidelines; however, it is noteworthy that there is a growing consensus that hazards identification, risk assessment, and management of risk to tolerable levels is a fundamental requisite to worker safety. If your organization is not already applying principles of risk management, then you may want to make plans to do so in the near future.

Authority	**Topic**
European Union (EU)/European Commission (EC)	Control of Major-Accident Hazards Involving Dangerous Substances (Directive 96/82/EC)
Organization for Economic Cooperation and Development (OECD)	OECD Guiding Principles for Chemical Accident Prevention, Preparedness, and Response
EU/EC	Personal Protective Equipment Directive (Directive 89/686/EEC)
EU/EC	Health & Safety at Work (Directive 89/391/EEC)
EU/EC	Directive on Indicative Occupational Exposure Limit Values (DIR 2006/15/EC) & Chemical Agents at Work Directive (DIR 98/24/EC)
EU/EC	Dangerous Substances Directive (Directive 67/548/EEC)
EU/EC	Directive on Pollutant Release and Transfer Register (EC/166/2006); Integrated Pollution Prevention and Control (IPPC Directive: 96/61/EC); Management of Quality of Ambient Air (96/62/EC)
EU/EC	Water Framework Directive (Directive 2000/60/EC); Quality of Drinking Water (98/83/EC)
EU/EC	Directive on Waste (2006/12/EC); Controlled Management of Hazardous Waste (91/689/EEC)
EU/EC	Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) (EC/2006/1907)

Authority	Topic
European Union (EU)/European Commission (EC)	Chemicals Act (Control of Major Accident Hazards Involving Dangerous Substances) Regulations 2015, S.I. No. 209 of 2015
United Nations (UN)	Recommendations on the Transport of Dangerous Goods
International Air Transport Association (IATA)	Dangerous Good Regulations
International Maritime Organization (IMO)	International Maritime Dangerous Goods (IMDG) Codes
ICAO (Agency of UN)	International Civil Aviation Organization Codes and Standards
UN	European Agreement Concerning the International Carriage of Dangerous Goods by Road (ADR)
UN	International Regulations Concerning the Carriage of Dangerous Goods by Rail (RID)
EU/EC	Transport of Dangerous Goods by Road (Directive 94/55/EC)
EU/EC	Transport of Dangerous Goods by Rail (Directive 96/49/EC)
EU/EC	Accidental Marine Pollution (2850/2000/EC); Maritime Safety: Prevention of Pollution from Ships (2002/84/EC); Protection of Groundwater Against Pollution (2006/118/EC)
Canada	Law C-21: An Act to amend the Criminal Code (criminal liability of organizations) (S.C. 2003, c. 21) – establishes criminal liability for organizations and individuals when they fail to take reasonable steps to prevent workplace accidents that affect workers or the public
Canada	Criminal Code Criminal Code (R.S.C., 1985, c. C-46) – amended to include provision of Law C-21 in 2008
United Kingdom	COMAH 2015 – Control of Major Accident Hazards (COMAH) Regulations (updated in 2015)

Authority	**Topic**
China – State Administration for Work Safety (SAWS)	AQ/T 3034-2010 Guidelines for Process Safety Management of Chemical Corporations – this regulation came into effect in 2011
China – State Administration for Work Safety (SAWS)	SAWS III [2013] No. 88 – guidance document to further strengthen company practices regarding process safety management
International Standards Organization (ISO)	ISO 9001:2000 – Quality Management Systems
International Electrotechnical Commissions (IEC)	Functional Safety – Safety Instrumented Systems for the Process Industry Sector IEC 61511-1 • Part 1: Framework, definitions, system, hardware and software requirements • Part 2: Guidelines for the application of IEC 61511-1 • Part 3: Guidance for the determination of the required safety integrity levels
ANSI/AIHA Occupational Health and Safety Management Systems: Z10-2005	Sets a benchmark provision requiring that processes be in place to identify and take steps to prevent or otherwise control hazards and reduce risks associated with new processes or operations at the design stage
Australian Safety and Compensation Council, Australian Government, 2006	Guidance on the Principles of Safe Design for Work
National Institute for Occupational Safety and Health (NIOSH), 2006	Announced an initiative on prevention through design
American National Standards Institute (ANSI/PMMI) B155.1-2006	Safety Requirements for Packaging Machinery and Packaging-Related Converting Machinery
Society of Fire Protection Engineers (SFPE), 2006	• Engineering Guide to Application of Risk Assessment in Fire Protection Design • Introduction to Fire Risk Assessment
Occupational Health and Safety Management Systems standard issued by the Canadian Standards Association	CSA Z1000-2006

Authority	Topic
Industrial Safety and Health Act of Japan, rev. April 2006	Stipulates, without penalty, that employers should make an effort to implement risk assessment
International Standardization Organization (ISO 14121-1)	Safety of Machinery – Principles for Risk Assessment, 2007
National Fire Protection Association (NFPA), 2007	Guidance Document for Incorporating Risk Concepts Into NFPA Codes and Standards
British Standards Institute BS-OHSAS 18001, 2007	Guidelines now read: “The organization shall establish, implement and maintain a procedure(s) for the ongoing hazard identification, risk assessment and determination of necessary controls.” The term tolerable risk was replaced by acceptable risk.
China’s State Administration of Work Safety, 2008	Published provisional regulations on risk assessment
U.K. Health and Safety Executive, 2008	Issued five steps to risk assessment: “The law does not expect you to eliminate all risk, but you are required to protect people as far as is ‘reasonably practical.’”
Industry Committee for Emergency Lighting Ltd	ICEL 1008: Emergency Lighting Risk Assessment
Institute for Research for Safety and Security at Work (Quebec, Canada), 2009	Machine Safety: Prevention of Mechanical Hazards
American Society of Safety Engineers (ASSE), 2009 Technical Report Z790.001	Prevention Through Design: Guidelines for Addressing Occupational Risks in the Design and Redesign Processes
Singapore Standard SS506, 2009	Occupational Safety and Health Management Systems, Part 1: Requirements
ANSI-ITAA GEIA-STD-0010, 2009	Standard Best Practices for System Safety Program Development and Execution
ISO/IEC 31010, 2009	Risk Assessment Techniques
EN ISO 12100-2010	Safety of Machinery: General Principles for Design Risk Assessment and Risk Reduction explicitly requires risk assessments
ANSI B11.0, 2010	Safety of Machinery: General Safety Requirements and Risk Assessments

C.3 HAZARDOUS MATERIAL AND HEALTH AND SAFETY INFORMATION

Hazardous Material Information	
European Inventory of Existing Commercial Substances (EINECS) No. (EU)	200-659-6
UN Number	UN 1230
Dangerous Goods Classification	
• Primary Classification	3
• Subsidiary Classification	6.1
• Packing Group	PG II
ADR Classification (transport by road)	
• Class	3
• Packing	II
• Danger Label Tanks	3+6.1
• Danger Label Packages	3+6.1
RID Classification (transport by rail)	
• Class	3
• Packing	II
• Danger Label Tanks	3+6.1
• Danger Label Packages	3+6.2
IMDG Classification (maritime transport)	
• Class	3
• Sub Risks	6.1
• Packing	II
• MFAG	19
ICAO Classification (air transport)	
• Class	3
• Sub Risks	6.1
• Packing	II

Health & Safety Information	
Exposure Limits	
TLV-TWA	262 mg/m^3
	(200 ppm)
TLV-STEL	328 mg/m^3
	(250 ppm)
OES-LTEL	266 mg/m^3
	(200 ppm)
OES-STEL	333 mg/m^3
	(250 ppm)
MAK	270 mg/m^3
	(200 PPM)
MAC-TGG 8 H	260 mg/m^3
VME-8 H	260 mg/m^3
	(200 ppm)
VLE-15	1,300 mg/m^3
	(100 ppm)
GWBB	266 mg/m^3
	(200 ppm)
GWK-15 min	333 mg/m^3
	250 ppm
EC	260 mg/m^3
	(200 ppm)
NFPA Classification	1B Flammable Liquid
NFPA Hazard Rating	
• Health	1
• Flammability	3
• Reactivity	0