



METHANOL INSTITUTE

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# Methanol Safe Handling Manual

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# 1 Introduction to the Manual

This chapter explains the purpose of this 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 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. However, this manual is not intended to be a substitute for applicable laws and regulations, nor does it alter the obligation of the user to comply fully with federal, state and local law. Each user will have specific circumstances relevant to its own safe use of methanol, and therefore must use its own independent judgment and discretion to determine how best to handle methanol safely. In doing so the user must consider its own management structure, product lines, location, and other factors that are unique to it.

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 available Fact Sheets on a number of topics related to

methanol safe handling, such as methanol use as fuel, emergency response, product stewardship, and health effects.

We understand that expertise in the safe handling of methanol is available in every corner of the globe. We hope to capture this expertise in future editions of this manual. Therefore, we welcome your comments, questions and feedback, so send us an email to [MI@methanol.org](mailto:MI@methanol.org). For the most recent edition of this Manual, visit our web site at [www.methanol.org](http://www.methanol.org).

## 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 also produce deleterious impacts to human health and the environment when not properly handled.

Methanol is naturally produced by living organisms, and 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 consumption in 2007 was 40,341,000 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 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 which 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 is located near Washington, D.C. For additional information or to find out more about the Institute and its programs, 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. Each user of this Manual must still use its own independent judgment and discretion in ensuring that it handles methanol safely/communicates appropriately, and in doing so must develop the specific systems that best fit its 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 and local law.

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## 2 Methanol General Information

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

### 2.1 What Is Methanol?

Also known as methyl or wood alcohol, the simple answer is that methanol is a colorless organic liquid at room temperature and pressure. 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. Potential future applications of methanol include its use as a hydrogen carrier for fuel cell technology applications 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 you use it and how much you use. Failure to control a small amount of methanol can be problematic; loss of control of a large quantity can be catastrophic. This section of the manual provides an overall view of methanol for both large and small users.

Five overriding considerations are of paramount importance when handling methanol.

1. Methanol is an easily ignited hydrocarbon that burns in 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, methanol vapor may collect in confined spaces and low-lying areas.
3. In certain specific circumstances, methanol vapor explodes on ignition.
4. Methanol is a toxin; ingestion of a small amount (between one and two ounces, approximately 30 to 60 milliliters) can cause death; lesser amounts are known to cause irreversible blindness. Do not eat it, drink it, breathe it, or stand over it.

5. Methanol is totally miscible in water. A 75% water and 25% methanol solution is considered to be a flammable liquid. This has important implications for fire fighting.

The methanol molecule contains a single carbon, and is thereby the simplest alcohol derived from normal, saturated hydrocarbons – namely, methane (CH<sub>4</sub>), ethane (C<sub>2</sub>H<sub>6</sub>), and propane (C<sub>3</sub>H<sub>8</sub>). The two- and three-carbon-derived alcohols are ethanol and propanol, respectively. 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 (CH<sub>3</sub>OH), ethanol (C<sub>2</sub>H<sub>5</sub>OH), and propanol (C<sub>3</sub>H<sub>5</sub>OH), have similar physical and chemical properties. As the number of carbon atoms that comprise alcohol molecules increases, the length of the straight carbon chain increases, the molecular weight of the alcohol molecule increases, freezing point temperatures decrease, and boiling point temperatures increase.

Alcohols are also structurally similar to water. Some properties of alcohols, specifically of methanol, resemble properties of water. Table 1 lists the structural formulas, systematic names, common names, and solid melting and boiling point temperatures for three representative alcohols.

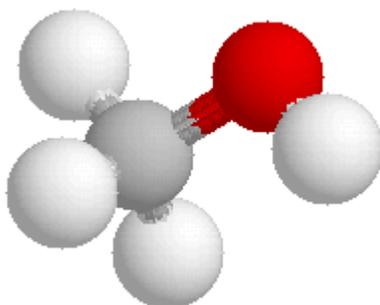


Figure 1. Methanol CH<sub>3</sub>OH

Table 1. Three Representative Alkane-Derived Alcohols

Molecular Structure	Systematic Name	Common Name	Liquid Freezing Point	Liquid Boiling Point
CH <sub>3</sub> OH	Methanol	Methyl alcohol; wood alcohol <sup>1</sup>	-144°F (-97°C)	149°F (65°C)
CH <sub>3</sub> CH <sub>2</sub> OH	Ethanol	Ethyl alcohol; grain alcohol <sup>2</sup>	-175°F (-115°C)	172.4°F (78°C)
(CH <sub>3</sub> ) <sub>2</sub> CHOH	2-Propanol (Isopropanol)	Isopropyl alcohol	-194.8°F (-126°C)	206.6°F (97°C)

<sup>1</sup> Prior to 1926, methanol was referred to as “wood alcohol.” During this period, methanol was produced by destructive distillation of wood.

<sup>2</sup> 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.

In summary, methanol is hazardous to life safety as it is flammable, toxic, and reactive with alkali metals and strong oxidants, and 100% miscible in water. These properties require careful handling and storage, as discussed in more detail in future sections.

## 2.2 The Methanol Life Cycle (Value Chain)

Methanol is produced, stored, and shipped in enormous quantities. World consumption in 2007 was around 40 million tonnes. Table 2 summarizes the major methanol export and import regions in 2006.

**Table 2. Summary of Global Methanol Industry in 2006 in Tonnes per Year**  
(Source: PCI-Ockerbloom & Co. Inc.)

Region	Import	Capacity	Production	Export
Caribbean	0	8153	7541	7012
Persian Gulf	1	8060	7756	5928
South America (Chile & Argentina)	0	4280	3566	3331
Africa	0	1758	1475	1447
New Zealand	1	530	404	267
North America (U.S., Canada, & Mexico)	7112	1715	1606	514
Western Europe	8062	3310	3176	3119
Asia (Japan, China, Taiwan, & S. Korea)	5427	9931	7623	206

### 2.2.1 Methanol Manufacture

With the exception of China, methanol producers are typically located in regions of the world that produce an excess of natural gas and/or industrialized countries that can access natural gas in large quantity at relatively low shipping cost.

As Table 2 shows, more regions export than import, and production lags behind capacity. North America exports about 33% of what it produces. Therefore, its consumption was something over 8 million tonnes in 2006. Western Europe exports most of its production; consumption was about 5 million tonnes. Western Europe, North America, and Asia are the principal regions of consumption. The Caribbean, the Persian Gulf, South America, and Africa are net exporters, with the majority coming from the Caribbean and the Persian Gulf regions. In 2007, China became the world's largest producer and consumer of methanol, with an annual average demand of around 10 million tonnes.

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 feed stock 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. These regions manufacture derivative

products: formaldehyde, resins, methyl amines, methyl chlorides, silicones, dimethyl terephthalate (DMT), terephthalic acid (TPA), and methyl methacrylates. North America, Western Europe, and a handful of Asian countries (Japan, China, Taiwan, and South Korea) consume methanol as chemical feed stock.

Technology for production of methanol will likely continue to evolve throughout this century as feed stock change, 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 the 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.
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, its next-larger alcohol molecule, and from less-expensive non-food-stuff feed stock.

#### **2.2.2.1 Recycling**

Methanol is an eminently recyclable material. As a solvent, it can be readily separated from contaminants 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 more chemically complex materials such as plastics, it can be recovered from these materials by chemically destructive processes, which decompose more 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 can be used 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 Section 1.2, methanol will be used to reduce waste from existing processes and reuse waste from other waste streams.

## 2.3 Uses of Methanol

Methanol markets have changed during the course of the past 15 years as usage and demand patterns have shifted. Evolving global economic, energy, and environmental realities will continue to drive the methanol market into the foreseeable future.

A principal historic change in methanol markets occurred during the 1990s, as a result of regulatory requirements for oxygenated gasoline. During this period, gasoline was oxygenated by addition of additives: namely MTBE (Methyl Tertiary Butyl Ether) and TAME (Tertiary Amyl Methyl Ether). These requirements began in California in the early to mid-1990s, and subsequently progressed throughout North America and Western Europe. The more widely used additive, MTBE, is synthesized from methanol feed stock and at one point accounted for about 37% of methanol consumption.

Initially, methanol was produced where consumed, but manufacture shifted to producing regions of the world with readily available natural gas feed stock reserves. Methanol-producing regions shipped methanol to MTBE plants in Europe and North America. Seeing a business opportunity, methanol-producing countries such as Saudi Arabia constructed their own MTBE manufacturing plants. Methanol import was supplemented and eventually largely supplanted by MTBE import. This change created methanol over capacity in North America and Europe, which resulted in plant closures in the late 1990s and early 2000s. It became more cost effective for established methanol producers to buy methanol on the open market rather than manufacture it domestically.

In the United States during the 2000 to 2006 time frame, issues surrounding MTBE became politicized and, although MTBE successfully reduced vehicle air pollution, inadequate containment, and improper handling of MTBE in some small refineries and retail stations led to the contamination of ground water, which has resulted in major lawsuits between water users and MTBE handlers. As of 2008, gasoline formulation in the United States has been modified by replacing MTBE with ethanol. Eventual substitution of methanol as a replacement for ethanol is anticipated.

During the first quarter of 2008, crude oil prices spiked over \$140 US 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 some staple food items. These circumstances provide an increased incentive to use methanol as a direct additive to motor fuel to reduce air emissions, and perhaps eventually as an alternate fuel for internal-combustion-engine automobiles to replace gasoline.

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

Globally, formaldehyde manufacture accounts for about 40% of methanol demand for production of urea-formaldehyde and phenol-formaldehyde resin glues and adhesives, which are used extensively as bonding agents in particleboard, plywood, and fibrous wood panels. Demand for these building materials has decreased sharply due to a housing market downturn. Figure 2 summarizes an approximate distribution of methanol usage in 2008. This distribution is expected to change, perhaps radically, in coming years.

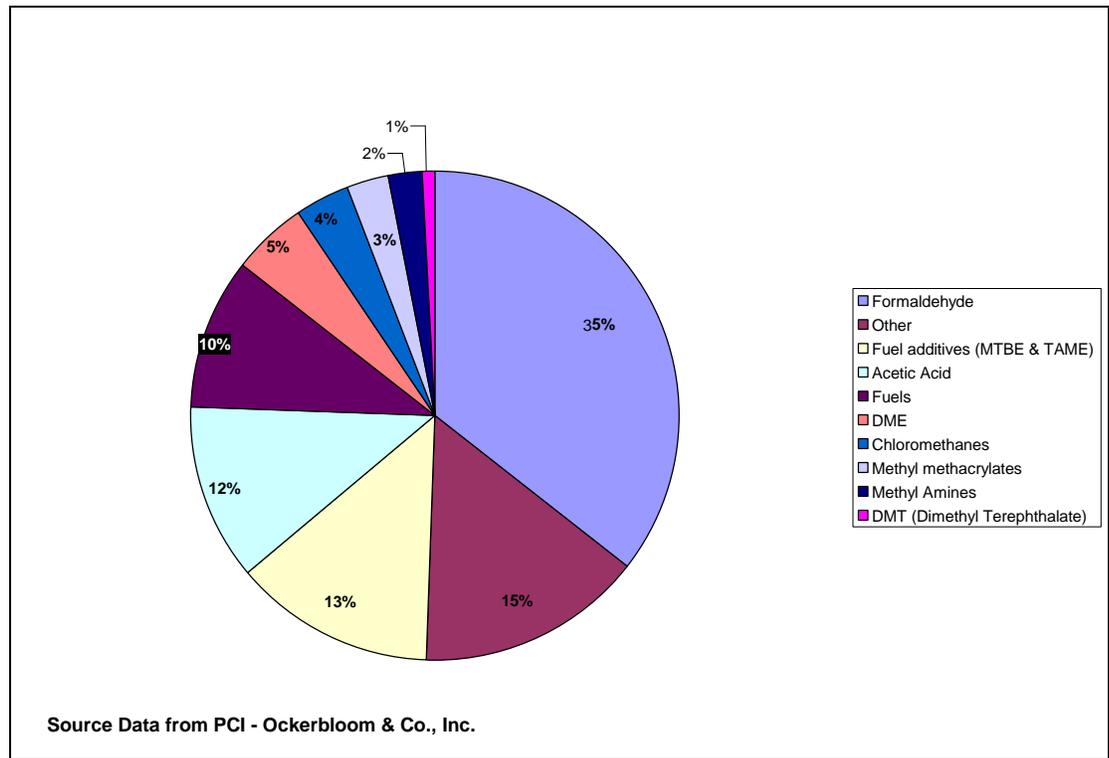


Figure 2. Approximate Distribution of Global Methanol Usage in 2008

### 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 use, followed by acetic acid production. Figure 3 summarizes the role of methanol in the production of intermediate chemical feed stock.

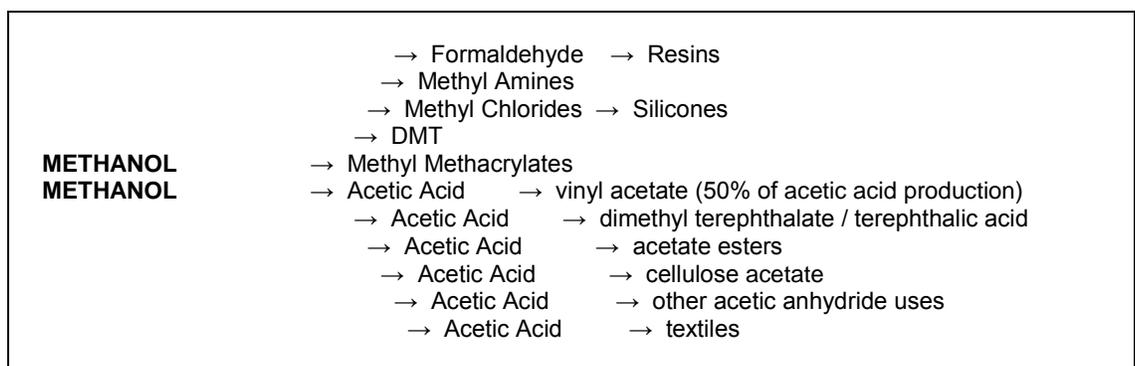


Figure 3. Methanol as Intermediate Chemical Feed Stock

### 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 past and the most recent 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] concluded 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 70-85% methanol content, not 100% pure methanol. As methanol becomes widely available as a motor fuel, these differences will likely be resolved.

The safety question over the use of methanol as a vehicle fuel centers on its potential for causing vehicle fires as compared to gasoline. According to a recent National Fire Protection Association (NFPA) study [43], while 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 are due to vehicle failure, such as leaks, loose wiring, 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.

The automobile racing industry has considerable hands-on experience in selecting and using motor fuels, including various methanol, ethanol, and gasoline blends. In racing, the most appropriate fuel depends on the type of race, and the type of race determines the characteristics of the car. For example, prior to 2006, NASCAR engines used 110-octane leaded gasoline, a fuel that is much different from street-legal automobiles, which use unleaded gasoline rated between 87 and 93 octane. In 2006, NASCAR switched to SUNOCO 260 GTX gasoline as the sanctioned racing fuel. The SUNOCO fuel is unleaded, with an octane of 99. Oxidant additives are prohibited. SUNOCO NASCAR-sanctioned fuel is entirely petroleum-derived and operates at compression ratios of 12:1.

By comparison, Indianapolis 500 (Indy) race cars used pure methanol prior to 2006 at which time the fuel was switched to a 90%/10% methanol/ethanol blend and then to a 98% ethanol/2% gasoline blend in 2007. Commercially available gasoline-methanol and gasoline-ethanol blends range from 10% to 30% methanol or ethanol. Each fuel is selected for a specific purpose and has advantages and disadvantages relative to other possible choices.

Methanol and, subsequently, ethanol fuels used in Indy cars have the advantage of enabling engines to operate at extremely high compression ratios, which produces more power for a given volume of engine displacement than a NASCAR engine. As a bonus, and contributing to its selection as the fuel of choice, methanol and its current replacement, ethanol, have multiple desirable safety features:

1. Methanol flame is low temperature and non-luminous, therefore, methanol fires generate substantially less radiant heat than gasoline fires, which have higher flame temperature and produce luminous flames.
2. 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.
3. The concentration of methanol in air necessary for combustion is approximately four times greater than that for gasoline. Coincidentally, the vapor pressure of methanol is lower, thereby generating fewer vapors. In other words, methanol must be raised to a

higher temperature in order to generate vapor concentrations necessary to support combustion in air.

4. 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 four times the volume of the methanol pool.

These considerations also apply to normal transportation-type driving 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 extinguishment are critical life safety considerations.

Indy racing officials elected to replace gasoline with methanol (and subsequently ethanol) to increase life safety of drivers and pit crew. The driving public may elect to use methanol and/or methanol blends as economic alternatives to gasoline. This change is anticipated to have the added benefits of increasing driver-occupant safety and reducing the already low likelihood of fuel station fires.

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.

The current world crude oil supply-demand situation will require substantial changes not only in fuel consumption, fuel formulation, but also in 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, from saving money to “going green.” Diesel fuel prices are continuing to increase globally, and biodiesel allows recycling of waste material and replacing a consumable resource with a renewable one, as well as diversifying 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<sup>3</sup> with pure methanol or 200-proof ethanol in the presence of sodium or potassium hydroxide catalyst. The chemical process is called trans-esterification. 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 waste, depending on circumstances. Once dried, glycerol can also be burned as fuel or potentially used as an additive in livestock feed.

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<sup>3</sup> Emphasis is placed on using vegetable oils because of spoilage of animal fat. Spoilage, in addition to being unpleasant, reduces the yield of the conversion process.

Methanol is used to process bio-waste material into biodiesel, a hydrocarbon fuel with properties similar to diesel fuel. Conversion can be accomplished on scales that range from 5-gallon-bucket 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 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 may or may not have 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 probably currently communicating with regulatory agencies administering regulations for health, 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 from the vessel 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:

1. 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.
2. Methanol must be stored in a bermed, diked or banded, 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 is 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."

3. 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.
4. Care must be taken in handling methanol, adding hydroxide, mixing hydroxide, and then introducing the methoxide into the waste oil.
5. Temperature control throughout the process is critical to safe and efficient operation. If the temperature rises too high, and agitation too vigorous, then fire and/or explosion is possible. If the temperature is too low and agitation too gentle, then the reaction will not go to completion.
6. 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.

### 2.3.4 Wastewater Denitrification

Wastewater collected in wastewater treatment plants characteristically contains high levels of nitrogen in the form of nitrates and ammoniated compounds ( $\text{NH}_3$  – anhydrous ammonia;  $\text{NH}_4\text{OH}$  – ammonium hydroxide, etc.). Bacteria convert the nitrogen in these compounds to nitrates, which, if discharged into the environment with the sewage effluent, have a devastating effect on fresh and salt water ecosystems manifested as overgrowth of algae, oxygen depletion, and subsequent suffocation of subsurface plants and animals. Denitrification is a process by which nitrogen is removed from treatment facility discharge. Removal is accomplished by a combination of chemical additives and bacterial degradation.

Addition of methanol to wastewater effluent accelerates action of anaerobic bacteria, which convert nitrates ( $\text{NO}_3^-$ ) to nitrogen ( $\text{N}_2$  gas), a harmless gas that makes up almost 80% of atmospheric air. Over 200 wastewater treatment plants in the United States alone are currently using methanol for denitrification. 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 US\$0.50 to US\$0.60 per pound of nitrogen removed, which is 12% of previously reported costs.

### 2.3.5 Emerging and Miscellaneous Uses

The current spike in the price of fuels is forcing drivers to alter their driving habits and change fuels and/or vehicles to cope with rising fuel costs. It is likely that additional pressure will be placed on developing alternate modes of transportation and power sources, including fuel cells and methanol-fired turbine engines.

#### 2.3.5.1 Direct Methanol Fuel Cell

Applications of direct methanol fuel cells (DMFCs) are being investigated, with positive results. At the time of this writing, the International Civil Aviation Organization has approved use of DMFCs to power personal devices such as laptop computers by passengers on board airplanes. Several development companies anticipate having DMFCs in commercial production by 2009 / 2010.

#### 2.3.5.2 Methanol to Hydrogen Fuel Cell

Methanol also shows promise as an electron transfer medium and source of hydrogen in hydrogen-based fuel cells. The use of on-board steam reformers in automobiles can convert liquid methanol into hydrogen gas and is intended to be a low-temperature / low-pressure source of motive power.

### **2.3.5.3 Turbine Engines**

Turbine engines currently operate on jet fuel and natural gas. The transition to methanol as a turbine fuel presents several challenges. Materials selection within the turbine must be investigated. Methanol's low heat of combustion is both an advantage and a disadvantage. The high octane allows high-pressure operation. The low heating value requires resizing many of the fuel delivery components within the engine.

In summary, established applications are being replaced by new ones. As a result, the need for experience in methanol shipping, storage, and handling will likely transfer from some well-established industrial segments to other newly established segments. The importance of accurate and widely available information for best practices, product stewardship, and responsible care and distribution of methanol is anticipated to become increasingly important in preventing and responding to accidental spills.



## 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 produced is transported between continents. The safety, reliability, and integrity of trans-ocean shipping and dock and marine terminal storage constitute a large portion of the loss exposure resulting from accidental and unmitigated release that is borne by the Methanol Industry.

#### 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 contact with methanol.

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.

#### 3.1.2 Rail Transport

Precautions for rail transport are much the same as those for ethanol, gasoline, MTBE, jet fuel (kerosene), and distillate, including grounding for protecting 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 2008 edition of the *Emergency Response Guidebook* (ERG2008) [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, ERG2008 recommends that responders isolate and consider evacuating in all directions from the release to a radial distance of one half mile (800 meters). First responders should be equipped with chemical protective clothing and a Self-Contained Breathing Apparatus (SCBA) in the event of a spill. Turnouts are appropriate for fire response, but not for spill response tasks that will place responders in contact with uncontained methanol. Ignition sources must be eliminated to a distance of at least 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 tankers apply equally for tankers attached to tractor haul trucks and to tank trailers towed by tractor haul trucks. Methanol transport truck haulage is subject to substantially the same precautions as are routinely exercised for gasoline transport tanker haulage.

## **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 tanks 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. 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.

### **3.2.1 Docks and Marine Terminals**

Storage facilities at docks and marine terminals are typically floating roof tanks, dedicated to methanol handling. These facilities are equipped with leak detection, alarm, and fire suppression, and spill response systems.

The larger concern is for unattended tank leaks. American Petroleum Institute codes, standards, and recommended practices should be referred to for 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 leak detection and toxic hazard.

### 3.2.3 Portable Containers (Totes and Drums)

Totes and drums can be problematic. The methanol industry has gone to considerable lengths to design and make satisfactory totes easily obtainable. Because the number of users of tote and drums far outnumbers the number of facilities with dedicated methanol 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 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 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](http://www.methanol.org), and click on the “Methanol Source Request” link. Complete and submit this on-line 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.
- Sources should be contacted regarding the intended application 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 having agreed upon facilities and provisions for receiving, storage, and local transfer, establish and train a local response team on actions to take in the event of a spill.
- Certain aspects of methanol handling require special provisions and protective measures. These include the following:
  - So far 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.
  - Use positive materials identification for gaskets, filters, hose material, etc.
  - Ensure procedures are in place to ground, and periodically verify grounding.
  - Ensure procedures are in place to protect from water up-take and accumulation.
  - Ensure procedures and provisions are in place for preventing methanol entry into the water table or aquifers.
  - Ensure procedures and equipment are in place for personnel protection.
  - Ensure procedures and equipment are in place for leak detection and alarm.
  - Ensure procedures and equipment are in place for onsite emergency response.
  - Ensure procedures and possibly specialized equipment are in place for offsite emergency responders.

- 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 34
  - 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 HAZOP, performed prior to delivery of the first tanker truck load, tote, or drum of methanol.
  - Methanex Corporation's Corporate Manual: Container Filling Best Practice, Document #CR3RC250.
  - ISO 9001: 2000 – Quality Management Systems

### 3.2.4 Electrical Classification

Electrical equipment 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. It is recommended that grounding straps be equipped with carbide-tipped clamps to ensure electrical contact through nonconductive 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.

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.

When being filled, metal containers (drums or totes) and the associated fill equipment pump should be bonded together and grounded. 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<sup>4</sup> connected to a clamp with hardened steel points and screws or a strong spring

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<sup>4</sup> A 1/4 to 3/8 flexible, bare bronze cable can be used for large grounding and bonding clamps.

that will penetrate paint, corrosion, and accumulated materials. Apply the bonding clamp on the top chime 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.

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 for ignition.
- 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).

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, it 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.

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 and combustion.

- ASTM E681 describes a standard test method for determining flammability limits.
- Perry's Chemical Engineers' Handbook, 6<sup>th</sup> 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, 2<sup>nd</sup> Edition, pp. 321-313, pp. 486-489, 1987.
- NFPA 30A, *Code for Motor Fuel Dispensing Facilities and Repair Garages*, 2008.
- 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 III 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

#### 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 the human diet from fresh fruits, vegetables, commercial beverages like fruit juices, beers, wines, and distilled spirits, and food additives aspartame and DMDC (dimethyl dicarbonate). Aspartame is an artificial sweetener, and DMDC is a yeast inhibitor used in tea beverages, sports drinks, fruit or juice sparklers, wines, and wine substitutes. Both additives are converted to methanol after consumption.

**Table 3. Methanol Levels in Foods and Beverages**

Sample	Methanol Level
Fresh and canned fruit juices (orange and grapefruit juices)	1-43 mg/l 11-80 mg/l 12-640 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

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 vapors may also be present in cigarette smoke at a level of 180 micrograms ( $\mu\text{g}$ ) per cigarette). 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 less than 3 mg/l blood (milligrams per liter blood). In controlled studies, humans breathing air containing 200 ppm (parts per million) methanol had blood levels below 10 mg/l.

Natural emission sources of methanol include volcanic gases, vegetation, microbes, and insects. Man-made methanol releases usually occur from usage of methanol-containing solvents and products, methanol production, end-product manufacturing, and storage and handling losses.

Another potential source of methanol emissions involves motor vehicle fuels. 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. 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.

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 feed stock for the production of other organic chemicals and a variety of consumer products, 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 (Methyl Tertiary Butyl Ether), 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 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 4. Added Body Burden of Methanol [2]**

Exposure/Dose	Added Body Burden of Methanol
Background in a 154 lb (70 kg) body	35 mg*
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**
Aspartame sweetened products 27 oz (0.8 liter) diet beverage	2-77 mg 42 mg
Ingestion of 0.2 ml of methanol	170 mg
Ingestion, 0.7-3 oz (25-90 ml)	Lethal (~20000-71000 mg)

\*Estimated from (0.73 mg/l) of blood

\*\*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 the 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:



### 4.1.5 Effects of Exposure

Methanol is a poison. At this time, there is no known method of mitigating its toxic effects. The principal concern is with acute exposure through any primary routes of entry. Health effects 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 poisonous nature of methanol and the difference between methanol, ethanol, and isopropyl alcohol.

#### 4.1.5.1 General Symptoms

The toxicity of methanol is the same, regardless of the route of 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. Signs of systemic poisoning may be delayed 8-36 hours after initial exposure. 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 in-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 and death.

#### 4.1.5.2 Acute Effects

The effects of acute, high-dose methanol exposure have been well-characterized in human 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 period 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, misty or blurred vision, to dramatically reduced visual acuity and total blindness.

The amount of methanol that can cause severe methanol poisoning is very small: Assuming that 100% methanol fuel is swallowed, the poisonous 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 two tablespoons (28 ml) for an adult.

#### 4.1.5.3 Chronic Effects

In contrast to the effects of acute, high-level exposure, relatively little is known about the effects of chronic, low-level methanol exposure. Based on the limited number of case reports and epidemiologic 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.

Most studies indicate that methanol does not cause cancer. Methanol is not currently listed by any international consensus body as being a carcinogen (e.g., IARC, NTP, NIOSH, ACGIH, or OSHA). Furthermore, there are no human data that demonstrate a link between methanol exposure and an increased incidence of birth defects or reproductive hazards. However, more recent review of available data on mice and rats indicates that inhalation or oral exposure to methanol at high doses is a developmental hazard. Since mice and rats metabolize methanol differently than humans, there is doubt whether these studies are at all predictive of human health effects.

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 dietary or occupational exposures. This value is not intended to represent the highest “safe” blood concentration. It is possible that substantially higher blood levels would not result in developmental toxicity.

## 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 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, and must be considered when determining equipment location, type, and capacity. If mechanical ventilation is used, spark-proof fans should be implemented.

### 4.2.2 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.

### 4.2.3 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 operated 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, and if the air concentration of methanol is known.

**Table 5. Respiratory Protection Guide**

Air Concentration of Methanol	Respiratory Protection
<200 ppm	No protection required.
200-250 ppm	Protection required if the daily time-weighted-average exposure is exceeded. A supplied air system must be used if protection is needed.
>250 ppm	A supplied air system must be used (i.e., positive-pressure SCBA).

### 4.2.4 Chemical-Resistant Clothing/Materials

Chemical-resistant clothing/materials should be worn if repeated or prolonged skin contact with methanol is expected. These may include 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 face-shield may be worn over goggles for additional protection, but not as a substitute for goggles.

Table 6 serves as guidance for proper personal protective equipment, depending on the situation presented.

**Table 6. 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 suit	Full chemical suit
Gloves (Silvershield or disposable nitrile)	Chemical-resistant rubber gloves	Chemical-resistant rubber gloves
Safety glasses with side shields (full face -	Full face respirator with organic vapor cartridge	SCBA / compressed air breathing apparatus (CABA)
Full boot cover	Chemical-resistant rubber boots	Chemical-resistant rubber boots

## 4.3 Safety Precautions

### 4.3.1 Routine Operations

Due to the flammability of methanol vapor, static electricity may ignite it. 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 to take. 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 with 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.
- Hydrants should be strategically placed with adequate hoses.
- 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 with lightning conductors that are securely grounded.

### 4.3.2 Special or High Hazard Operations

#### 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 atmosphere that is oxygen-deficient, toxic, or combustible, therefore, requiring them to be classified as “permit-required” for entry by OSHA. 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 IDLH (Immediately Dangerous to Life or Health) concentration, and the Upper Explosive Limit (UEL) is 36% (360000 ppm) by volume. At concentrations in air below the LEL, there is not enough methanol vapor to spread a flame. At concentrations in air above the UEL, there is too much methanol and not enough oxygen to spread 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.

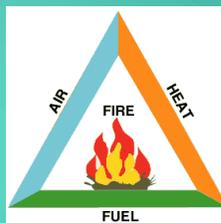
In confined spaces, ventilation systems may be necessary in order to keep airborne concentrations of methanol below the LEL and below permissible exposure limits. Before entering a confined space where methanol may be present, check to make sure that an explosive concentration does not exist.

#### **4.3.2.2 Hot Work**

Methanol is extremely flammable. 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. 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 promotes rapid mixing with air; non-turbulent release retards mixing with air. The specific gravity of unmixed vapor is 1.1 compared to air at 1.0. Pure methanol has a low flash point of 54°F (12°C) and a wide flammability range (6-37 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 slight to substantial mixing range with air. The minimum ignition energy (MIE) for methanol in air is 0.14 milijoules (mJ) compared to 0.2 mJ for gasoline and 0.017 for hydrogen (H<sub>2 gas</sub>) [33]. Local hot spots can exceed the flash point and methanol can be ignited. When methanol catches fire, it burns with a clear blue flame that is very difficult to see in bright sun light. Methanol may be on fire and you may not be able to discern the hazard of a fire by looking for a flame.

### ***The Fire Triangle:***



The 3 elements required to have a fire are:

1. Ignition source (such as heat, or sparks)
2. Fuel (methanol is a fuel), and
3. Oxygen (air is a source of oxygen).

Fire Prevention: Break the triangle by removing one of the elements (especially the ignition source).

Methanol has the potential to catch fire when hot work is performed near methanol sources. 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. 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.

#### **4.3.3 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 in itself 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.

## 4.4 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 Material Safety Data Sheet (MSDS) 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 exposed area with copious amounts of tepid water for at least 15 minutes. Contaminated clothing and shoes should be removed under the shower. Wash 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 15 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 18 to 24 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 and 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) is also available to treat methanol poisoning.



## 5 Managing Methanol Safely: Process Safety

This chapter summarizes the “Process Safety Management” system of administering highly hazardous materials, which includes methanol, as mandated in the United States by Federal OSHA according to provisions set forth in 49 CFR 1910.119, the so-called “OSHA Process Safety Management standard [60].” This is by no means the only system used successfully to manage chemical hazards; however, it has proven to be effective in the 15 years it has been in effect, provided the principles are applied diligently and intelligently.

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* [50], the European Directive on the *Control of Major-Accident Hazards Involving Dangerous Substances* (Directive 96/82/EC), as well as the Association Française de Normalisation (AFNOR), Deutsches Institut für Normung E.V. (DIN), International Organization for Standardization (ISO), American Petroleum Institute (API), and the American Society of Mechanical Engineers (ASME). The OSHA Process Safety Management Standard was selected as a model because it is an overview of the management duties and responsibilities that must necessarily 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 packaging 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.

Process safety management 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 or not your facility is or would be regulated under the provision of the OSHA Standard. The point is not regulation, but responsibility. The basic structure laid out in the Standard is time proven to provide an effective framework for safe manufacture, storage, and use of hazardous chemicals. You are encouraged to make good use of this.

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

PSM consists of 14 management elements. Each element addresses a particular aspect of the process to manage chemicals. Each element is stand-alone, but also projects into and strengthens every other element. As Table 7 shows, elements can be arranged into one of seven groupings: knowing, doing, responding, recovering, learning, verifying, and protecting. Elements are organized within groupings based on the premise that, in order to safely operate and maintain a chemical processing asset, whether a two-person laboratory, a water treatment plant, or a large volume synthesis plant, it is necessary to (1) know what you are doing before you do it, (2) do it, (3) respond to and recover from contingencies, (4) learn from mistakes, (5) verify management controls are functioning as intended, and (6) protect proprietary property.

**Table 7. The Organization of Process Safety**

Grouping	PSM Element	Grouping	PSM Element
<b>Know</b>		<b>Respond and Recover</b>	
	Employee Participation		Emergency Planning and Response
	Process Safety Information	<b>Learn</b>	
	Process Hazards Analysis		Incident Investigation
	Operating Procedures	<b>Verify</b>	
	Training		Process Safety Audits
<b>Do</b>		<b>Protect</b>	
	Contractors		Trade Secrets
	Pre-Startup Safety Review		
	Mechanical Integrity		
	Hazardous Work Permitting		
	Management of Change		

Each element of PSM is applied over and over, through time, in a serial sequence that 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 of each element of the Standard.

## 5.1 Employee Participation

The guiding principle regarding employee participation is that the employees are the persons who must know the most and with the greatest level of detail regarding the process in order to operate and maintain process system equipment safely and efficiently. PSM specifies three actions to facility management regarding employee participation in managing process safety.

1. Employers are to develop a written plan for employee participation.
2. Employers are to consult with employees regarding implementation of all elements and aspects of process safety.
3. Employers are to provide open access to all information developed for the purpose of managing process safety.

In effect, all aspects of a process safety program belong to facility employees; employers have the responsibility and the duty of creating, supporting, and funding the program and verifying that the program functions as anticipated and produces the intended result. Employees do not know what they do not know, and it is the employer's responsibility to inform all employees of the risk of working around methanol and how to manage those risks. When accidents do occur, it is usually because the individuals handling the methanol or performing work around methanol were unaware of the risks. This points to a failure of management to properly train and/or supervise the employees.

## 5.2 Process Safety Information

The overriding premise that drives the necessity of process information is that specific and accurate information is essential in understanding how chemicals behave within the control limits for a process. Three types of information are to be collected, organized, and made available to employees:

1. Information pertaining to the hazards of the chemicals within the process,
2. Information pertaining to the technology of the process (including safe control parameter limits), and
3. Information pertaining to the equipment that is used in the process.

The purpose of insisting that employees become familiar with this information is to ensure that operators, maintenance personnel, and their supervisors:

- Know and understand the properties and behavior of process chemicals in all potential operating circumstances including transients, deviations, excursions, upsets, startups, emergency shutdowns, and normal shutdowns.
- Understand how process technology drives process excursions in abnormal operating circumstances caused by interruption of utilities, equipment failure, and/or human error.
- Appreciate equipment pressure, temperature, and containment limits during abnormal conditions.
- Verify that equipment design and construction complies with "recognized and generally accepted engineering practices."

## 5.3 Process Hazard Analysis

Process hazard analyses (also variously referred to as hazard evaluations, risk assessments, or hazard identification techniques) are required because circumstances and perceptions change over time. Process Hazard Analyses (PHAs) are conducted periodically to, in effect, bring the process equipment up to date.

This element of the OSHA Standard stipulates that PHAs are to be performed on all aspects of the process using an analysis technique that is appropriate to the complexity of the process. The PHA is to identify, evaluate, and verify hazards involved in the process due to chemicals, failure to control the process within the intended operating envelope, equipment breakdown, or human error. The PHA team verifies that each of the potential circumstances is safeguarded in depth by layers of protection, that accidental release to the environment is mitigated, and that emergency response in the event of accidental release is prompt, appropriate, and effective. If any of these is deemed to be inadequate due to nonexistence, unreliability, or inadequate design, then recommendation is made of alternatives for correcting identified deficiencies. Correction is to be made in a timely manner.

## 5.4 Operating Procedures

In order to operate the process safely, operators must know the boundaries between safe and unsafe conditions. Likewise, they must know how and when to perform specific tasks associated with equipment operation and process control.

Employers are to provide written operating instructions that guide operators through the steps necessary to start up, operate, shut down, and emergently shut down the process under normal and abnormal operating conditions. Procedures should clearly state maximum and minimum safe operating limits for temperature, pressure, level, fluid flow-rate, heater firing rate, etc.

Operating procedures are to be revised when even a not-in-kind change is made within the process. Procedures are to be updated and verified as accurate on an annual basis.

## 5.5 Training

Operating personnel are to be trained in interpreting and applying the written operating procedures. As a practical matter, training includes both classroom and one-on-one, on-the-job training. For large complex processes, electronic process control simulators may be used in the same way as electronic-hydraulic simulators are used for pilot flight training. For small, simple processes, operator training may include table top exercises.

Training is to be repeated when a not-in-kind change is made within the process. Refresher training is to be given every three years.

Employers are to maintain a record of each employee's training and proof that the employee not only took, but also understood, the training at a minimum level that is considered to demonstrate understanding and operating proficiency. Likewise, employers are to implement controls that ensure operators are day-to-day "fit for duty."

## 5.6 Contractors

Historically, contractor employees who are at a facility for short periods of time on an irregular basis to perform specialized services have anomalously high accident rates. Some contractor-involved incidents involve only contractors; others also involve facility employees. In a chemical laboratory, this may consist of a craft workman, such as a plumber or an electrician. During a chemical manufacturing plant turnaround, this may consist of a crew of several hundreds of contractor-employed workers. The circumstances are the same in both cases. The workmen are unfamiliar with hazards within this particular workplace, and make mistakes that result in injury or hazardous release.

Plant management addresses this situation at several levels. First, contractors are carefully screened prior to being engaged to perform work at the facility. If a contractor has a poor safety record on previous jobs, then consideration is given to locating a contractor who has a good safety record. Once a contractor has been screened and selected, contractor employees are safety trained regarding hazards that are specific to the facility. The contractor is also required to perform certain safety-directed activities on a daily basis with its crew members. These include training contractor employees, daily safety meetings (so-called tailgate meetings), recordkeeping, notification of hazardous contract work, and incident reporting and investigation. This aspect of contractor management is particularly important for anyone performing hot work around methanol.

## 5.7 Pre-Startup Safety Review

Presuming that a process unit or equipment item has required repair, and has been taken out of service while the repair is being made, process safety management requires that a review be done to verify that both the equipment item(s) and the organization are in an operational-ready condition. A pre-startup safety review is to be conducted whenever a modification in process chemicals, technology, or equipment requires updating process safety information.

Prior to “return-to-service,” which is defined as “the introduction of highly hazardous chemical,” the employer is to confirm the following:

- Construction tasks are complete, and construction activity is terminated.
- Equipment is in accordance with design specifications.
- Process safety information is updated.
- Safety, operating, maintenance, and emergency procedures are in place and are adequate.
- A process hazards review appropriate to the complexity of the process and the modification has been performed, and resulting recommendations have been resolved and/or implemented.
- Requirements for management of change are satisfied.
- Each employee involved in operating and maintaining the process is trained regarding the change.

## 5.8 Mechanical Integrity

The mechanical integrity element of process safety focuses on the maintenance function (equipment inspection, testing, and repair) as it pertains to “fitness for service” or “fitness for

continued service.” Accordingly, this element sets criteria for preparing written maintenance procedures; training maintenance employees; documenting results of employee training; and equipment inspection, testing, and repair (deficiency correction).

Provisions within this element include warehousing of spare parts and replacement materials. The employer is to ensure that maintenance materials, spare parts, and equipment are suitable for the process application in which they will be used. This may include positive materials identification and verification that specifications are satisfied and consistent with design requirements.

In a chemical manufacturing plant, this element pertains to duties of the purchasing, warehousing, inspection, and maintenance functions. Provisions within this element apply generally to all types of equipment and specifically to pressure vessels, storage tanks, piping systems, relief and vent systems, emergency shutdown systems, control systems, pumps, and other equipment, such as compressors, turbine engines, turbo-generators, etc.

## 5.9 Hazardous Work Permits

Maintenance, inspection, and testing may require facility and contract employees to work in so-called hazardous circumstances. Within the context of process safety, hazardous circumstance encompasses immediate and proximate hazards associated with the work environment. These include confined space entry, lock-out/tag-out of energy sources, elevated work, sub-grade work, line breaking, hot-tapping, hot work, over-head lifts, crane relocation, etc.

Process safety mandates that employers and employees be informed and aware of the location and hazards associated with all work tasks pertaining to inspection, testing, and maintenance of equipment. Therefore, work is to be scheduled and permitted prior to taking place. Both scheduling and permitting are to establish a written record of what is being done, where it is being done, when it is being done, and the hazards associated with the task or the work environment. Hazardous work permitting assures both employees and employers that all reasonable measures are being taken to safeguard workers assigned to perform hazardous work.

## 5.10 Management of Change

Management of change addresses the issue of configuration management. It is occasionally necessary to modify the configuration of a process system in order to improve performance, reliability, or efficiency. Within the context of process safety, maintenance and repair activity assumes one of two states specific to item or component replacement: (1) in-kind replacement and (2) not-in-kind replacement.

In-kind replacement is any repair that substitutes another part, component, or equipment item for an existing item that meets or exceeds the design basis and fabrication specifications for the original part, component, or item. Because this state does not change or otherwise affect the design basis and performance capability of the system into which it is placed, it does not constitute a “change.”

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

The management of change procedure developed to satisfy this element of process safety addresses the following considerations:

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

The following actions are to be taken accordingly:

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

## 5.11 Emergency Planning and Response

Plan for, prepare for, train for, and respond to facility emergencies: accident, injury, accidental release of highly hazardous chemicals, subsequent fires and explosions, and other damage- and exposure-causing spills and incidents. Determine what might happen, and where it might occur. Install appropriate detectors and early warning devices. Have established evacuation procedures, rendezvous points, and headcount procedures. Establish mitigation measures, such as fixed fire monitors, sprinkler systems, deluge systems, automatic rapid transfer and isolation systems, blast walls, and the like, to contain, control, and localize damage. Inspect and test alarms, mitigations measures, and safety systems regularly, as recommended by suppliers.

Establish command, control, communicate, and manage measures necessary to assess the situation, call for backup, render first aid, and administer emergency medical care.

Work with your local first responders (police, fire, emergency medical care and possibly military) so that they are aware of the emergency planning and response procedures you have put in place, and so that they can provide you with feedback. Local fire departments are generally interested in participating in fire drills at chemical manufacturing sites to give the firefighters experience and so that they can better understand your facility. If the first time a fire truck pulls into your facility is to respond to an emergency, staff may lose precious time in driving to the right site. Involving your local first responders in fire drills will help build familiarity with the site and your operations that could save lives and property.

## 5.12 Incident Investigation

Despite best intentions, diligent prevention efforts, and appropriate mitigation and effective response, accidents will occur; people will be injured; air, soil, and water media will be contaminated; and capital equipment will be damaged and destroyed. Practices and procedures advocated by process safety can dramatically reduce the number and severity of accidents. It is unlikely that it will prevent every possible incident scenario from occurring.

Given this expectation, it is important to learn from past mistakes. Hence, incident investigation is an essential element of an effective process safety management system. Employers are to have personnel on hand who are trained in implementing written procedures for investigating accidents: releases, toxic releases, spills, fires, explosions, and especially minor incidents or situations that were discovered before an accident occurred, also called “near misses.”

A structured incident investigation and root cause analysis process should be implemented. Corrective actions should be developed that address the root causes and that are aimed at preventing recurrence of the incident.

The following guidance is provided for incident investigation:

1. Initiate an investigation as promptly as possible, and certainly within 48 hours.
2. Membership of the investigation team should include the following:
  - persons knowledgeable in the process;
  - contract employees, if the incident involved a contractor;
  - persons trained in forensic investigation;
  - persons trained in interviewing; and
  - persons or consultants trained in air dispersion modeling, fire modeling, explosion modeling, and failure analysis.
3. Prepare a written investigation report with recommendations.
4. Establish a team to address findings, and resolve or implement recommendations.
5. Review the report with employees and contractors whose job tasks are relevant to the findings.
6. Inform employees and contractors of lessons learned.
7. Retain and subsequently archive the report.

## 5.13 Process Safety Audits

Periodically (at least every three years) conduct a facility-wide audit to determine if procedures, provisions, and practices for process safety are in place, they are known and understood by employees, and they are adequate, functional, effective, and efficient. The audit 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
- Expertise and experience in safety auditing.

The audit team is to deliver a written audit report to the employer that assesses strengths and weaknesses in the various program elements. The employer is to promptly respond to each of the audit findings, and correct and document that deficiencies have been corrected. Audit reports should be retained and archived.

## 5.14 Trade Secrets

Trade secrets and proprietary information that is considered intellectual property of the employer is not precluded from inclusion within the process safety program. Neither is its inclusion revocation of the rights and privileges to secrecy thereof.

Trade secrets and information that is considered proprietary to the employer is to be clearly identified in writing by the employer. Intellectual property is to be protected by confidentiality agreement between the employer and the employees and contract employees who must have knowledge of and use that information in their duties for implementing various elements of a process safety program. Specifically this includes persons responsible for the following:

- Conducting process hazard analyses;
- Preparing operating procedures;
- Developing maintenance, inspection, and testing procedures;
- Conducting incident investigations;
- Doing emergency planning and response; and
- Performing process safety audits.

As mentioned before, process safety is founded on the principle that knowledge is power. As a methanol user, one aspect of your product stewardship is to use this chemical in a safe and responsible manner. You are encouraged to make good use of this knowledge.

## 5.15 Implementing Process Safety

A key step in managing methanol safely is to identify the risks posed by the material in order to design safety into the process. This is done through 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 the most widely used fuel, gasoline, which is also volatile and flammable.

Methanol's physical and chemical properties have several advantages over gasoline with regard to fire safety. Methanol has a lower volatility, vapor density, and heat release rate, and a higher flammability requirement 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."

There are some important differences, as well. One is that methanol can ignite at ambient temperatures in enclosed spaces, such as fuel tanks, while gasoline produces too much vapor to ignite in enclosed spaces. This particular hazard would necessarily be addressed in fuel tank design and location to ensure that the tank is isolated from all foreseeable ignition sources. The same process would be used to identify and resolve other risks from the operation of the facility, such as health and environmental issues.

### 5.15.1 What Is a "Hazard"?

The term "hazard" is a commonly used word. Within the context of risk assessment, the term has a more specific meaning. As used in this guide, a hazard is a threat that is posed by a

substance as an inherent characteristic of that substance. Typically, hazards are classified by type. Chemical hazards are classified as to the nature of the threat: fire, toxicity, reactivity, chemical or thermal instability, or chemical incompatibility. For example, methanol is classified as flammable and toxic. Persons handling, using, or storing methanol must take precautions to avoid manifesting the hazard. A hazard is a property of a substance that is characteristic of that substance.

### **5.15.2 What Is a “Risk”?**

The word “risk” is also commonly used. As used in this guidance, it has a very specific meaning. Risk is the frequency, likelihood, or probability of a sequence of events that results in a consequence, where the consequence is a manifestation of a chemical hazard. Mathematically, risk is calculated as the product of frequency or probability times consequence severity. Conversationally, the risk of a particular consequence, an explosion for example, is that probability of an explosion.

### **5.15.3 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 or task, and the equipment that is used in the process or that will be used to accomplish the task.

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

The third step is to conduct the review, making recommendations to improve control of the hazards. All aspects of the hazards review should be documented, including the list of recommendations.

The report is subsequently filed and archived, and the recommendations are either implemented, discussed and revised, or discussed and rejected. The risk of a particular consequence is assessed before and after implementation of the recommendation. In general, engineering safeguards are more expensive but more reliable; administrative safeguards are less expensive, but subject to becoming less reliable over time.

Appendix A 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), as well as list of the documents that contain process safety information for the technology and equipment of the process.

Many hazard identification 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.

### **5.15.4 Process Hazard Assessment Documentation**

Process hazard assessments must be documented, and this documentation must be preserved throughout the life of the facility. In general terms, the documentation should indicate what was reviewed, what questions were asked, what hazard was being safeguarded, how the scenario was developed, what the accident scenario consisted of, what corrective action was selected, and the benefit of the corrective action.

## 6 Fire Safety

This section provides information about fire safety characteristics that are peculiar to methanol and possibly different from other common fuels, such as gasoline, diesel, and jet fuel (hydrotreated kerosene).

It is particularly difficult to extinguish fires involving gasoline, diesel, and methanol. The focus of this discussion is on controlling and extinguishing methanol fires, although it also applies to fires involving methanol in the presence of gasoline or diesel. Additional information on properties of methanol that relate to fire safety is presented in Appendix B.

### 6.1 Fire Detection and Protection

Broadly speaking, all fires have a common trait. They begin as little fires and become larger. The objectives of fire protection are to contain, control, and extinguish. Success is best achieved using three aspects of fire response: (1) early detection, (2) immediate response, and (3) appropriate action.

All fires release heat; most fuel fires display flames and generate smoke. Fires involving pure methanol are not like most fires; they generate less heat, flames are nearly invisible to the naked eye during daytime, and there is very little smoke. Early detection of methanol fires requires different technology than early detection of gasoline and diesel fires.

#### 6.1.1 Vapor Control

The first measure in early detection of methanol fires must necessarily rely on the presence of methanol vapor. If methanol vapor is present, one must assume that ignition is possible. Once ignition occurs, 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, and whether vapor is confined or unconfined. If 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 explosion is more likely. If ambient temperature is below the flash point, if potential ignition sources are low energy, and if vapor can readily escape to atmosphere, then explosion is less likely.

##### 6.1.1.1 Storage Tank Safety Features

Best practice for tank storage (in particular, of large volumes) of methanol uses internal or external floating roofs to minimize methanol vapor space within the tank and to reduce the amount of air that can mix with that vapor and control the volume of vapor emission from tanks. Alternatively, inert gas blanketing can be used to prevent formation of explosive atmospheres within tank vapor spaces. Dry nitrogen is the preferred inert gas for blanketing.

Blanket gas should be free of carbon dioxide to avoid corrosion in the presence of moist air, and to avoid product contamination that could increase methanol acidity.

It is recommended that the outside of methanol tanks be painted with heat reflecting paint. This measure will reduce vapor losses from the tanks.

#### **6.1.1.2 Pressure Relief Systems**

Tank internal pressure can be controlled using pressure/vacuum relief valves or vacuum breakers. Vents may or may not be configured with flame arresters, depending on the specific circumstances of the hazard. Pressure relief valves are sized to a fire case and, if possible, should be piped to relieve into a flare header. If configured to relieve to atmosphere, then it is strongly recommended that Process Safety Valves (PSVs), be configured to breathe to atmosphere through flame arresters. In addition to fire safety, it is recommended that local regulations for limiting hydrocarbon emissions be considered when configuring tank vents and pressure relief devices.

Overflow pipes are not recommended. Methanol liquid is known to collect and drip from the pipes when ambient temperature is below storage temperature. Accumulation of condensed liquid methanol may create a fire hazard or qualify as an environmental release.

#### **6.1.2 Heat Detection**

The second early detection measure for a methanol fire is early detection of heat. When dealing with methanol, the adage “where there is smoke there is fire” must be modified to “where there is heat there is fire.” A number of technologies are available that scan for temperature. Consider investigating and testing these for your specific needs.

#### **6.1.3 Smoking, Vehicle Access, and Miscellaneous Ignition Sources**

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 fire-safe rating prior to being used in a methanol-containing area.

As a rule of thumb, allow at least 20 feet (7 meters) of “no ignition source” perimeter around storage areas containing individual small volume containers of methanol (i.e., cans, buckets, barrels, and totes). Allow at least 50 feet (17 meters) of “no ignition source” perimeter around storage and logistics areas containing and/or handling larger volumes of methanol (i.e., individual tanker trucks, rail cars, and small storage tanks). Allow at least 200 feet (70 meters) of “no ignition source” perimeter for logistics terminals that simultaneously load or unload multiple trucks, multiple rail cars, barges, ships, and large-volume storage tanks.

In the event a tanker truck, rail car, or storage tank is involved in a fire, evacuate to a distance of at least one half mile (850 meters) in all directions. Methanol is toxic; therefore, structural fire fighters' protective clothing is not effective in responding to a methanol spill and fires.<sup>5</sup>

## 6.2 Fire Control

Key elements of essential protection are immediate and appropriate response and maintaining control of the fire.

### 6.2.1 Fire vs. Explosion

Fire events, though undesirable, are preferable to explosion events. Process hazard analysis must consider which is more likely in each circumstance: a fire or an explosion. If the judgment is explosion, then consideration should be given to changing circumstances, process conditions, or process configuration, so that fire is the most likely consequence of ignition. If this is not an option, then it is essential that all potential ignition sources be eliminated and that no mobile ignition sources are allowed to enter the area.

### 6.2.2 Extinguishing Materials

Streams of water can be used to cool surrounding process equipment. Normally used foam is not appropriate for alcohol fires. The solvent properties of methanol cause normal fire fighting foam to degrade. Methanol fires must be attacked with alcohol-resistant foam.

Consider automated application of dry powder or carbon dioxide extinguishing material. If this is not practical, then consider automated application of fine water spray or fog. Methanol is 100% miscible in water by volume. Methanol water solutions and aerosols are flammable to 75% by volume composition of water. In other words, it takes between three and four times the volume of water as of methanol to extinguish a methanol fire. If water is chosen as the first response, the provisions must be made for preventing the methanol-water solution from spreading and carrying the fire into other parts of the facility.

## 6.3 Fire Ground Safety

Fire ground command must be vigilant to prevent fire teams from becoming surrounded by or partially immersed in methanol-water flammable solutions. Remember, the fact that methanol does not produce a visible flame in daytime hours can be a hidden hazard that may potentially become a life safety issue.

### 6.3.1 Confined Space Fires

Flammable methanol-water solutions must be prevented from entering confined spaces, such as sewers and drains. Non-burning, flammable methanol-water solutions must be prevented from contacting other ignition sources and hot equipment that could cause these solutions to ignite.

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<sup>5</sup> Refer to 2008 Emergency Response Guidebook for additional guidance.

Burning and non-burning, flammable methanol-water solutions must be kept away from other fuel sources, such as vehicles.

### **6.3.2 Fire Brigades**

Although the composition and capabilities of a fire brigade are outside the scope of this manual, this section touches on some of the key issues that fire brigades must keep in mind when responding to methanol fires.

#### **6.3.2.1 Outside Responders**

Most facilities relying on this manual will not have their own fire brigade and must rely on outside sources for fire fighting. This in no way compromises response effectiveness, provided there is provision for early detection, alarm, and rapid callout. Offsite responders must be aware that they are responding to a methanol fire, and must 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.

#### **6.3.2.2 Personal Protection Equipment**

Fire responders must wear the following minimum Personal Protection Equipment (PPE):

- Turnouts (fire resistant uniform) with helmet, gloves, and boots
- Full face, positive pressure SCBA
- Communication equipment

#### **6.3.2.3 Fire Responder Training**

Fire responders must be trained and equipped to fight methanol fires. In order to combat a methanol fire, it is essential that alcohol-resistant foam be used directly on the fire, and that water be used thoughtfully and intelligently. If too much water is used to cool surrounding equipment, and if water runoff mixes with burning methanol, then the dilution can create a so-called “running fire.”

Special provisions may be necessary to accommodate response by an outside party. This should be determined and accommodated by the facility prior to introducing methanol into the facility.

## 7 Emergency Response

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

Effective emergency response starts by developing an Emergency Preparedness Plan 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 Emergency Response Plan (ERP) includes regular drills and annual reviews to ensure that the plan is fully implemented and kept current.

### 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, 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; 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 a bermed, diked, or bunded, well-ventilated area that, if designed in accordance with NFPA 30, shall be capable of containing at least 110% of the volume of the largest methanol storage tank in the contained area. Following a leak inside the containment area, the 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.

Operation and maintenance procedures to prevent leaks and spills should include periodic visual inspections and nondestructive testing of the condition of tanks, valves, pipes, hoses, and dikes, as well as preventative maintenance of mechanical, electrical, and structural

components, and detection and alarms systems. The methanol handling, containment, and control system must be maintained so as to be continually “fit for continued service.” Written procedures for loading and transferring methanol, as well 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); a plastic (non-sparking) shovel to disperse the sorbent materials; yellow caution tape or other barrier devices to isolate the area; and a drum or container to place the collected waste material. Personal protection equipment for the responders should, at a minimum, include chemical splash goggles and face shield, butyl or nitrile gloves, rubber boots, chemical resistance coveralls, and 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 and first aid kits should be positioned nearby.

## 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, as well as surprise, drills at least once a year, or more often if possible.

### *Steps if a Spill Occurs*

The first steps to take if a spill occurs are:

1. Stop or reduce the release of material, if it can be done safely.
2. If there are noxious vapors, evacuate and notify supervisor or emergency coordinator.
3. Eliminate all sources of ignition.
4. Evacuate all persons not wearing protective equipment from the area of the spill or leak until cleanup is complete.
5. Notify supervisor or emergency coordinator of the spill.
6. Do not walk through spilled product. Avoid skin contact and inhalation.
7. Stay upwind and keep out of low-lying areas.
8. For large spills and fires, immediately call your fire department.

The following emergency equipment shall be present on site:

- Fire extinguishers
- Industrial first aid kit
- Portable eye-wash station, capable of supplying 15 minutes of water
- Emergency shower
- Ample supply of potable water for washing, as well as for drinking purposes
- Emergency communication devices, such as mobile phones, or two-way radios
- Vehicle suitable for emergency transport

## 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 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 paved 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 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.

Water spray can knock down methanol vapors but may not prevent ignition in closed spaces. AR-AFFF may be applied to the spill for vapor suppression and to diminish the fire hazard.

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 in order to prevent fires or explosions. 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.

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, 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 exposures to chemical and physical hazards, the spill area should be divided in three concentric circles centered on the Exclusion Zone (EZ) (hot zone), where the spill is contained. This is surrounded by a Contaminant Reduction Zone (CRZ), which includes the only access point for entry of response personnel and equipment, as well as the decontamination corridor for cleaning personnel and equipment exiting the hot zone. The Support Zone 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. See Chapter 8 Environmental Protection.

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 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 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 Commander, who will direct the response efforts.

Depending on the size and magnitude of the event, an Incident Command (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 exclusion zone 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 exclusion zone (hot zone). Intrinsically safe (explosive-proof) cellular telephones or two-way radios (for areas with no cellular phone service) should be available to all ER personnel.

## 8 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. Methanol in the atmosphere comes primarily from industrial sources. Some methanol is also distributed into water. 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.

### 8.1 Air Emissions

The relatively high vapor pressure of pure methanol causes it to volatilize readily to the air. If released below ground, it will concentrate in the soil gas within the pore spaces. In the atmosphere, methanol vapor reacts with nitrogen oxides (NO<sub>x</sub>) to generate methyl nitrate. As a volatile organic compound (VOC) methanol can contribute to formation of petrochemical smog. Methanol is broken down by sunlight and has a half-life of 17 to 18 days. It is also easily biodegradable. After 5 days, the estimated removal from the environment is 75%-82%, and up to 95% in 20 days.

According to the United States TRI, 175.23 million pounds (75,483 tonnes) of methanol were released on- and offsite from facilities in all industries in the U.S. in 2006. Approximately 82% of the emissions were released into the air, and less than 3% into surface waters. The largest emitter in 2006 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.

## 8.2 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 miscible in water, 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 (low water-octanol partition coefficient) and will not readily evaporate. 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 will readily biodegrade under a wide range of geochemical conditions.

In the event of a release to groundwater, methanol will eventually dissolve completely to a relatively low concentration. The initial dilution concentration will depend on the size of the spill area, the soil water moisture content, and the depth to the water table. After the initial source zone dilution and mixing, the final concentration of methanol will depend on the degree of dispersion of the plume in the particular environment.

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 soil, surface water, and groundwater quickly biodegrade under both aerobic and anaerobic conditions.

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 3000 mg/l, methanol is readily degraded in a wide range of subsurface conditions. However, methanol concentrations above 10000 mg/l can inhibit the microbial population and lower the degradation rate. The EPA has determined that methanol has a limited persistence in the environment.

## 8.3 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 3 (CCL-3) released by EPA in February 2008.

## 8.4 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 1000 mg/l and mostly above 10000 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 bug) 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 bioaccumulate significantly in animals higher up in the food chain.

Methanol's effects on mammals come 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 the release area and prevent exposure. However, methanol is a component of antifreeze, which can be highly toxic when consumed by household pets, such as dogs and cats.

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 tended to be lower than for humans, while the oral lethal doses were much higher for animals than for humans.

## 8.5 Climate Effects

More methanol is produced from natural gas than from any other source. A well-operated, existing methanol production plant using natural gas as feed stock has an efficiency of approximately 68%. The upper limit of efficiency of methanol production from this fossil feed stock consisting 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 or by electrical energy via hydroelectric or wind power with energy efficiencies of only 55%-60%, compared to the conventional natural gas manufacturing process.

In the 1990's, a typical methanol manufacturing plant would emit approximately 0.9-1.0 tonnes of carbon dioxide (CO<sub>2</sub>) for every tonne of methanol produced. In addition to the environmental concerns, large CO<sub>2</sub> emissions represent operational inefficiencies in a methanol plant, since the carbon emitted as CO<sub>2</sub> is not available for making methanol molecules. For these reasons, methanol plants began and continue to focus on efficiency improvements that reduce CO<sub>2</sub> emissions.

Through the implementation of efficiency improvements, and through replacing of older facilities with newer plants that use more efficient technologies, over the last decade methanol plants have been able to significantly reduce CO<sub>2</sub> emissions by up to 40%; some facilities report emissions as low as 0.54 tonnes of CO<sub>2</sub> per tonne of methanol produced. This is equivalent to emitting 3.8 lb of CO<sub>2</sub> per gallon (0.45 kg of CO<sub>2</sub> 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 CO<sub>2</sub> from biomass-derived fuels originates from the air and the emissions are not counted in an emission inventory or a life cycle analysis.

## 8.6 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 product, 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.

## 9 Product Stewardship

This chapter presents the Methanol Institute's product stewardship philosophy and outlines the major elements of a Product Stewardship Management System. A Fact Sheet called "Implementing Product Stewardship" provides additional information.

### 9.1 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. This role is consistent with the Responsible Care® Ethic [14], which is the guiding principle applied globally, and specifically ascribed to by several Methanol Institute member companies. It is a voluntary 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.

*According to the American Chemistry Council, Responsible Care companies have reduced environmental releases by 78% and achieved an employee safety record that is more than 5 times safer than the average of the United States manufacturing sector.*

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.

## 9.2 Product Stewardship Management System

Similar to safety and environmental management systems, such as ISO 14001 and 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:

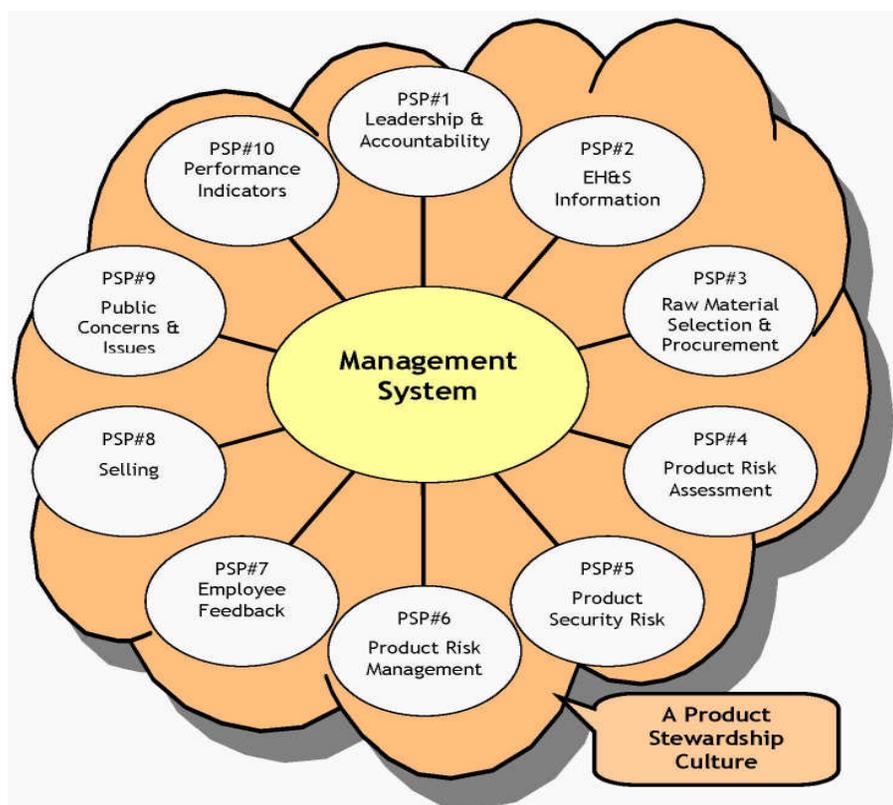
- Train, correct and reward people,
- Constantly seek a better way,
- Audit to make sure the system is working, and
- Track and report on performance, and use this feedback to drive improvement.

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.

## 9.3 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.



**Figure 4. The Product Stewardship Practices**

(Courtesy of the Canadian Chemical Producer's Association, Product Stewardship Guide, December 2003, with permission)

### 9.3.1 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; and
- 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.

### 9.3.2 PSP #2: Environmental, Health, and Safety Information

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. Collect information from available sources, including internal research and development, industry partners, academia, and government sources. 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](http://www.methanol.org) can be a useful tool for developing an EH&S information database.

### **9.3.3 PSP #3: Raw Material Selection and Procurement**

Assess how raw materials and purchased finished product impact the risk of the products prior to new purchases or on a recurring basis. Incorporate risk management and use of the most efficient materials and components in procurement decision-making processes; empower employees to cease supply agreements when risks are judged to be too high. Actively seek input and advice from suppliers on their product and risk management experiences.

### **9.3.4 PSP #4: Product Risk Assessment**

Designing and reformulating new products or applications presents an ideal opportunity to reduce risk to people and to create more environmentally friendly products. Take action wherever possible to lower product energy and material intensities across the life cycle. On a regular basis or on receipt of new information or changed regulations, reassess the risk to ensure the interpretation of the data is still appropriate.

### **9.3.5 PSP #5: Product Security**

Companies should establish a security plan that protects against the deliberate misuse of company products and raw materials as a result of terrorism, activism, vandalism, and malicious acts. The extent and rigor of actions with respect to terrorism will vary depending on the degree of potential risk, as determined by guidance from national, provincial, or local governments.

### **9.3.6 PSP #6: Risk Management**

Assess product risks prior to new sales, and cease sales when risks are judged to be too high, either on an individual customer basis or in the market as a whole. Take corrective action to reduce identified high-risk issues, if the assessed risks are not being managed appropriately or are not considered to be acceptable.

### **9.3.7 PSP #7: Employee Training and Education**

Include product stewardship education into existing employee training and education programs throughout the company, and provide additional training to employees who have been assigned product stewardship responsibilities. Promote feedback from employees on social, EH&S, and ethical concerns they may have.

### **9.3.8 PSP #8: Selling**

Promote two-way communication with downstream second parties, which will enable companies to understand market expectations for the product and social, EH&S, and ethical concerns. Provide balanced and accurate information on EH&S issues to second parties. Ensure 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. 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 your downstream distributors and customers is a good way to promote product stewardship. If you need additional copies, or would like the Methanol Institute to forward this manual directly to your downstream partners, contact us at [MI@methanol.org](mailto:MI@methanol.org).

### 9.3.9 PSP #9: Public Concerns and Issues

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

### 9.3.10 PSP #10: 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.

## 9.4 Responsible Distribution

Responsible Care is the guiding principle, as discussed. The concept of Responsible Distribution<sup>®</sup> specifically extends this principle as it relates to all aspects of the distribution of chemicals, chemical products, and chemical services. Like Responsible Care, some member companies of the Methanol Institute specifically ascribe and adhere to Responsible Distribution as well. Methanol is distributed globally, and awareness and adherence to the Codes of Practice for Responsible Distribution is important in terms of managing hazards and minimizing risks with the use of methanol. As presented by the Canadian Association of Chemical Distributors [13], Responsible Distribution generally requires the following:

- 1. Ensure general compliance.**

A company shall have written policies, standards, and procedures to govern all aspects of the responsible distribution of chemicals, chemical products, and chemical services.

- 2. Manage risk.**

A company shall have an active program to continually improve safety and environmental performance. Key elements of risk management include (but are not limited to): regular hazard and risk review of processes; establishing written standards and procedures for bulk and packaged storage and handling (e.g., spill containment and cleanup; product segregation; operation and maintenance of on-premise vehicles; selection, labeling, and management of containers and shipping vehicles, etc.); providing employees and contractors with information pertaining to the hazards and risk associated with distribution activities (e.g., handling chemicals, cleaning tanks and drums, transferring goods from one container to another; packaging, etc.).

- 3. Communicate information.**

The company shall have a program to communicate information to employees, customers, contractors, sub-distributors, and suppliers.

- 4. Comply with legal requirements.**

A company shall have a program to comply with legal requirements and to ensure that employees work in accordance with the law.

- 5. Interact with interested parties.**

A company shall implement a program to assist and work with interested parties (employees, organizations, and governmental and community bodies) to identify issues and set standards for the continual improvement of chemical distribution.

**6. Manage sub-distributors.**

A company may have an oral or written contract outlining the terms and conditions for the distribution and/or sale of the product where there is no change to the product, package, and/or labeling, as originally supplied by the member company. The member company shall implement a program to educate, assist, and assess all sub-distributors.

**7. Manage suppliers.**

A company shall implement a program to educate, assist, assess, and approve suppliers of chemicals, chemical products, and chemical services to encourage compliance with this Code of Practice.

## 10 Risk Communication

### 10.1 What Is Risk Communication?

When one first considers 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 well, 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. The focus of this chapter is to introduce the tools and principles for effectively communicating information about risks, as well as hazards, about the industry in non-crisis situations.

It is important to keep in mind two other key definitions in the context of risk communication in non-crisis situations, 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.

## 10.2 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, or 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.

## 10.3 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 three basic steps to effective risk communication:

### 1. Determine the communication goal.

Communication goals about a particular methanol business, work location, new technology, etc. 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 assume 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.**

Always take the time to make a clear and concise message, using the most appropriate means of delivery for the audience intended to receive the message. It sounds simple, but the importance of planning the message and understanding the audience cannot be overstated. Whenever possible, get input from representatives of the key audience to solicit feedback and to better understand their concerns in order to ensure the message achieves the primary objectives of informing and persuading your audience. 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 (e.g., whether training should be provided in a language other than or in addition to English).

**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.

## 10.4 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 one hundred American football fields 14 feet (4.25 m) deep,” are much more meaningful to average listeners than talking about 250000 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 actually 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.

## 10.5 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 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.

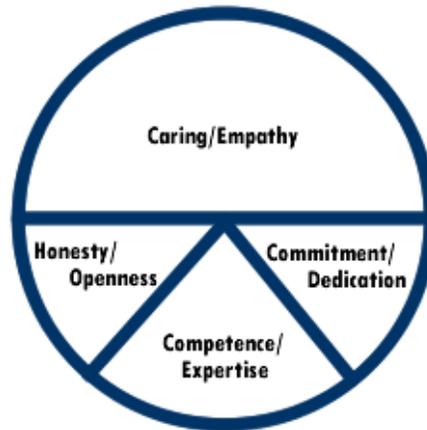
Risks Perceived To...	Are More Accepted Than...
Be voluntary	Risks perceived as being imposed
Be under an individual’s control	Risks perceived to be controlled by others
Have clear benefits	Risks perceived to have little or no benefit
Be distributed fairly	Risks perceived to be unfairly distributed
Be natural	Risks perceived to be manmade
Be generated 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

## 10.6 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 factors in

assessing trust and credibility are: empathy and caring, competence and expertise, honesty and openness, and dedication and commitment.

Trust and credibility are central to effective communication about topics of high concern. 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!

## 10.7 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.

# 11 Glossary

## 11.1 Terms, Abbreviations and Acronyms

### -A-

**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.

**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.

**alkane(s)** 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 psi.

**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.

**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 are exposed to direct flames of a fire. Contact of fire 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 relieve 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 1900 liters) per minute is required to cool the tank.

**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 1055 Joules.

**bunded** An enclosure to contain either a reclaimed area, or a chemical or other hazardous substance if it spills.

**-C-**

**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.

**carcinogen** A substance that causes cancer; a substance or agent capable of causing producing cancer in mammals.

**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).

**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-3** United States EPA's Contaminant Candidate List 3, released in February 2008. See *Contaminant Candidate List*.

**C or ceiling** The concentration value of an airborne substance that is not to be exceeded during any part of the working exposure.

**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).

**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 point temperatures less than 73°F (22.78°C) and boiling point temperatures less than 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 less than 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 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.

**coma** A profound state of unconsciousness in 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.

**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.

**corrosive** (adj) a substance as 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.

## -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 explosion that burns furiously and persistently. Vapor cloud explosions are typically deflagrations, not detonations. Strictly speaking, most deflagrations are not explosions, but are very fast fires. 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.

**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 which 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.

**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.

**Drinking Water Advisory** A non-regulatory concentration of a contaminant in water that is likely to be without adverse effects on health and aesthetics.

## **-E-**

**EH&S** Environmental Health and Safety.

**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.

**EZ** Exclusion Zone; also known as “hot zone.”

## **-F-**

**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.

**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 and 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.

**functional groups** Structural molecular fragments of organic compounds that are found in all members of a given class of compounds and which are centrally involved in the chemical reaction of a chemical class.

## -G-

**gal** gallon; a commonly used abbreviation for an English (Imperial) unit of volume; also called the Imperial gallon, it is the volume that exactly contains 10.0 lb of water at standard temperature and pressure.

**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.

**g/cm<sup>3</sup>** 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/m<sup>3</sup>** grams per cubic meter; a metric unit of concentration measure (weight/volume) expressed in units of grams of weight per cubic meter volume.

**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-

**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.

## -I-

**IARC** The International Agency for Research on Cancer, a scientific group that classifies chemicals according to their cancer-causing potential.

**IC** Incident Command.

**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

**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.

## -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: 1000 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-**

**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 is required as in Level A protection but 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.

**-M-**

**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.

**methanol (methyl alcohol, wood alcohol)** Methanol (CH<sub>3</sub>OH) 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 which 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/m<sup>3</sup>** a metric unit of concentration measure (weight/volume) expressed in units of milligrams of weight per cubic meter of volume.

**MI** Methanol Institute.

**MIE** Minimum Ignition Energy.

**miscible** A liquid or gas that will evenly dissolve in another liquid or gas; 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.

**M.P.** melting point; a commonly used abbreviation for the melting point temperature of a solid material.

**MSDS** Material Safety Data Sheet.

**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-**

**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/canutec/en/GUIDE/ERGO/ergo.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, *Flammable and Combustible Liquid Code*.

**NFPA #30A** A National Fire Protection Association, *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.

**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).

**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.

## -P-

**partition n 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.

**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.

**producer gas (air gas)** A mixture of carbon monoxide (CO) and nitrogen (N<sub>2</sub>) made by passing air over very hot carbon. Usually some steam is added to the air and the mixture contains hydrogen (H<sub>2</sub>). Producer gas is used as a fuel in some industrial processes.

**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 Valves.

## **-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

**running fires(s) [running liquid fire(s)]** 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.

**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.

**STEL** Short-Term Exposure Limit; pertains to inhalation exposure of a toxic aerosol.

**-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.

**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 are usually expressed as parts per million (ppm) or milligrams per cubic meter ( $\text{mg}/\text{m}^3$ ). 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 2000 pounds.

**tonne** The metric unit of weight (mass) equal to 1000 kilograms.

**tote** A portable vessel widely used for containment during shipping and storage of relatively small amounts of bulk liquid methanol. 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. Dimensions of the tote are 42 inches by 48 inches by 48 inches (approximately 1.1 m by 1.2 m by 1.2 m). Tare weight (weight empty) is 510 lb (231 kg); gross weight full is 2800 lb (1270 kg).

**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.

**TWA** Time Weighted Average.

**-U-**

**UEL** Upper Explosive Limit (upper flammable 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. (See *flammable range*, LEL.)

**UFC** An acronym for Uniform Fire Code of the United States (NFPA 1).

**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.

**U.S. gal** United States or U.S. gallon of liquid. A U.S. gallon is the volume that contains exactly 8.34 lb of water at standard temperature and pressure.

**-V-**

**Vol% or v/v%** Volume percent; a measure of concentration that relies on relative volume rather than relative weight (mass).

**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.

**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.

**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-**

**WMO** World Meteorological Organization.

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# A Process Safety Information

## A.1 Technology of the Process

The following information items should be collected and reviewed as process safety information that pertains to the technology of the process.

Process description	Operating parameter limits
<ul style="list-style-type: none"> <li>▪ Feed materials</li> </ul>	<ul style="list-style-type: none"> <li>▪ Pressure, temperature, flow rate</li> </ul>
<ul style="list-style-type: none"> <li>▪ Chemistry</li> </ul>	<ul style="list-style-type: none"> <li>▪ Maximum and minimum safe operating limits</li> </ul>
<ul style="list-style-type: none"> <li>▪ Chemical kinetics (if relevant)</li> </ul>	<ul style="list-style-type: none"> <li>▪ Maximum time at maximum and minimum limits</li> </ul>
<ul style="list-style-type: none"> <li>▪ Intermediate products</li> </ul>	
<ul style="list-style-type: none"> <li>▪ Reactants / catalysts</li> </ul>	
<ul style="list-style-type: none"> <li>▪ Utility requirements (steam, natural gas, merchant gases, special heat transfer media, etc.)</li> </ul>	
<ul style="list-style-type: none"> <li>▪ Special circumstances (very high pressure, very high temperature, cryogenic temperatures, etc.)</li> </ul>	
<ul style="list-style-type: none"> <li>▪ Potential runaway reactions</li> </ul>	
<b>Process Flow Diagram</b>	
<ul style="list-style-type: none"> <li>▪ Major equipment items (name and item number)</li> </ul>	
<ul style="list-style-type: none"> <li>▪ Heat and material balance</li> </ul>	
<ul style="list-style-type: none"> <li>▪ Typical operating parameters</li> </ul>	
<ul style="list-style-type: none"> <li>▪ Special alloys</li> </ul>	
<ul style="list-style-type: none"> <li>▪ Utility requirements</li> </ul>	

## A.2 Equipment

The following information items should be collected and reviewed as process safety information that pertains to system equipment.

Process unit description	Carseal / chainlocked valve list
<ul style="list-style-type: none"> <li>▪ Name of process unit</li> </ul>	<ul style="list-style-type: none"> <li>▪ Valve number</li> </ul>
<ul style="list-style-type: none"> <li>▪ Block diagram of important unit operations</li> </ul>	<ul style="list-style-type: none"> <li>▪ Valve description</li> </ul>
<ul style="list-style-type: none"> <li>▪ Feed material, intermediates, products</li> </ul>	<ul style="list-style-type: none"> <li>▪ Scenario safe-guarded against</li> </ul>
<ul style="list-style-type: none"> <li>▪ Chemistry</li> </ul>	<ul style="list-style-type: none"> <li>▪ Normal position</li> </ul>
<ul style="list-style-type: none"> <li>▪ Recycle strategy for reprocessing off-spec material</li> </ul>	<ul style="list-style-type: none"> <li>▪ Circumstances for changing position</li> </ul>
Piping and instrument diagrams	Scenario protected against
Piping specifications	<ul style="list-style-type: none"> <li>▪ Consequences of opening or closing</li> </ul>
List of item-numbered equipment	Special operating conditions or regulatory restrictions
Equipment name	Piping inspection data
Equipment tag number	Pressure vessel inspection data
Equipment nameplate capacity (vol, wt, processing rate)	Plot plan
Equipment operating conditions	Electrical single line diagrams
Maximum / minimum safe operating limits	Programmable logic controller (PLC) logic
Manufacturer	PSV inspection/test/rebuild records
Date placed in service	Area electrical classification
Anticipated life	Location of electrical substations
Control parameter safe operating limits	Location of electrical switch gear
Equipment design / fabrication codes	Utility requirements
Maintenance, testing, and inspection	Operating procedures
Maintenance procedures	Safety systems (firewater, detectors, etc.)

## B Properties of Methanol / Methyl Alcohol

### B.1 Physical Properties

#### CH<sub>3</sub>OH

- 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/m<sup>3</sup>; 1 mg/m<sup>3</sup> = 0.76 ppm

#### B.1.1 Solid

CH<sub>3</sub>OH<sub>(solid)</sub> T < -98°C (-144°F); P = 1 atm (14.7 psia)

#### B.1.2 Liquid

CH<sub>3</sub>OH<sub>(liquid)</sub> -98°C (-144°F) < T < 65°C (149°F); 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 (68°F)
- 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 air)	166 g/m <sup>3</sup>
➤ 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)	126 mm Hg @ 25°C (77°F)
➤ Vapor pressure @ PTotal=(14.7 psia)	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

## 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)
10	-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** $\text{CH}_3\text{OH}_{(\text{vapor})}$  $65^\circ\text{C} (149^\circ\text{F}) < T; P = 1 \text{ atm} (14.7 \text{ psia})$ 

- Relative density of vapor saturated air (air = 1):
  - 1.01 @ 20°C (68°F)
  - 1.02 @ 30°C (86°F)
- Density of vapor relative to air (air = 1.0): 1.1
- Viscosity
  - 9.68  $\mu\text{Pa s}$  @ 25°C (77°F)
  - 13.2  $\mu\text{Pa s}$  @ 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<sup>3</sup>/kg-mol
- Critical density 0.2715 g/cm<sup>3</sup>
- Critical compressibility factor 0.224
- Accentric factor 0.556
- Henry's Law Constant  $4.55 \times 10^{-6} \text{ atm}\cdot\text{m}^3/\text{g}\cdot\text{mol}$
- Airborne Saturation Concentration 166 g/m<sup>3</sup>
- Airborne Concentration Conversion:
  - 1 mg/ml = 764 ppm @ 25°C (77°F) at 1 atm, 14.7 psia, 760 mm Hg
  - 1 ppm = 1.31 mg/m<sup>3</sup> @ 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 <sub>3</sub> OH                                    |
| ➤ Molecular weight                                 | 32.04 grams/mole                                      |
| ➤ Elemental composition by weight                  |   |
| ○ Oxygen   | 50.0 wt%  |
| ○ Carbon   | 37.5 wt%  |
| ○ Hydrogen   | 12.5 wt%  |
| ➤ Solubility CH <sub>3</sub> OH (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. [R. Manwaring, *et al.*, *Chem. Ind.*, 1973, p. 172].
- 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 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 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, but 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, and 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: but nevertheless deserving of 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 even 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 three hundred 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.
- Many resins, nylons, and rubbers, such as neoprene, nitrile (Buna-N), and ethylene propylene (EPDM), are suitable, though some are more 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, but 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.
- First time hose and piping must be washed with water and then methanol to ensure that contaminants are removed before being placed in service.
- Methanol is one of the few specialized environments which 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	wt % Water Sustained Exposure
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

Intermittent exposure = short term non continuous exposure

Sustained exposure = long term continuous exposure

## B.4 Structure and Properties

- Index of refraction, nD 1.328 @ 20°C (68°F)
- Dielectric constant,  $\epsilon_r$  32.66 @ 20°C (68°F)
- Bond angle all 109.5°
- Magnetic susceptibility  $5.3 \times 10^{-7}$  cm<sup>3</sup>/g

## 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°C (60.1°F) open cup TOC method
➤ Auto-ignition T at P = 1 atm (14.7 psia)	385°C (725°C) <sup>6</sup>
➤ Explosive Limits in air at ambient T and P	6-36 vol% <sup>7, 8</sup>
➤ Explosive Range	30 vol%
➤ Flame	non-luminous blue flame
➤	not visible to naked eye in daylight
➤ Flammable Methanol-Water Mixtures:	down to 21 vol% (25 wt%) methanol
➤ Stoichiometric air/fuel weight ratio	6.45
➤ CH <sub>3</sub> OH(vapor) in stoichiometric air/vapor mixture	12.3 vol%

### B.5.1 Fire Extinguishing Media

- Carbon dioxide
- Dry chemical
- Alcohol resistant foam- Aqueous Film Forming Foam (AR-AFFF) with 6% proportioning with water
- Water mist or fog<sup>9</sup>

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<sup>6</sup> Methanex Corporation & Terra Industries among others indicate auto-ignition temperature as 464°C (867°F).

<sup>7</sup> 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.

<sup>8</sup> 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 %.

<sup>9</sup> 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.

## B.6 Thermodynamic Properties [58]

➤ 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 ( $S^\circ_{liquid}$ )	127.19 J/mol K
➤ Standard Entropy of Solid 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 ( $\Delta H_{trs, X_{line} \rightarrow L}$ )	3.159 kJ/mol @ 175.4 K
➤ Specific heat	2.51 kJ/kg K; 0.6 Btu/lb-°F
➤ Heat Capacity Ratio, $\gamma = C_p/C_v$	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



## 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)

Regulation / Code	Relevant Section or Part
	Section 1910.1200 – Hazard Communication
Environmental Regulations -- 40 CFR	Part 61 – National Emissions Standards for Hazardous Air Pollutants
	Part 68 – Clean Air Act/Accidental Releases
	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
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
	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

Regulation / Code	Relevant Section or Part
	Part 192 – Transportation of Natural and Other Gas by Pipeline: Minimum Federal Safety Standards
	Part 195 – Transportation of Hazardous Liquids by Pipeline
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
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 primary international regulations, standards, and guidelines 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.

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)
	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, Authorisation and Restriction of Chemicals (REACH) (EC/2006/1907)
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)

Authority	Topic
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)
International Standards Organization	ISO 9001:2000 – Quality Management Systems

## C.3 Hazardous Material and Health & Safety Information

Hazardous Material Information		Health & Safety Information	
<b>EINECS No. (EU)</b>	200-659-6	<b>Exposure Limits</b>	
<b>UN Number</b>	UN 1230	TLV-TWA	262 mg/m <sup>3</sup> (200 ppm)
<b>Dangerous Goods Classification</b>		TLV-STEL	328 mg/m <sup>3</sup> (250 ppm)
o Primary Classification	3		
o Subsidiary Classification	6.1	OES-LTEL	266 mg/m <sup>3</sup> (200 ppm)
o Packing Group	PG II	OES-STEL	333 mg/m <sup>3</sup> (250 ppm)
<b>ADR Classification (transport by road)</b>		MAK	270 mg/m <sup>3</sup> (200 ppm)
o Class	3	MAC-TGG 8 h	260 mg/m <sup>3</sup>
o Packing	II	VME-8 h	260 mg/m <sup>3</sup> (200 ppm)
o Danger Label Tanks	3+6.1	VLE-15	1,300 mg/m <sup>3</sup> (1000 ppm)
o Danger Label Packages	3+6.1	GWBB-8 h	266 mg/m <sup>3</sup> (200 ppm)
<b>RID Classification (transport by rail)</b>		GWK-15 min.	333 mg/m <sup>3</sup> 250 ppm
o Class	3	EC	260 mg/m <sup>3</sup> (200 ppm)
o Packing	II		
o Danger Label Tanks	3+6.1	NFPA Classification	1B Flammable Liquid
o Danger Label Packages	3+6.1	NFPA Hazard Rating	
<b>ADNR Classification (transport by inland waterways)</b>		o Health	1
o Class	3	o Flammability	3
o Packing	II	o Reactivity	0
o Danger Label Tanks	3+6.1		
o Danger Label Packages	3+6.1		
<b>IMDG Classification (maritime transport)</b>			
o Class	3		
o Sub Risks	6.1		
o Packing	II		
o MFAG	19		
<b>ICAO Classification (air transport)</b>			
Class	3		
Sub Risks	6.1		
Packing	II		