METHANOL INSTITUTE

Methanol Safe Handling Manual

January, 2013

www.methanol.org

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Chapter

1

1 Introduction to the Manual

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

1.1 Purpose of the Manual

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

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

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

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

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

In addition to the manual, we have Fact Sheets available on a number of topics related to methanol safe handling. These include methanol use as fuel, emergency response, product stewardship, and health effects.

1.2 The Methanol Value Chain

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

Natural sources of methanol include volcanic gases, vegetation, microbes, and insects, and it is also manufactured from a variety of inorganic and organic sources. Most methanol is produced from natural gas in large, integrated chemical manufacturing plants located in regions where hydrocarbon feed stocks are plentiful, such as the Persian Gulf, the Caribbean, South America, Africa, and Russia. In China, in particular, most methanol is produced from coal. Although methanol is consumed throughout the world, the largest users are in regions that have high industrial development, such as Western Europe, North America, and Asia (Japan, China, Taiwan, and South Korea). World consumption in 2010 was an estimated 45,198,000 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 that generate heat to fuel other reactions.

1.3 Methanol Institute Product Stewardship Policy

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

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

1.4 Methanol Institute Contact Information

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

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1.5 About the Authors

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1.6 Disclaimer

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

Chapter

2

2 Methanol General Information

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

2.1 What Is Methanol?

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

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

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

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

Five overriding considerations are important when handling methanol:

1. Methanol is a flammable, easily ignited liquid that burns and sometimes explodes in air.
2. The molecular weight of methanol vapor is marginally greater (denser) than that of air (32 versus 28 grams per mole). As a result, and depending on the circumstances of a release or spill, methanol liquid will pool and vapor may migrate near the ground and collect in confined spaces and low-lying areas. It is expected that methanol vapor, being near neutral buoyancy, will dissipate readily from ventilated locations. Do not expect it to dissipate from non-ventilated locations such as sewers and enclosed spaces. If ignited, methanol vapor can flash back to its source.
3. In certain specific circumstances, methanol vapor may explode rather than burn on ignition. Methanol containers are subject to Boiling Liquid Expanding Vapor Explosion (BLEVE) when heated externally.

4. Methanol is a toxin; ingestion of a small amount (between one and two ounces, approximately 30 to 60 milliliters) may cause death; lesser amounts are known to cause irreversible blindness. Do not swallow methanol liquid, do not breathe methanol vapor, do not walk in pooled liquid, and do not allow vapor or liquid to contact skin. Methanol absorbs through the skin and other tissues directly into the blood stream.
5. Methanol is totally miscible in water and retains its flammability even at very high concentrations of water. A 75v% water and 25v% methanol solution is considered to be a flammable liquid. This has important consequences for firefighting.[1] Methanol is a chemical solvent, which has important implications for materials selection and also for firefighting.

The methanol molecule contains a single carbon, and is thereby the simplest alcohol that can be derived from normal, saturated hydrocarbons – namely, methane (CH_4), ethane (C_2H_6), and propane (C_3H_8). 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_3OH), ethanol (C_2H_5OH), and propanol (C_3H_5OH) – have similar physical and chemical properties, but very different toxicity hazards. As the number of carbon atoms in alcohol molecules increases, the length of the straight carbon chain increases, the molecular weight of the alcohol molecule increases, freezing point temperature decreases, and boiling point temperature increases.

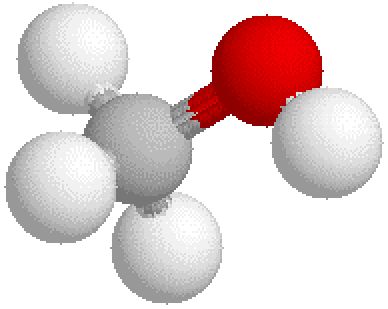

Figure 1. Methanol CH_3OH

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

Table 1. Three Representative Alkane-Derived Alcohols

Molecular Structure	Systematic Name	Common Name	Liquid Freezing Point	Liquid Boiling Point
CH_3OH	Methanol	Methyl alcohol; wood alcohol[2]	-144°F (-97°C)	149°F (65°C)

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

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

CH_3CH_2OH	Ethanol	Ethyl alcohol; grain alcohol[3]	-175°F (-115°C)	172.4°F (78°C)
$(CH_3)_2CHOH$	2-Propanol (Isopropanol)	Isopropyl alcohol	-194.8°F (-126°C)	206.6°F (97°C)

If mishandled, methanol poses hazards to life safety. It is flammable, toxic, reactive with alkali metals and strong oxidants, and 100% miscible in water. These properties necessitate specific measures in handling 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. As a result of the world-wide economic downturn, supply and demand have remained more or less flat; however, a number of large plants have been constructed and brought online in late 2009 and the first quarter of 2010, which has added 4.0 million tonnes of natural-gas-derived methanol.

Table 2. Summary of Estimated Global Methanol Capacity Additions in 2010 (Excluding China) in Tonnes per Year

Region	Import	Added Capacity	Total Capacity	Production	Export
Caribbean	0	0	8,153	7,541	7012
Middle East/Persian Gulf (Brunei=0.9; Egypt=1.3; Oman=1.0)	1	3.2	8,063.2	7,759.2	5,931.2
South America (Chile & Argentina; Venezuela=0.9)	0	0.9	4,281	3,567	3,332
Africa	0	0	1758	1475	1447
New Zealand	1	0	530	404	267
North America (U.S. & Canada)	7,112	0	1,715	1,606	514
Western Europe	8,062	0	3,310	3,176	3,119
Asia (Japan, China, Taiwan, & S. Korea)	5,427	0	9,931	7,623	206

2.2.1 Methanol Manufacture

Methanol producers are typically located in regions of the world that produce an excess of natural gas, areas that mine large amounts of coal, and/or industrialized countries that can access natural gas in large quantity at relatively low shipping cost. Natural gas supplies are

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

increasing as a result of new drilling and hydro-fracturing technology, which allow development of previously unrecognized low-cost reserves. These additional reserves, when added to conventional reserves, are creating a shift in the availability of natural gas. This has resulted in construction of gas to liquid processing plants in Asia and the Middle East. In the United Arab Emirates, the liquid product is a high grade of kerosene, which is being used as a replacement for petroleum-derived jet fuel.

Another market trend is caused by the cost of manufacturing methanol from natural gas versus other sources such as coal. Because it is less expensive to manufacture methanol from gas than from coal, high-cost coal-to-methanol producers are curtailing production, particularly in China, in order to take advantage of lower-cost imported methanol (Saudi Arabia, New Zealand, Malaysia, and Indonesia).

As Table 2 shows, more regions export than import, and production lags behind capacity. Prior to the recent economic downturn, North America exported about 33% of what it produced. Consumption was something over 8 million tonnes in 2006, but dropped substantially by 2010. Western Europe exports most of its production; consumption was about 5 million tonnes but has also decreased. Consumption in Western Europe and North America has decreased as a result of the slowdown in new construction and production of automobiles. 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 annual average demand of around 10 million tonnes. This appears to mark a turning point in global supply and demand. It also marks a point at which the price of methanol began closely tracking the cost of crude oil. At $310/tonne, the price of methanol is approximately equivalent to the cost of crude at $80/bbl of oil equivalent.

Table 3: MMSA Global Methanol Supply and Demand Balance, 2005-2010E

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	2005	2006	2007	2008	2009	2010E	AAGR 05-10E
Methanol supply							
Name plate capacity	43,349	46,061	52,089	59,117	65,475	73,104	11.0
Adjustments	--	--	--	--	--	(1,250)	
Total capacity	43,349	46,061	52,089	59,117	65,475	71,854	10.6
Macro operating rate	82.5%	78.7%	74.9%	68.1%	64.3%	62.9%	
Production	35,773	36,267	39,034	40276	42,106	45,198	4.8
Imports	18,943	19,387	19,279	20,231	22,503	22,331	3.3
Total supply	54,716	55,654	58,313	60,507	64,609	67,528	
Methanol demand							
Formaldehyde	13,714	14,481	15,086	15,160	14,193	14,800	1.5
Acetic Acid	3,588	3,849	4,003	4,278	4,244	4,585	5.0
Methyl Tertiary Butyl Ether (MTBE)	8,671	7,056	7,094	7,001	6,738	6,943	-4.3
Methyl Methacrylate	1,201	1,249	1,329	1,328	1,261	1,322	1.9
Dimethyl terephthalate (DMT)	603	537	488	487	467	468	-4.9
Methanethiol (Methyl Mercaptan)	373	394	416	432	425	439	3.3
Methylamines	1,065	1,099	1,140	1,167	1,132	1,201	2.4
Methyl Chloride (Chloromethane)	1,525	1,572	1,686	1,713	1,692	1,764	3.0
Alternative fuels							
Gasoline blending & combustion	1,075	2,244	2,799	3,091	4,903	5,775	40.0
Biodiesel	264	410	817	909	832	998	30.5
DME	176	327	932	1,824	3,338	3,428	81.2
Fuel cells	5	5	7	10	5	5	0.5
Methanol-to-Olefins	0	3	5	7	7	302	0.0
Others	3,499	3,059	3,169	3,038	2,834	3,167	-2
Total	35,759	55,673	58,251	40,445	42,072	45,198	4.8
Exports	18,943	19,387	19,279	20,231	22,503	22,331	3.3
Total country demand	54,701	55,673	58,251	60,676	64,575	67,528	
Net	14	(19)	62	(168)	34	--	

The global methanol market in 2010 and the foreseeable future will likely be driven by supply and demand in China as China's high-cost, coal-based sources go offline, and by energy-related applications in the transportation sector and the power sector. Methanol is experiencing increased application as a replacement for gasoline in China in taxis and public transportation such as buses. This is beginning to occur also for personal automobiles, though more slowly.

Demand for fuel oxygenates such as Methyl Tertiary Butyl Ether (MTBE) and TAME remains flat, as does demand for formaldehyde and acetic acid. Increases in demand appear to be coming from increased use of methanol as a gasoline replacement, for biodiesel, and for Dimethyl Ether (DME), a liquid fuel similar to Liquefied Petroleum Gas (LPG).

Increased demand for DME is most likely due to use in the power generation sector, use as a blend material with LPG, and use as an alternative to diesel fuel.

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

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

2.2.2 Sustainable Production

Sustainable production of methanol derives from three specific chemical characteristics:

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

In small amounts and low concentrations, methanol is a naturally occurring material. It is a natural byproduct of most bacterial-driven bio-decomposition cycles. Chemical plants have the ability to replicate and accelerate these natural processes. As a result, methanol, or more appropriately, bio-methanol, can be manufactured from natural materials even more easily and efficiently than ethanol, the next-larger alcohol molecule, and from less-expensive non-food-stuff feedstock.

2.2.2.1 Recycling

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

2.2.2.2 Reuse

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

2.2.2.3 Waste Management

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

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

2.3 Uses of Methanol

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

During the first quarter of 2008, crude oil prices spiked over $140 U.S. per barrel. At the same time, natural gas (methane) prices (in the United States in particular) lagged behind crude oil prices. Use of food crops to produce ethanol fuel has been blamed in part for driving supply and demand of some staple food items. These circumstances provide an increased incentive to use methanol as a replacement for ethanol as a direct additive to motor fuel to reduce air emissions, and perhaps eventually as an alternate for gasoline in automobiles.
This may well become a major factor in supply and demand in both developed and developing countries, particularly for Asia.

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

Globally, formaldehyde manufacture has accounted for about 40% of methanol demand for production of urea-formaldehyde and phenol-formaldehyde resins, glues, and adhesives. These are used extensively as bonding agents in particleboard, plywood, and fibrous wood panels. Demand for these building materials has decreased sharply due to a downturn in new construction. At present, the distribution of methanol demand is changing radically. This is expected to continue during the next decade.

2.3.1 Chemical Intermediates

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

→ Formaldehyde → Resins
→ Methyl Amines
→ Methyl Chlorides → Silicones
→ DMT
METHANOL → Methyl Methacrylates

METHANOL → Acetic Acid → vinyl acetate (50% of acetic acid production)
→ Acetic Acid → dimethyl terephthalate/terephthalic acid
→ Acetic Acid → acetate esters
→ Acetic Acid → cellulose acetate
→ Acetic Acid → other acetic anhydride uses
→ Acetic Acid → textiles

Figure 2. Methanol as Intermediate Chemical Feedstock

2.3.2 Fuel Applications

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

Methanol was recognized at that time as a potential replacement for crude-oil-derived gasoline. During the intervening years between the 1970 and the recent 2010 price spike, various agencies and organizations have assessed the hazards, challenges, and benefits of using methanol as a motor fuel. A study by the United States Environmental Protection Agency (EPA) [63] concludes that methanol is a safer motor fuel than gasoline. Other studies have concluded that hazards posed by the motoring public’s use of methanol are greater than those of gasoline. An important factor often not considered in the discussion is the proportion of methanol used in a fuel blend. Most current blends envisioned for vehicle fuel range from 5-15% up to 70-85% methanol content, not 100% pure methanol. As methanol becomes widely available as a motor fuel, these differences will need to be resolved.

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

The automobile racing industry has considerable hands-on experience in selecting and using motor fuels, including various fuel grade 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 that used in 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:

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

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

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

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

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

2.3.3 Biodiesel Fuel Production

Biodiesel is diesel fuel that has been sourced from biodegradable materials, specifically vegetable waste, or rendered oils, rather than from petroleum distillate.

There are many reasons for making biodiesel, which range from saving money to “going green.” Diesel fuel prices are continuing to increase globally, and have recently approached $5.00 per gallon in some areas of the United States. Biodiesel allows recycling of waste material and replacing a consumable resource with a renewable resource. It also diversifies the fuel supply base away from solely petroleum-based fuels. Regardless of the motivation, biodiesel production involves using neat (100% pure) alcohol, typically either methanol or ethanol.

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

When methanol is used to process bio-waste material into biodiesel, it produces a hydrocarbon fuel with properties similar to diesel fuel. Conversion can be accomplished on scales that range from 30-gallon capacity trash-can-sized batches, to continuous processes operated intermittently, to continuously operated plants with capacities ranging from 4 million to 100 million gallons (15000 to 378000 cubic meters) per year.

Typically, people using methanol to produce biodiesel in small-scale batch applications are not trained chemists. Operators are likely unaware of the hazards and regulatory compliance necessary to manufacture fuel safely and legally. These individuals may not be trained or experienced in handling concentrated hazardous chemicals such as lye (sodium/potassium hydroxide, Na/KOH) and methanol.

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

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

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

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

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

A variety of precautions must be observed:

- Methanol must be stored in a dedicated location, where it is protected from heat and ignition sources. All electrical systems must be fully enclosed and explosion proof. In order to prevent the methanol from absorbing moisture, it must be stored in a sealed container. If the container is sealed, there should be an allowance for thermal expansion; otherwise, large changes in temperature may cause the methanol to expand and rupture the container.
- Methanol must be stored in a bermed, diked or bunded, well-ventilated area, which, if designed in accordance with NFPA 30 [45], shall be capable of containing at least 110% of the volume of the largest methanol storage tank in the contained area. Best practice dictates considerably more than 110%. Following a leak inside the containment area, the resulting methanol pool should be completely covered with alcohol-resistant foam. If the containment area is adequately sized, the methanol spill can be diluted with at least four parts water to one part methanol to reduce the risk of fire. Insufficient freeboard within the bermed area can result in overflow of the berm and a so-called “running fire.” Running fires are difficult to control.
- It is desirable to preheat the waste oil prior to reaction with methoxide. This must be done carefully to prevent oil spattering and accidental ignition when the methanol hydroxide reactant is added.
- Care must be taken in handling methanol, adding hydroxide, mixing hydroxide, and then introducing the methoxide into the waste oil.
- Temperature control throughout the process is critical to safe and efficient operation. If the temperature rises too high, and agitation is too vigorous, then fire and/or explosion are possible. If the temperature is too low and agitation too gentle, then the reaction will not go to completion.
- The potential for spills is consistent throughout the process. A closed reactor, whether batch or continuous, is preferable to a reactor that is open to the atmosphere.

2.4 Emerging Uses of Methanol

Previously mentioned applications account for most of the world’s current methanol consumption. Although consumption has leveled off during the recent world economic downturn, methanol’s use is anticipated to increase due to new applications in emerging technologies and increased demand in developing countries during the 2010 to 2020 time frame.

Four of these new uses are discussed here:

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

The current spike in the price of fuels is forcing drivers to alter 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.

2.4.1 Wastewater Denitrification

Wastewater effluent from municipal waste treatment plants characteristically contains high levels of nitrogen in the form of nitrates and ammoniated compounds (NH_3 – anhydrous ammonia, NH_4OH – ammonium hydroxide, etc.). Nitrogen is an excellent fertilizer, which enhances plant growth in soils and water. Overactive plant growth may damage ecosystems if the effluent is released into natural waters, such as streams, rivers, lakes, and even the ocean. Methanol denitrification is a simple, effective, and comparatively inexpensive method of removing excess nitrogen and inhibiting plant growth.

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

Denitrification is a natural process, which occurs within surface water, ground water, and near surface soils. Within the context of wastewater effluent conditioning, denitrification is a liquid phase biochemical reduction reaction which is facilitated by the presence of methanol. Under anaerobic (oxygen free) conditions, microorganisms such as bacteria convert nitrogen-containing compounds, (for example, ammonium (NH_4), ammonia (NH_3), nitrates (NO_3^{-1}), nitrites (NO_2^{-1}), and proteinaceous organic nitrogen) into elemental nitrogen (N_2). The overall chemical reaction is

$$6\ NO_3^{-1} + 5\ CH_3OH_{(l)} \rightarrow 5\ CO_{2(g)} + 3\ N_{2(g)} + 7\ H_2O_{(l)} + 6\ OH^{-1}_{(l)}.$$

Elemental nitrogen atoms combine and form a gas ($N_{2(g)}$) which escapes into the atmosphere, thereby reducing availability of nitrogen within the wastewater discharge. Limiting the amount of nitrogen available as fertilizer slows down plant growth. Oxygen uptake likewise decreases, and dissolved oxygen becomes more available throughout the water column.

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

The metabolic energy necessary for microorganisms to break the nitrogen-oxygen chemical bond can be obtained from a carbon-containing biodegradable substrate material, such as methanol, or from dissolved oxygen ($O_{2(g)}$). By forcing anoxic conditions, the reduction conversion reaction is forced to occur at the nitrogen-oxygen bond, rather than the oxygen-oxygen bond, thus purging nitrogen and preserving oxygen within the system.

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

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 U.S. $0.50 to $0.60 per pound of nitrogen removed, which is 12% of previously reported costs.

2.4.2 Direct Methanol Fuel Cells

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

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

Direct methanol fuel cells function in a manner similar to, but distinct from, that of a lead acid battery. They use a polymer membrane instead of an aqueous electrolyte. The membrane serves the purpose of an electrolyte and transfers hydrogen ions (H^+) or protons, produced at the anode to the surface of the cathode. In direct methanol fuel cells, hydrogen ions are generated by direct oxidation of methanol (CH_3OH) at a catalyzed anode. The oxidation reaction generates hydrogen ions, which diffuse through the membrane to the cathode. Electrons from the anodic oxidation reaction circulate through an external electrical circuit as current, and carbon dioxide (CO_2) is generated at the anode as a gaseous waste product.

Oxidation-reduction reactions necessary to generate hydrogen ions at the anode and water at the cathode occur in the vapor or liquid phase, depending on cell design. A mixture of steam and methanol is injected under pressure and at elevated temperature into the anode compartment. An anode with a highly specialized catalytic coating enhances the kinetics of a direct chemical reaction, which breaks the carbon-hydrogen bonds of methanol molecules into hydrogen ions, and re-combines carbon with oxygen in the form of carbon dioxide (CO_2). A solid polymer membrane transports hydrogen ions generated at the anode to the cathode. The cathode, also a pressurized gas chamber, contains compressed air. Oxygen within the air reacts with the hydrogen ions on the catalyzed surface of the cathode to complete the reduction portion of the reaction by forming water vapor. Using highly advanced catalyst and polymer materials a direct methanol fuel cell essentially burns methanol at the anode and reduces hydrogen ions at the cathode, generating an electrical current and forming carbon dioxide and water vapor.

Anode (Methanol) noble metal catalyzed oxidation rxn:	$CH_3OH + H_2O_{(steam)} \rightarrow CO_2 + 6H^+ + 6e^-$
	$\downarrow$
Polymer Electrolyte conveys H^+ (Protons) from anode to cathode:	$6H^+$
	$\downarrow$
Cathode (Oxygen as Air) reduction rxn:	$6H^+ + 3/2O_2 + 6e^- \rightarrow 3H_2O$

Methanol fuel is an easily handled liquid, and the products of the oxidation-reduction reaction are water and carbon dioxide absent NO_x and SO_x contaminants.

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

Direct methanol fuel cells are an outgrowth of indirect fuel cells, which use hydrogen (H_2) as the fuel rather than methanol. Direct methanol cells provide several advantages compared to indirect fuel cells. In direct methanol fuel cells, the fuel is liquid and easily stored and transferred. In indirect fuel cells, hydrogen is used directly or is generated by chemical stream reforming. Storage of hydrogen gas is difficult and potentially hazardous; addition of a steam reformer increases the complexity of the cell.

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

The number of direct methanol fuel cells is increasing by about 2000 units per year. Currently there are well over 10,000 units in the field. Most of these units are less than 1.5 kW. About three quarters of these are being used in portable applications, with the remaining quarter being used in niche transportation applications in marine and submarine vessels, scooters, motorbikes, and as niche units in transportation vehicles. The majority of units are installed in North America, Europe, and Japan, although developing countries are applying this technology at an increasing rate. When fully developed, consumption of methanol direct fuel cells may be driven by consumer electronics, or possibly even as an alternative source of power in hybrid automobiles. In the latter application, it is conceivable that both the fuel cell and an internal combustion engine would run on methanol as fuel.

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

Manufacturers are developing modularized component-based configurations, which can be exchanged to replenish various cell components as they become depleted or wear out. The International Civil Aviation Organization has approved use of DMCs to power passenger personal devices, such as laptop computers, while on-board airplanes. Several development companies have direct methanol fuel cells commercial productions at this time.

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

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

2.4.3 Turbine Engines

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

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

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

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

Air monitoring requirements for methanol-fueled turbines are less than those for natural gas and distillate fueled turbines. Air quality control has become an increasingly expensive operating issue as air quality standards have become increasingly more stringent. There are multiple disadvantages of firing with refined hydrocarbon fuels: capital cost of monitoring equipment, increased operating cost, cost of uncertainty and penalties associated with non-compliance, shortened mean time between failures and associated increased maintenance cost, shortened life of turbine components, and increased lifetime cost associated with system unavailability. Taken together, methanol may have significant economic and operating advantages over conventional fuels.

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

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

The principal technical considerations are discussed below.

- *Methanol has a low heating value compared to natural gas and currently used distillate turbine fuels.* A greater volume of methanol must be combusted in order to produce the same base load output (brake horsepower) as that of natural gas or distillate fuel. Turbine fuel storage, and transfer and combustion systems may need to be modified to accommodate appropriately larger fuel volume. Testing indicates that turbine operability and performance with methanol fuel is equivalent to that of natural gas and distillate; air quality is superior.
- *Methanol has low lubricity.* Distillate has inherent lubricity because of the nature of the carbon-hydrogen molecules that comprise the fuel and the presence of small amounts of sulfur. Testing is in progress on additives that will increase methanol lubricity.
- *Methanol has a low flash point (very low vapor pressure at low temperature), which affects cold weather starting and operation and the need for explosion safeguards.* Cold weather starting issues can be circumvented by starting up with conventional

fuels. The explosion issue requires modification of engine configuration. Testing is being done for several methods of resolving the explosion issue.

- *Methanol liquid is electrically conductive compared to natural gas and distilled fuels.* Conductivity increases corrosion of alloys commonly used to handle natural gas and distillate fuel. This is particularly true for aluminum and titanium alloys. Additives are being tested to inhibit corrosion. Alternatively, commonly used materials may be replaced with more corrosion-resistant materials. Aluminum and titanium alloys should not be used in methanol or methanol vapor service without a rigorous mechanical integrity program.
- *Methanol is a solvent, which attacks some plastics, resins, and fiberglass compounds.* A variety of compatible materials are available to replace incompatible materials. Special care must be taken in selection and storage of gaskets, "O" rings, and other parts that prevent leakage.
- *Methanol absorbs water from the atmosphere.* Unlike gasoline, neat methanol and gasoline-methanol blend fuels absorb moisture from the air. Moisture absorbed by neat methanol is fully miscible, and is retained as a single phase that does not affect combustion. Moisture absorbed by gasoline-methanol blends forms an immiscible phase, which sinks, thereby accumulating in the bottom of tanks and piping low spots. If the amount of water is small, presence of an immiscible phase has little or no effect on the combustion properties of the blended fuel. Large amounts of water-phase material interfere with combustion, and in extreme circumstances may result in flameout.

2.4.4 Offshore Platforms

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

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

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

Methane hydrate, methane clathrate, hydro-methane, methane ice, "fire ice," and natural gas hydrate are synonyms for a solid clathrate compound that traps a large amount of methane within its crystal structure of frozen water, thereby forming a porous ice-like solid. A typical composition of methane clathrate hydrate is 1 mole of methane for every 5.75 moles of water at an observed density of 0.9 g/cm^3. One liter of methane clathrate contains 168 liters of methane gas at standard temperature and pressure. Clathrates contain sufficient amounts of methane to ignite and burn in air, hence the name “fire ice.”

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

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

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

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

2.4.5 Methanol Specifications

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

Chapter

3

3 Transportation and Storage of Methanol

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

3.1 Methanol Transportation

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

3.1.1 Ocean-Going Transport

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

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

Accidental releases into open ocean are to be avoided, but are considered to pose less of a threat to the environment than crude oil, bunker fuel, gasoline, or diesel fuels. Solubilization of pure (100%) methanol in water is rapid and complete. The accompanying dilution reduces methanol concentrations to a level that is nontoxic to marine life in less than one mile, even for large catastrophic releases.

3.1.2 Rail Transport

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

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

In the event of derailment, first responders should treat methanol as highly flammable and highly toxic. The 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 tank cars apply equally for tankers attached to tractor haul trucks and for tank trailers towed by tractor haul trucks. Methanol transport by truck haulage is subject to substantially the same precautions as are routinely exercised for gasoline transport.

3.2 Methanol Storage

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

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

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

3.2.1 Docks and Marine Terminals

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

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

3.2.2 Tank Farms

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

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 fabricate satisfactory totes that are easily obtainable. Because the number of users of tote and drums far outnumbers the number of facilities with dedicated bulk storage and handling systems, this manual stresses the importance of safe methanol handling for tote and drum containment. It is strongly suggested that handlers consult methanol providers concerning their selection of containment. Unlike tank farms, where personnel seldom have direct contact, users of totes and drums are typically subject to spillage, need for immediate response, and subsequent cleanup.

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

- Methanol should be purchased only from reputable sources. The Methanol Institute provides a service to link methanol customers with methanol suppliers. Visit the MI web site at www.methanol.org, and click on the “Methanol Source Request” link. Complete and submit this online form, providing information on your methanol needs, and your information will be shared with MI members representing the leading global methanol producers and distributors. These suppliers will then contact you directly to discuss price and supply.
- Providers should be consulted regarding the intended application and circumstances of use before committing to a sales contract. Many merchant chemical companies are equipped and willing to extend their services in order to assure safe use of the chemicals they sell.
- After agreeing on facilities and provisions for receiving, storage, and local transfer, establish and train a local response team in the actions that are necessary and prudent in the event of a spill.

- Certain aspects of methanol handling require special provisions and protective measures. These include the following:
    - As much as possible, methanol should be stored and used in a dedicated area that is specifically marked off and appropriately labeled. This area should have safety measures readily available to employees working in the area. The area should be designated as a hazardous area, and protective measures should be immediately available in the event of spillage, exposure, and ignition.
    - The area designated for methanol handling should be equipped with an effective audible alarm, which will summon assistance in a timely manner.
    - Use positive materials identification for gaskets, filters, hose material, and similar supplies.
    - Replace gaskets, hoses, and “O” rings periodically, *before* they are expected to degrade or fail.
    - Ensure that procedures are in place to ground, and periodically verify grounding.
    - Ensure that procedures are in place to protect from water uptake and accumulation.
    - Ensure that provisions and procedures are in place to prevent spilled methanol from entering drains, manholes, and confined spaces.
    - Ensure that procedures and provisions are in place for preventing methanol entry into the water table or aquifers.
    - Ensure that procedures and equipment are in place for personnel protection and exposure mitigation. This should include eye wash and shower stations.
    - Ensure that procedures and equipment are in place for leak detection and alarm.
    - Ensure that procedures and equipment are in place for onsite emergency response.
    - Ensure that 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 Hazard and Operability Study (HAZOP), performed prior to delivery of the first tanker truckload, 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 within the proximity of methanol storage and handling must be explosion proof to meet National Electrical Code (NEC) requirements [42]. Positive pressure may be required to ensure that methanol-free areas, such as smoking rooms and control systems and electrical switch gear, are protected.

3.2.5 Grounding and Bonding

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

It is recommended that grounding straps be equipped with carbide-tipped clamps to ensure electrical contact through 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. Refer to API and NFPA publications for specific guidance.

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

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

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

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

Be aware of the following:

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

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

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

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

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

- ASTM E681 describes a standard test method for determining flammability limits.
- Perry's Chemical Engineers' Handbook, 6th Edition, McGraw-Hill Book Company, San Francisco, Sec. 3, pp. 256-257, 1984.
- NFPA-325, *Guide to Fire Hazard Properties of Flammable Liquids, Gases and Volatile Solids*, 1994.
- Glassman, I., Combustion, 2nd Edition, pp. 321-313, pp. 486-489, 1987.
- NFPA 30A, *Code for Motor Fuel Dispensing Facilities and Repair Garages*, 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 II Division 1, Hazardous Locations*.
- UL 1604 *Electrical Equipment for Use in Class I and II, Division 2, and Class III Hazardous (Classified) Locations*.

- DOD-HDBK-263, Electrostatic Discharge Control Handbook.
- IEC 60050-426:1990, IEC 60079-4:1975, IEC 60079-4A:1970, IEC 60079-20:199.

Chapter

4

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 small concentrations in the human diet from fresh fruits, vegetables, commercial beverages like fruit juices, beers, wines, and distilled spirits. The food additives Aspartame (an artificial sweetener) and Dimethyl Dicarbonate (DMDC) (a yeast inhibitor used in tea beverages, sports drinks, fruit or juice sparklers), as well as wines, release small amounts of methanol when metabolized in the human body. Table 4 illustrates examples of methanol levels in common foods and beverages, compared to background levels in the human body.

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

Sample	Methanol Level
Fresh and canned fruit juices (orange and grapefruit juices)	1-640 mg/l *(average of 140 mg/l)*
Beer	6-27 mg/l
Wines	96-329 mg/l
Beans	1.5-7.9 mg/kg
Lentils	4.4 mg/kg
Carbonated beverages	~56 mg/l
Human body background level	0.5 mg/kg (0.73 mg/l in blood)

Non-dietary potential exposure to methanol (primarily through inhalation) can result from using certain consumer products, such as paints, windshield washer fluids, antifreeze, de-icers, and adhesives that contain methanol as a solvent. Methanol vapors may also be present in cigarette smoke at a level of 180 micrograms (µg) 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 between .025 to 4.7 mg/l in blood (milligrams per liter in blood). In controlled studies, humans breathing air containing 200 ppm (parts per million) methanol had blood levels below 10 mg/l.

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

Occupational (workplace) exposure is likely to cause the highest daily exposure to methanol. Occupational exposures typically occur through inhalation of methanol vapors during production or use. About 70% of the methanol produced in the United States is used as feedstock for the production of other organic chemicals and a variety of consumer 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, acetic acid, and other industrial chemicals. The Occupational Safety and Health Administration (OSHA) Time-Weighted-Average (TWA) Permissible Exposure Limit (PEL) to methanol is 200 ppm for an 8-hour day and 40-hour week.

Concentrations of methanol vapors measured in the breathing zone of workers during refueling of methanol-powered transit buses are generally less than 10 ppm. Concentrations of methanol vapors measured in the breathing zone of mechanics changing fuel filters (2-minute procedure) for these buses averaged approximately 50 ppm.

4.1.2 Accidental Sources of Exposure

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

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

Table 5. Added Body Burden of Methanol [32]

Exposure/Dose	Added Body Burden of Methanol
Background body burden in humans	35 mg*
Skin contact of hand in liquid methanol, 2 min	170 mg
Inhalation, 40 ppm methanol for 8 hr	170 mg
Inhalation, 150 ppm for 15 min	42 mg**
Ingestion of 12 oz (0.34 liter) of Aspartame sweetened diet beverage	21 mg
Ingestion of 0.2 ml of methanol	170 mg
Ingestion, 0.7-3 oz (25-90 ml) of methanol	Lethal (~21000-70000 mg)

*Estimated from methanol body burden of 0.5 mg/kg body weight for a 70 kg person
**Assuming 100% absorption in lung (60%-85% more likely)

4.1.3 Routes of Exposure

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

4.1.4 Methanol Metabolism

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

Human metabolism of methanol:

Step 1 **Step 2** **Step 3**
Methanol → Formaldehyde → Formate → $CO_2 + H_2O$

4.1.5 Effects of Exposure

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

4.1.5.1 General Symptoms

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

4.1.5.2 Acute Effects

The effects of acute, high-dose methanol exposure have been well characterized in human cases of alcohol poisoning and in animal studies. Generally, the affected individual experiences a short period of intoxication with a mild depression of the central nervous system, followed by a 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, to misty or blurred vision, to dramatically reduced visual acuity and total blindness.

The amount of methanol that can cause severe methanol exposure is very small: Assuming that 100% methanol fuel is swallowed, the lethal dose is less than one teaspoonful (4 ml) for a one-year old infant, one and one half teaspoons (6 ml) for a 3-year- old child, and less than two tablespoons (28 ml) for an adult.

4.1.5.3 Chronic Effects

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

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

Methanol is not currently listed by any international consensus body or government agency (e.g., IARC, NTP, NIOSH, ACGIH, or OSHA) as being a carcinogen. EPA's Integrated Risk Information System (IRIS) is conducting a human health hazard and dose-response assessment of methanol. A draft IRIS Toxicological Review of Methanol released for external peer review in December 2009 concluded that the weight of evidence is consistent with a determination that methanol is likely to be carcinogenic to humans. This is defined as "an agent that has tested positive in animal experiments in more than one species, sex, strain, site, or exposure route, with or without evidence of carcinogenicity in humans." In March 2011, EPA placed the external peer review of the draft IRIS Methanol Toxicological Review on hold, following a report from the National Toxicology Program (NTP), which recommended a review to resolve differences of opinion in the diagnoses of certain tumors reported in a methanol research study completed by a European research institute. EPA and the National Institute of Environmental Health Sciences plan to jointly sponsor an independent Pathology Working Group (PWG) review of select studies conducted at the Institute.

According to the draft IRIS Toxicological Review, "there is no information available in the literature regarding the observation of cancer in humans following chronic administration of methanol." Likewise, there are no human data that demonstrate a link between methanol exposure and an increased incidence of birth defects or reproductive hazards. However, 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 uncertainty as to the predictive value of these studies to 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 methanol PEL. However, this value is not intended to represent the highest "safe" blood concentration.

4.2 Exposure Control

4.2.1 Engineering Controls

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

4.2.1.1 Ventilation

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

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

4.2.2 Exposure Monitoring

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

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

Portable Gas Monitor

Gas detection tubes

(Courtesy of Drägerwerk AG with permission)

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

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

4.2.3 Personal Protective Equipment

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

4.2.4 Respiratory Protection

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

Table 6. Respiratory Protection Guide

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

4.2.5 Chemical-Resistant Clothing/Materials

Chemical-resistant clothing/materials should be worn if repeated or prolonged skin contact with methanol is expected. These may include 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 7 serves as guidance for proper personal protective equipment, depending on the situation presented.

Table 7. Personal Protective Equipment Selection

Low risk of vapor/low risk of volume splash	High risk of vapor/low risk of volume splash	High risk of vapor/high risk of volume splash
Fire retardant clothing	Full chemical resistant suit	Full chemical resistant, impermeable suit
Gloves (Silvershield or disposable nitrile)	Chemical-resistant rubber gloves	Chemical-resistant rubber gloves
Safety glasses with side shields	Full face supplied air respirator	SCBA or compressed air breathing apparatus (CABA)
Full boot cover	Chemical-resistant 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 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 an atmosphere that is oxygen-deficient, toxic, or combustible, therefore requiring them to be classified by OSHA as “permit-required” for entry. Deaths in confined spaces have occurred in the workplace because the atmosphere within the confined space was not tested prior to entry and/or continually monitored. *Confined space entry procedures must comply with all applicable Federal and local codes and regulations.*

In addition to the potential for an oxygen-deficient atmosphere, accumulation of methanol vapors in confined spaces may lead to explosion if ignited. The Lower Explosive Limit (LEL) of methanol is 6% (60000 ppm) by volume, which is 10 times the Immediately Dangerous to Life or Health (IDLH) concentration, and the Upper Explosive Limit (UEL) is 36% (360000 ppm) by volume. At concentrations in air 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

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

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

Pure methanol has a low flash point of 54°F (12°C) and a wide flammability range (6-36 vol%). Flash point is defined as the minimum temperature at which the vapor pressure of a liquid is sufficient to form an ignitable mixture with air near the surface of the liquid. Flammability range is the concentration range within which a mixture of air and methanol vapor is capable of igniting, providing availability of an ignition source. The extent of the flammability range means that methanol vapor can be ignited throughout a wide range of concentrations in air [33]. The minimum ignition energy (MIE) for methanol in air is slightly lower than that of gasoline. Local hot spots can exceed the flash point and methanol can be ignited. When methanol catches fire, it burns with a clear blue flame that is very difficult to see in bright sunlight. Methanol may be on fire and you may not be able to discern the hazard of a fire by looking for a flame.

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

4.4 First Aid Measures

First aid is the immediate temporary treatment given to an exposed individual before the services or recommendations of a medical professional are obtained. Prompt action is essential. If necessary, medical assistance must be obtained as soon as possible. A 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 the exposed area with copious amounts of tepid water for at least 15 minutes. Contaminated clothing and shoes should be removed under the shower. Wash the area thoroughly with soap and water. Seek medical attention if irritation or pain persists or if symptoms of toxicity develop. Wash contaminated clothing and shoes before reuse.

4.4.3 Eye Contact

In case of contact with eyes, immediately irrigate the eyes with copious amounts of tepid water for at least 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, 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.

Chapter 5

5 Managing Methanol Safely: Process Safety

This chapter summarizes the “Process Safety Management” system of administering highly hazardous materials. According to provisions set forth in 49 CFR 1910.119, the so-called “OSHA Process Safety Management Standard” [60], methanol is classified as a highly hazardous material if it is connected to the process and consists of at least 10,000 lbs (1,508 gallons). This is by no means the only system used successfully to manage chemical hazards; however, it has proven to be effective in the 20 years during which it has been in effect, provided the principles are applied diligently and intelligently. A copy of the Standard can be obtained free of charge over the Internet on the U.S. OSHA web site.

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 for the *Methanol Manual* because it gives 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 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 Process Safety Management 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 the principles set down in the Standard.

Process safety is founded on the principle that knowledge is power, power enables control, and 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 necessary to safely manage chemical hazards. Each element stands alone, but also projects into and strengthens every other element. As Table 8 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 that management controls are functioning as intended, and (6) protect proprietary property.

Table 8. The Organization of Process Safety

Grouping	PSM Element	Grouping	PSM Element
Know		**Respond and Recover**	
	Employee Participation		Emergency Planning and Response
	Process Safety Information	**Learn**	
	Process Hazards Analysis		Incident Investigation
	Operating Procedures	**Verify**	
	Training		Process Safety Audits
Do		**Protect**	
	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 have the most detailed knowledge 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 produce the intended result. Employees do not know what they do not know. It is the employer’s responsibility to inform all employees of the hazards and risks associated with methanol and how to effectively control those risks. When accidents occur, and it is likely that they will, it is usually because the individuals handling the methanol or performing work near methanol storage and handling areas are unaware of the risks. Accidents indicate lapses of management control in properly training and supervising employees.

5.2 Process Safety Information

Having specific, accurate, and detailed information about the process is necessary at all levels of the organization in order to understand how chemicals behave within the control limits and abnormal conditions for a process. Three types of information must 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).
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, shutdowns, and emergency shutdowns.
- Understand how process technology drives process excursions in abnormal operating circumstances caused by interruption of utilities, equipment failure, human error, and external weather and geologic events such as earthquakes, tsunamis, floods, and hurricanes.
- Know and respond to equipment pressure, temperature, and containment limits during abnormal conditions.
- Ensure that equipment design and construction comply with “recognized and generally accepted engineering practices.”
- Verify that workers are fit for duty and that equipment is fit for continued service.

5.3 Process Hazard Analysis

Process hazard analyses (PHAs) – also variously referred to as hazard evaluations, risk assessments, or hazard identification techniques – are required because circumstances and perceptions change over time. PHAs are conducted periodically to verify that sufficient safeguards are in place to protect against abnormal operating conditions and to avoid accidental release of process materials to the workplace, adjacent communities, and the environment.

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 identifies, evaluates, and verifies that hazards arising from the process, and from inventories of hazardous chemicals that are connected to the process, are controlled within the intended operating envelope. It also insures that abnormal circumstances that arise as a result of equipment breakdown and/or human error do not jeopardize worker and contractor health or cause harm to the facility or the environment. 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 absence, unreliability, or inadequate design, then recommendation is made to correct identified deficiencies. Correction should be made in a timely manner.

5.4 Operating Procedures

In order to maintain safe operations, operators must know the boundaries between safe and unsafe operating conditions. Likewise, they must know how and when to perform specific tasks associated with equipment operation and process control during normal operations, as well as in the event of abnormal circumstances.

Employers must provide written operating instructions that guide operators through the steps necessary to startup, operate, shutdown, 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, heater firing rate, heater stack gas composition, tank and vessel volume, and other important environmental conditions.

Operating procedures should be revised whenever a not-in-kind change is made within the process. Procedures must be updated and verified as accurate on an annual basis.

5.5 Training

Operating personnel must 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 should be repeated when a not-in-kind change is made within the process. Refresher training must be given every three years.

Employers must 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 demonstrates understanding and proficiency. Likewise, employers must implement controls that ensure operators are “fit for duty” whenever they are on duty within the plant.

5.6 Contractors

Historically, contractor employees who are at a facility for short periods of time on an irregular basis to perform specialized services such as turnarounds have anomalously high accident rates. Some contractor-involved incidents involve only contractors; others also involve contractors and facility personnel. 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. Workmen who are unfamiliar with the hazards in their workplace are prone to making mistakes, which cause injury and/or uncontrolled accidental release of hazardous chemicals.

PSM stipulates that plant management address 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 identifying 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 and the chemicals present. The contractor is also required to perform certain safety-directed activities on a daily basis with crew members. These include contractor employee training, daily safety meetings (so-called tailgate meetings), recordkeeping, notification of hazardous contract work, preparation of job cards, and incident reporting and investigation. These measures are particularly important for workers performing hot work or confined space entry near methanol.

5.7 Pre-Startup Safety Review

If a process unit or equipment item requires repair, and the process unit or equipment item is out of service while the repair is being made, then process safety management requires that a review be done to verify that both the equipment item(s) and the organization are in an operation-ready condition. A pre-startup safety review is 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 chemicals,” 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 workers, documenting results of employee training, and equipment inspection, testing, and deficiency correction.

Provisions within this element include warehousing of spare parts and replacement materials. The employer must ensure that maintenance materials, spare parts, and equipment are suitable for the process application in which they will be used. This may include labeling, 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: 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 perform work in so-called hazardous circumstances. Within the context of process safety, hazardous circumstances encompass immediate and proximate hazards associated with the work environment: confined space entry, lock-out/tag-out of energy sources, elevated work, sub-grade work, line breaking, hot-tapping, hot work, overhead lifts, crane relocation, and other work tasks that require safeguards to prevent injury.

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 must 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, how it is being done, who is doing the work, 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. Occasionally, it is 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 activities assume 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 for an existing item another part, component, or equipment item that meets or exceeds the design basis and fabrication specifications of 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 the design basis and fabrication specifications of an original part, component, or item.

The procedure for management of change 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.
- Modifications 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 should be taken:

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

5.11 Emergency Planning and Response

It is important to plan for, prepare for, train for, and respond to facility emergencies. This includes accidents, injuries, accidental release of highly hazardous chemicals, subsequent fires and explosions, and other damage- and exposure-causing spills and incidents. When you are planning, determine what might happen, and where and how it might occur. Install appropriate detectors and early warning devices. You will also want to establish evacuation procedures, rendezvous points, and headcount procedures. It is important to include in your plan mitigation measures, such as fixed fire monitors, sprinkler systems, deluge systems, automatic isolation systems, blast walls, and similar measures. These measurements help to contain, control, and localize damage. Be sure to inspect and test alarms, mitigation measures, and safety systems regularly, as recommended by suppliers.

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

It is very helpful to work with 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 a better understanding of the facility. If the first time a fire truck pulls into a facility is to respond to an actual emergency, staff may lose precious time in driving to the site of the incident and in understanding the situation at hand. 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 the best intentions, diligent prevention efforts, appropriate mitigation, and effective emergency 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. However, it is unlikely that these practices 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 should have personnel on hand who are trained to investigate accidents (for example, releases, toxic releases, spills, fires, explosions, and especially minor incidents or situations that were discovered before an accident occurred, also called “near misses”).

Accidents should be categorized based on severity and the response that is required. A structured incident investigation and process of root cause analysis should be implemented for all but the least damaging accident events. Corrective actions should be developed that address the root causes and that are aimed at preventing recurrence.

The following guidance is provided for incident investigation:

1. Initiate an investigation as promptly as possible, certainly within 48 hours.
2. Include the following members in the investigation team, as applicable:
    - persons knowledgeable in the process.
    - contract employees, if the incident involved a contractor.
    - persons trained in forensic investigation.
    - persons trained in interviewing.
    - 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

At least every three years, if not more frequently, conduct a facility-wide audit to determine whether procedures, provisions, and practices for process safety are in place. These practices should not only be known and understood by employees, but should also be 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.
- Expertise and experience in safety auditing.

The audit team should deliver a written audit report to the employer that assesses strengths and weaknesses in the various program elements. The employer should 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 are considered intellectual property of the employer are not precluded from inclusion within the process safety program. Neither is such inclusion a revocation of the rights and privileges to secrecy thereof.

Trade secrets and information that are considered proprietary to the employer must be clearly identified in writing by the employer. Intellectual property should be protected by confidentiality agreements 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.
- Conducting emergency planning and response.
- Performing process safety audits.

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

5.15 Implementing Process Safety

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

As an example of a very simple risk assessment, let us compare the hazardous properties of methanol to gasoline, the most widely used fuel, which is also volatile and flammable.

Methanol's physical and chemical properties provide users with several fire safety advantages compared to gasoline. Methanol has lower volatility, lower vapor density, a lower heat release rate, and a lower flammability limit than gasoline. The United States Federal EPA states that: "These properties together make methanol inherently more difficult to ignite than gasoline, and less likely to cause deadly or damaging fires if it does ignite."

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

5.15.1 What Is a "Hazard"?

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

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

5.15.2 What Is a “Risk”?

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

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

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

5.15.3 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, and the design basis and condition of the equipment.

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

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

A report is subsequently prepared and the recommendations either are implemented or discussed further; after possible further discussion, the recommendations either are revised or rejected. The risk of a particular consequence is assessed before and after implementation of the recommendation. In general, engineering safeguards are expensive and reliable.

Administrative safeguards are inexpensive; however, they are subject to much lower reliability, especially over time.

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

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

5.15.4 Process Hazard Assessment Documentation

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

Chapter

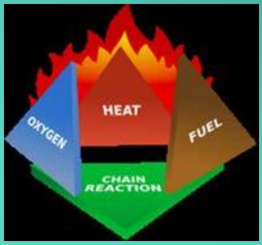
6

6 Fire Safety

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

It is particularly difficult to extinguish fires involving gasoline or diesel when in the presence of 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.

The Fire Tetrahedron



The four elements required to have a fire are:

1. Ignition source (such as heat or sparks).
2. Fuel (e.g., methanol).
3. Oxygen (air is a source of oxygen).
4. Chemical chain reaction (combustion that provides energy to keep the fire going).

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

6.1 Fire Detection and Protection

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

All fires release heat, and most fuel fires display flames and generate smoke. Fires involving pure (neat) methanol are not like most commonly encountered fires. Methanol fires produce less heat (have a low flame temperature); transfer less heat to surroundings (flames are non-luminous); are difficult to see (flames are nearly invisible to the naked eye during daytime, and there is little or no smoke); can initiate under unexpected circumstances (flammability limits are between 6 vol% and 36 vol% in air); are difficult to extinguish with water (100% miscible); and are flammable to 75 vol% water.

Early detection of methanol fires requires different technology from early detection of gasoline and diesel fires. If methanol ignition occurs in daylight hours, it is unlikely that the fire will be detected visually until it spreads to adjacent materials that emit a luminous flame or a visible plume of smoke. Two instrumentation technologies are available for early detection of a methanol fire. The first is vapor detection. If a methanol source is emitting large quantities of vapor, it is only a matter of time before ignition and flashback occurs. With luck, the source of vapor can be isolated and mitigated before the vapors ignite. The second technology is thermal imaging, which has been used for many years to identify hot spots and loose connections in electrical systems. It works equally well on methanol fires. A video of a methanol tanker truck fire and boiling liquid expanding vapor explosion (BLEVE) provides an excellent demonstration of the usefulness of the thermal imaging technique in protecting life safety of fire ground personnel. (http://www.firefighternation.com/videos/methanol-tank-truck-fire)

Immediate response is the second objective. Methanol has a low flame temperature, which, when combined with non-luminous flames, substantially reduces the rate of radiant heat flux. Low flame temperature combined with low heat flux allows fire fighters to approach the fire more closely than would be possible with a gasoline or diesel fire. This fact provides advantages and disadvantages.

The advantage is that small fires can be attacked with handheld extinguishers. The disadvantages are that it can be difficult to determine the location and intensity (burn rate) of the fire. To make a reasonable determination, it is necessary to use a thermal imaging device. When the location of the fire cannot be determined with a high degree of confidence, it is possible to locate the first line of defense too close to the fuel source. Uncertainties associated with locating and characterizing methanol and methanol-gasoline blend fires require a slow and deliberate approach. This is particularly true if there is any possibility of a BLEVE, or thermally induced rollover of the contents of a storage tank. It is highly desirable to determine a plan of attack using a bird’s eye view of the fire as seen with a thermal imaging device. Overhead imaging capability will save lives when fighting methanol and methanol-gasoline fires.

The third objective, “appropriate action,” is particularly important when fighting methanol fires. Methanol fires require special procedures:

- Methanol is 100% miscible in water; a mixture of 75% water and 25% methanol is a flammable liquid capable of supporting combustion.
- Methanol has a greater affinity for water than for gasoline. In the presence of water, the methanol in methanol-gasoline blended fuels partitions from the gasoline into a heavy, methanol-water phase, which forms beneath the gasoline. This can be an extremely treacherous situation in a storage tank. Methanol blends require special

measures to avoid thermally induced rollover of the contents of the tank and a subsequent tank explosion. Do not use water as a suppressant on methanol-blended fuel fires. Use only high temperature, alcohol compatible foam, such as film-forming fluoroprotein foam – specifically alcohol-resistant aqueous film-forming foam (AR-FFFP). In addition, allow substantial standoff distance from the fire, and continue applying foam long after the fire appears to be out. Methanol fires are known to restart if foam suppression is discontinued too soon.

- For small fires involving neat methanol or nearly pure methanol, water may be used as the suppressant. However, the water must be in the form of a fog or fine droplet water spray, and there must be sufficient freeboard space to increase the volume of the methanol-water solution by a factor of four. Otherwise, the volume of firewater necessary to suppress the fire may cause the fire to spread.
- If foam is used as the suppressant, then the foam must be an alcohol-compatible foam (AR-AFFFP). Otherwise the solvent property of methanol will attack and destroy the foam.
- Methanol is a strong polar solvent. Many plastics and synthetic fabrics soften and rapidly degrade when in contact with methanol.
- Finally, methanol is a toxic poison, which must not be ingested, inhaled, or contacted with skin. Methanol absorbs through the skin. SCBA breathing equipment worn with conventional turnouts does not provide sufficient protection against the toxicity of methanol, methanol water solutions, or methanol vapor. SCBA with a level “B” chemical resistant suit to prevent skin absorption may be required in such cases.

In summary, as a methanol transporter, user, or handler, it is necessary to make special provisions for responding to accidental releases. Methanol hazards are flammability and toxicity. However, it is the physical characteristics that determine what constitutes an appropriate response. The physical and chemical properties of methanol and methanol-blended fuels are distinct from one another. An appropriate response to a methanol fire will not be an appropriate response to a methanol-gasoline fire.

6.1.1 Vapor Control

The first measure in early detection of methanol fires relies on the presence of methanol vapor. If methanol vapor is present in concentrations at or near the lower flammability limit (6 vol%), then you must assume that ignition is possible. If ignition occurs, then combustion will ensue as either a fire or an explosion. The route by which ignition is manifested depends on ambient temperature, the energy of the ignition source, whether the vapor has traveled as a near-neutrally buoyant dense gas, and whether accumulated vapor is confined or unconfined. If ambient temperature is above the flash point, and if there is a large amount of vapor space in a container, tank, room, building, or enclosure, then flashback and explosion are likely. If ambient temperature is below the flash point, if potential ignition sources are low energy, and if vapor can readily dissipate to the atmosphere, then explosion is less likely.

In order to control whether the consequence is a fire or an explosion, it is necessary to control vapor concentration and vapor ventilation. To control the vapor, it is necessary to control the liquid, or the availability of oxygen in the vapor space above the liquid.

6.1.1.1 Storage Tank Safety Features

Best practice for tank storage of methanol in large volumes uses internal floating roof tanks to minimize methanol vapor space within the tank and to reduce the amount of air that is available to mix with the vapor. It is also necessary to control the vapors that are emitted from the tank. If the vapor space of the tank is not padded with an inert gas, then the tank vents must be equipped with flame arresters. Verify that the flame arrester components are not fabricated from aluminum alloy. Methanol is corrosive to aluminum alloys. There is a reported instance of a tank fire that occurred as the result of a release of excessive vapor from a tank. The flame arrester had aluminum alloy components that degraded and failed over a 13-year-period. Clearly, facility preventive maintenance was insufficient. Inert gas blanketing or padding adds an additional level of protection against ignition within the tank vapor space. Because nitrogen gas ($N_{2\ (g)}$) is an asphyxiate, special precautions should be taken for accessing the tank roof and for entering purged tanks.

Nitrogen padding has the added advantage of preserving methanol purity. Dry nitrogen is the preferred 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 and corrosivity.

It is further recommended that ignition sources be strictly controlled within the proximity of methanol storage, regardless of whether containment is in tanks or portable containers. The outside of methanol tanks should 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 relief/vacuum breaker valves. Vents may or may not be configured with flame arresters, depending on the specific circumstances; however, arresters are the preferred configuration.

Pressure relief valves are sized to a fire case and, if possible, should be piped to relieve into a flare header. If configured to relieve to the atmosphere, then it is strongly recommended that Process Safety Valves (PSVs) be configured to breathe to the 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 overflow pipes when ambient temperature is below storage temperature. Any accumulation of condensed liquid methanol in the bermed area creates a fire hazard and may 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 read “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 explosion-proof ratings for use in a methanol containment 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 (e.g., 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 (e.g., individual tanker trucks, rail cars, and small storage tanks). Allow a minimum of 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 that 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 does not offer effective protection in responding to methanol spills and fires.[6] Be aware that the odor threshold of methanol is well above the toxic exposure limit.
- Portable containers, tanker trucks, rail cars, and storage tanks are all subject to BLEVE. Establish safety precautions that are cognizant of overpressure, radiant heat flux, and toxic exposure hazards.

6.2 Fire Control

Key elements of 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. Accident scenario consequence analysis, associated with process hazard analysis and risk assessment, 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. Methanol vapor is known to flashback to the source. Verify that hazard zone perimeters are adequate. In assessing scenario consequence severity, it is necessary to consider exposure to overpressure and radiant heat flux.

6.2.2 Extinguishing Materials

If a portion of a facility is engulfed in fire, then streams of water can be used to cool adjacent process equipment. Normal Aqueous Film-forming Foam (AFFF) fire suppression foam is not appropriate for alcohol fires. The solvent properties of methanol cause normal firefighting foam to degrade. Methanol fires must be attacked with AR-AFFF.

For small fires in a contained space, 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. Methanol-water solutions and aerosols are flammable up to 75 vol% water. A greater volume of water – at least four times greater than the volume of methanol – is required to extinguish a methanol fire. If water is chosen as the first response fire suppression medium, then provisions must be made to prevent the resulting methanol-water solution from (1) entering drains and manholes and (2) spreading and carrying the fire into other parts of the facility.

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

6.3 Fire Ground Safety

Fire ground command must be vigilant to prevent fire teams from becoming surrounded by or partially immersed in flammable methanol-water solutions. Because 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 ignition sources and hot equipment that could cause these solutions to ignite.

Burning and non-burning 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 firefighting. This in no way compromises response effectiveness, provided there is provision for early detection, alarm, rapid callout, and instrumented, as well as visual fire assessment. Offsite responders must be: aware that they are responding to a methanol fire and be trained and equipped in the same way as an in-house fire brigade. It is recommended that facility operators contact their local first responders and set up site visits and fire drills to increase familiarity with the site.

Responders will benefit from having aerial and fire ground thermal imaging capability. Responders must either bring their own or be provided access to AR-AFFF alcohol-compatible fire suppression foam.

6.3.2.2 Personal Protection Equipment

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

- Methanol compatible 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, that foam be applied for a substantial period of time after the fire is out, and that water is 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.” Application of water within the interior of a tank will not suppress a methanol fire and more likely exposes responders to a tank explosion resulting from thermally induced rollover and expansion of tank contents.

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

Responders should have portable thermal-imaging equipment available for use on the fire ground and in the air over the fire ground. Responders must be trained in using the instrumentation, and incident command must be trained to take advantage of thermal-imaging capabilities.

6.4 Methanol-Gasoline Blended Fuels Fire Safety

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

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

6.4.1 Properties of Methanol-Gasoline Blended Fuels

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

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

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

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

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

6.4.2 Methanol-Gasoline Blended-Fuel Fires

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

Gasoline burns with a luminous flame; therefore, the gasoline portion of the fire is easily recognized. The 15/85 fuel blend burns with a slightly luminous flame. The methanol-water phase may be under the gasoline, where it is prevented from burning, or it may begin burning when the floating gasoline layer is consumed. The methanol-water phase will burn with an invisible, non-luminous flame. Responders may believe that the application of foam has suppressed the fire; however, methanol fires are persistent. It is in fact necessary to apply foam for an extended time after the fire is out. Two to three times as much AR-AFFF foam is required to maintain fire suppression as is required to initially extinguish the flames. This means that foam inventory needs to be sufficient to cover a spill to considerable depth.

It is important to remember that a gasoline fire requires conventional AFFF for effective fire suppression. On the other hand, a methanol or methanol-water fire requires AR-AFFF or film-forming fluoroprotein (FFFP) foam for effective suppression. A 15M/85G blend requires FFFP to combat the higher temperature of a gasoline fire and resist solvent attack of methanol.

AFFF foams have no alcohol resistance. They immediately break down when exposed to alcohol. The AR-AFFF foam has low heat and temperature resistance. The AR-AFFF degrades when exposed to high temperatures associated with a gasoline fire.

If AFFF foam is applied to a methanol fire, and if AR-AFFF foam is applied to a gasoline fire, then both foams are ineffective, and responders will have to rely on water spray and/or let the fire burn itself out.

Application of the wrong foam in the wrong place at the wrong time may cause fire intensity to increase, with the result that tank roll over and/or BLEVE become very real possibilities. At this point, responders have lost control of the fire ground, and the likelihood increases that someone may be injured unless a decision is made to increase standoff distance.

6.4.3 Response to Methanol-Gasoline Blended-Fuel Fires

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

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

- How does the incident commander decide which monitors and which hose crews get which foam at what times?
- What types of foams are needed, and are foam inventories sufficient?
- How is the incident commander going to track fire propagation?
- How are hot spots identified?

- How will the commander know if a BLEVE or tank rollover is imminent?
- How long should the incident commander continue applying foam after the fire is initially extinguished?
- What is the best strategy: fight the fire, or withdraw and allow the fire to burn itself out?
- At what point in the response must the decision to withdraw be made, what information is necessary to make it, and who is going to make it?

Chapter

7

7 Emergency Response

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

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

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

7.1 Spill Prevention

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

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

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

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

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

Workers must be trained to handle methanol in a safe manner. Systems and procedures that protect the employees, the plant, and the environment should be implemented.

Spill kits must be available in all areas where methanol is handled, stored, or used. A complete spill kit must include:

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

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

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

7.2 Spill Response

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

Steps if a Spill Occurs

The first steps to take if a spill occurs are:

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

7.3 Release Containment

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

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

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

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

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

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

Outdoor releases of methanol vapors will likely disperse relatively quickly. Isolating the area 328 to 656 ft (100 to 200 meters) from the spill source in all directions and staying upwind of the release plume are the appropriate response measures. If a tank truck or rail car is involved, expand the isolation area to one half mile (800 meters) from the release source. The purpose in expanding the radius of the exclusion limit is to protect personnel against overpressure, radiant heat flux, and shrapnel in the event of a BLEVE.

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

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

7.3.1 Site Control Zones

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

7.4 Spill Cleanup and Remediation

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

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

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

7.5 Spill Notification and Reporting

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

Spill notification may trigger requirements to remediate the spill area and restore any damage to the environment, in addition to penalties and fines.

7.6 Incident Investigation and Recordkeeping

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

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

7.7 Incident Command Structure

During a small spill that can be handled within the facility, the onsite Emergency Response Commander (ERC) has primary responsibility for responding to and correcting emergency situations and for taking appropriate measures to ensure the safety of site personnel and the public. The ERC is also responsible for ensuring that corrective measures have been implemented, appropriate authorities have been notified, and follow-up reports have been completed. Possible actions may include evacuation of personnel from the release area. Facility personnel are required to report all spills, fires, injuries, illnesses, and property damage to the ERC.

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

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

7.7.1 Communications

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

Chapter

8

8 Methanol Incidents and Safeguards

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

8.1 Overview of Methanol Incidents

Many major incidents of methanol spills, fires, and explosions have been reported in the international media, and compilations of private reports and some public agencies are available on the Internet. However, a comprehensive list of incidents and accidents involving methanol that have occurred throughout the global supply chain is not available in a centralized database at this time. The widespread uses of methanol from chemical intermediates and solvents to alternative fuels make this a complex task.

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

Table 9. Types of Methanol-related Incidents by User Sector (1998-2011)

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

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

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

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

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

Table 10 below shows the rates of injuries and fatalities caused by the methanol-related accidents reported.

Table 10. Methanol Incident Fatalities and Injuries by User Sector (1998-2011)

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

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

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

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

8.1.1 Common Causes of Incidents

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

8.1.2 Routine Operations and Maintenance

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

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

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

8.1.3 Transportation Activities

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

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

8.1.4 Pipeline Incidents

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

8.2 Key Findings

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

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

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

- Insufficient understanding of the physical, chemical, and flammable properties of methanol.
- Methanol container, hose, or pipeline integrity not preserved.
- Methanol vapors allowed to accumulate or released in flammable concentrations.
- Inadequate spill containment capability.
- Obvious ignition sources, such as hot work, not recognized or controlled.
- Ignition sources such as static electricity, electric arc from non-explosion-proof equipment or installations, friction and mechanical sparks, or exothermic chemical reactions not identified or difficult to control.
- Inadequate equipment maintenance.
- Standard Operating Procedures for routine operations not followed or inadequate.
- Process safety measures not in place or not followed.
- Fire prevention systems not in place, inadequate, or not operational.
- Inadequate Emergency Response planning, training, equipment, and/or supervision.
- Failure to recognize the magnitude of the hazard or developing event and to take appropriate and timely life safety protection measures.

8.3 Conclusions

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

- Conditions conducive to catastrophic events exist in all phases of the methanol value chain, including the manufacture, transportation, distribution, storage, and processing sectors, as well as in educational, recreational, and residential settings.

- Serious incidents from the use, transportation, or storage of methanol can and do occur in large and small operations with widely differing levels of technical capability.
- Emergency Response and Spill Prevention capabilities, training, and equipment are essential elements of safe methanol handling, as many spills have resulted in fires and explosions.
- The majority of incidents, and many fatalities, could have been prevented by implementing proper Hot Work Permit procedures prior to welding or grinding activities.
- Mechanical integrity and proper preventive maintenance of equipment for methanol service is of key importance for all methanol users.
- Understanding the importance of corrosion causes and prevention in methanol service conveyance systems, pipelines, and storage tanks is essential. This is of particular importance in marine terminals, tank farms, chemical plants, loading racks, and for all industrial users.
- Recognition, identification, and control of potential ignition sources must be emphasized in all situations where methanol is present and releases are possible. This should include sources of heat, fire, friction, electrical arc, static electricity, sparks, chemical reactions, and physical process conditions, among others.
- Industrial methanol users, and the biodiesel manufacturing industry in particular, will benefit from implementing process safety management practices and procedures for routine and special operations, as well as emergency conditions.
- Operator training in the physical, chemical, and flammable properties of methanol is an essential element in safe handling, in particular for industrial and transportation workers.

8.4 Safeguards

To reduce the probability and consequences of a catastrophic incident, methanol users must have the right tools to help them recognize the particular hazards of the type of operation or activity they are involved in and to identify the appropriate safeguards to control those hazards. In the chemical industry, this is best achieved through a safety management system composed of three elements: people, equipment, and procedures. One key concept of the systems approach is to realize that if we change anything in the system, we effectively change the system, and this allows unsafe or hazardous situations to occur.

All good systems require proper planning, operator training, and implementation. In order for the safety management system to be successful, the procedures must be complete, written, regularly updated, and rigorously followed. The process must have the right equipment that is properly maintained and documented, and the people must be properly trained in the procedures and the equipment and supervised to do their job safely and effectively.

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

8.4.1 Process Safety Management

PSM is one safety management system that has been in effect in the chemical industry for more than 20 years. In the United States, most facilities that store, process, or use 10,000 lbs (1,508 gallons) or more of methanol are required by OSHA to implement PSM. The intent of PSM is to know, understand, and control hazards of chemicals, process technology, and equipment used in large and small chemical operations and activities. PSM consists of 14 management elements that work together in a systematic fashion. Each element addresses a particular aspect of the process necessary to safely manage chemical hazards. However, the elements of PSM can be scaled to the specific situation of the facility and implemented by all facilities as needed. There are other models of chemical process safety in use around the world that can be effectively adopted by methanol users. The PSM process is described in detail in Chapter 5 of this manual.

8.4.2 Corrosion Prevention

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

8.4.3 Hot Work Permit Program

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

8.4.4 Fire Prevention and Response

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

8.4.5 Employee Training

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

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

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

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

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

Chapter

9

9 Environmental Protection

This chapter discusses the environmental impacts of methanol.

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

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

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

9.1 Environmental Fate and Transport

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

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

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

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 surface waters can quickly biodegrade under aerobic conditions. However, for releases where fine soil, low hydraulic conductivity, low nutrient, and anaerobic conditions prevail, methanol degradation in soil or groundwater can be very slow.

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

9.2 Air Emissions

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

According to the United States Toxics Release Inventory (TRI), 116.8 million pounds (53,000 metric tons) of methanol were released on- and off-site from facilities in all industries in the U.S. in 2009. Approximately 87% of the emissions were released into the air, and less than 2.5% into surface waters. The largest emitter in 2009 was the pulp and paper industry.

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

9.3 Groundwater Effects

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

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

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

9.4 Impacts to Drinking Water

Methanol is not currently listed as a contaminant on the United States EPA's National Primary Drinking Water Regulation (NPDWR), the National Secondary Drinking Water Regulation (NSDWR), or the Drinking Water Health advisories. Methanol is listed as a candidate on the Contaminant Candidate List 3 (CCL-3) released by EPA in February 2008.

9.5 Biological Effects

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

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

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

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

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

9.6 Climate Effects

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

In the 1990s, a typical methanol manufacturing plant would emit approximately 0.9-1.0 tonnes of carbon dioxide (CO_2) for every tonne of methanol produced. In addition to the environmental concerns, large CO_2 emissions represent operational inefficiencies in a methanol plant because the carbon emitted as CO_2 is not available for making methanol molecules. For these reasons, methanol plants began and continue to focus on efficiency improvements that reduce CO_2 emissions.

Over the last decade, methanol plants have been able to reduce CO_2 emissions by up to 40%. This has been accomplished through the implementation of efficiency improvements and through replacement of older facilities with newer plants that use more efficient technology. Some facilities report emissions as low as 0.54 tonnes of CO_2 per tonne of methanol produced. This is equivalent to emitting 3.6 lb of CO_2 per gallon (0.43 kg of CO_2 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 $CO_2$from biomass-derived fuels originates from the air, and the emissions are not counted in an emission inventory or a life cycle analysis.

9.7 Waste Treatment and Disposal

Waste methanol in concentrations equal to or greater than 24% by weight meets the EPA's definition of an ignitable hazardous waste. Product-grade methanol, when disposed, is a listed hazardous waste. Waste methanol, or water contaminated with methanol, is considered a hazardous waste and must never be discharged directly into sewers or surface waters. It may only be disposed of at a licensed facility permitted to handle Hazardous Waste as defined in the United States Resource Conservation and Recovery Act (RCRA). Contaminated products, soil, or water with methanol must be moved only by registered transporters in approved containers. The recommended disposal method for methanol is incineration for heating value recovery. Concentrated liquid methanol can be used as secondary fuel in systems compatible with water-soluble waste. Waste methanol is also amenable to reclaiming by filtration and distillation.

Chapter

10

10 Product Stewardship and Sustainability

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

10.1 Product Stewardship and Responsible Care

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

10.2 Product Stewardship Management System

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

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

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

10.3 Product Stewardship Practices

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

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

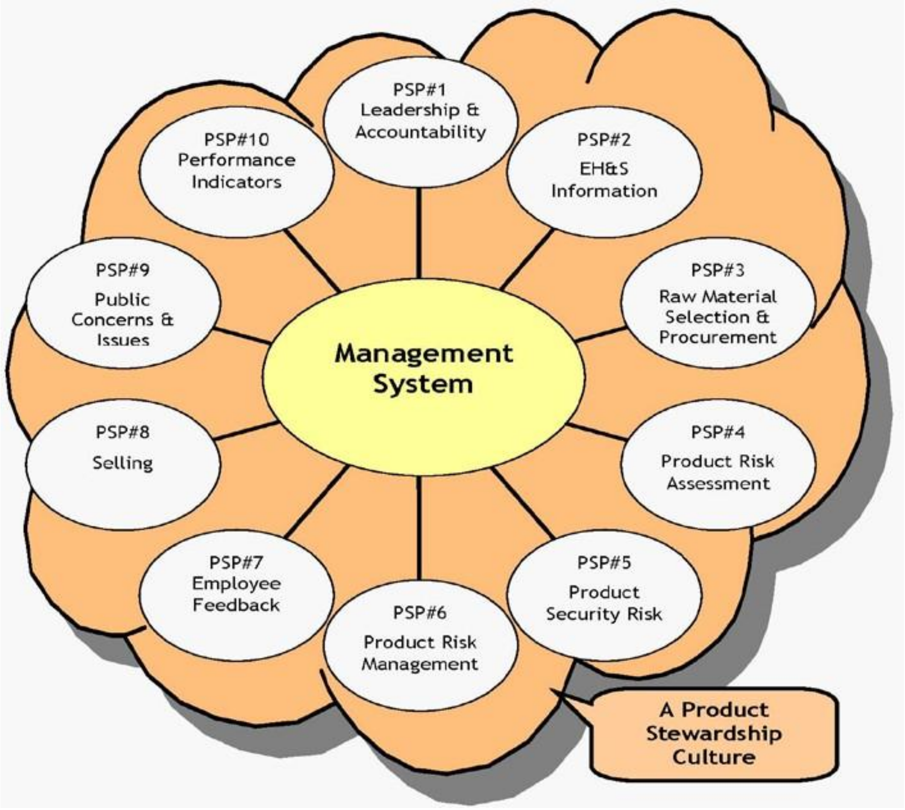

Figure 3. The Product Stewardship Practices

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

10.3.1 PSP #1: Leadership and Accountability

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

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

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

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

10.3.3 PSP #3: Raw Material Selection and Procurement

Prior to changing purchasing practices of raw materials and finished products, assess on a regular basis any potential impacts and risks that could occur. Incorporate risk management and use 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. It is best to actively seek input and advice from suppliers on their product and risk management experiences.

10.3.4 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.

10.3.5 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.

10.3.6 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.

10.3.7 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.

10.3.8 PSP #8: Selling

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

10.3.9 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.

10.3.10 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.

10.4 Responsible Distribution

Responsible Care is the guiding principle, as already discussed. The concept of Responsible Distribution® 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 of 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, and other procedures); and 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, and other distribution activities).

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.

10.5 Sustainability

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

10.5.1 A Primer on Sustainability

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

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

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

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

10.5.2 Alternative Energy

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

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

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

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

Iceland-based Carbon Recycling International (CRI) is manufacturing “renewable methanol” by first using geothermal energy to produce hydrogen from water, then combining it with captured carbon dioxide emissions from geothermal electricity generation to produce methanol. CRI has operated a demonstration facility in Iceland since 2007 and is building a commercial 1.3 million gallon per year production plant in Svartsengi, Iceland.

At the research and development stage, researchers at the University of Southern California are working on a technology to strip carbon dioxide from the atmosphere to produce methanol.

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

Chapter

11

11 Risk Communication

11.1 What Is Risk Communication?

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

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

- High concern, high stress
- Emotionally charged, or
- Controversial

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

Risk communication also has applications at home, at work, and in the community as the following definition suggests:

Risk communication is the art of putting science in the hands of people, in a way they can use (USEPA [64]).

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

In this context, it is important to keep in mind two other key definitions – the concepts of “Hazard” and “Risk.” When we are considering the global use of methanol, hazard and risk may be considered as follows:

- The "**hazard**" associated with methanol is its intrinsic ability to cause adverse effects.
- The "**risk**" is the probability that such effects will occur in the various applications in which methanol will be used and discharged (or the exposure scenarios for use of methanol).

This entire manual focuses on the hazards of methanol and the means used to limit those hazards and thereby the risk of exposure of methanol to workers, the community, and the environment.

This chapter emphasizes the application of risk (and hazard) communication pertaining to the distribution and use of methanol in the context of the second definition above: *putting science in the hands of people in a way they can use.*

The need may arise for a more detailed look at risk communication in crisis situations. The Methanol Institute has a *Crisis Communication Guidebook* that includes a more detailed review of risk communication principles for use during crisis situations, including dealing with the media.

11.2 Why Is Risk Communication Important?

Effective and thoughtful risk and hazard communication can build trust and confidence in the employee population and the community at large. This is crucial in order to prevent inaccurate or potentially damaging public response in the event of a crisis.

Also, recall in the Product Stewardship chapter, the concepts of the Responsible Care Ethic and Responsible Distribution. A key principle of each is sharing information with affected parties, whether they are employees, nearby communities, political interest groups, sub-distributors, or suppliers. Planning your message to be consistent with the principles of Responsible Care and/or Responsible Distribution, as well as achieving the basic tenets of risk communication, go hand in hand.

While we are not focused on crisis situations in this chapter, the risks and hazards of methanol are real. When we are addressing issues of people's health and safety, it is important to realize that these are matters of high concern to people.

11.3 Risk Communication Basics

The first definition of risk communication above stated that risk communication is a "science-based" approach of communication. Indeed it is. Effective risk communication requires planning and preparation. There are four basic steps to effective risk communication:

1. Determine the communication goal.

   Communication goals about a particular methanol business, work location, new technology, or other situation are numerous in non-crisis situations, such as sharing a new procedure with a supplier, training new employees in a manufacturing process, informing a neighborhood community about a new alarm procedure at a plant, etc. Is the goal to inform your audience and/or to persuade them to act? Write down the purpose of the communication and any desired outcome prior to constructing the message.

2. Know the audience.

   For example, if information is planned to be shared with a neighboring community or a work crew within a plant, request input from a representative(s) of the community or work crew, rather than assuming what their concerns may be. This is applicable for all communications, whether routine (such as information bulletins, training classes, etc.) or high-stress situations. Getting input from the audience, particularly with regard to concerns about health and safety, will not only be enlightening for the entity preparing the message, it can also help build credibility with the audience, which is crucial in risk communication.

3. Develop the components of the communication – the message and the medium.

   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 better understand their concerns. Select a medium for communicating that will reach the most people, and take care not to inadvertently leave groups out. For example, communicating important information (such as what to do when a shelter-in-place alarm is activated) via a web bulletin to an economically disadvantaged community is likely not an effective means of communicating such an important message. Make sure that language barriers are considered and planned for in order to reach the most people.

4. Make sure the information provided is accurate and timely.

   This is particularly important when communicating in a crisis situation, but applies to all risk and hazard communication. Ensuring that the person delivering the message is competent is critical to building and maintaining credibility with the audience.

11.4 Communicating Complex Technical and Scientific Information

Scientific information will be more useful to the audience, and greater communication success will be achieved, if the information provided is relevant and easily understood. To help audiences understand the issues, create well-targeted messages. Also be sure to use clear, non-technical language to discuss risks and other specific information indicating the nature, form, severity, or magnitude of the risk.

The following are some ways to clearly communicate complex scientific or technical information:

- Always use consistent names and terms (e.g., switching from parts per million to parts per billion can result in alarm because the higher numbers may be noticed, but not the unit of measure).
- Avoid acronyms and jargon, and provide careful definitions in advance. Never assume an audience “knows what you are talking about.”
- Use familiar frames of reference to explain how much, how big, or how small, and try to create a mental picture of such measures as “parts per billion” or “tons per day.”

  Numeric analogies, such as “the United States produces enough garbage in a day to fill 100 American football fields 14 feet (4.25 m) deep,” are more meaningful to average listeners than talking about 250,000 tons or tonnes of garbage per day. However, examples should not be trite or condescending or overly dramatic. Take the time to develop meaningful examples and calculations.
- Acknowledge uncertainty. Recognizing and admitting uncertainty is simply the reality of most risk communication situations, but especially in a crisis situation. Saying “I do not know” is an acceptable response and can build credibility.

  If an audience demands 100% certainty, they are more than likely questioning the underlying values and process, not the science. Try to identify the real concerns behind the demand for certainty and address them. For example, the statement, “If you’re not certain, how can we know we’re being protected?” is not a question about data but rather about personal and family safety. That is the issue to be addressed.

11.5 Understanding the Public's Perception of Risk

A key barrier is the term "risk" itself – how it's measured, described, and ultimately perceived. Interested parties perceive risk differently, and people do not believe that all risks are of the same type, size, or importance.

Perceptions of the magnitude of risk are influenced by factors other than numerical data (see table below from the U.S. Department of Health and Human Services (USDHHS) [61]). Understanding these factors will help determine the degree of risk with which a message may be perceived and assist in crafting an appropriate communications strategy.

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

11.6 Earning Trust and Building Credibility

The ability to establish constructive communication will be determined, in large part, by whether an audience perceives the person delivering the message to be trustworthy and believable. Consider how people form their judgments and perceptions.

Key elements in trust and credibility, and their relative importance, are depicted as follows:

(Courtesy of the Center for Risk Communication, with permission)

Do not underestimate the absolute requirement that people need to know that you care before they care what you know!

11.7 Looking for Opportunities to Get Your Message Out

Do not wait for a crisis situation to begin the process of risk communication. In fact, the more thorough and thoughtful an industry, company, government body, etc., can be about the issues they deal with and how the public may perceive the risks, the better prepared that entity will be in any crisis situation. Some opportunities to reach out may include, but are not limited to, the following actions:

- Submit letters to the editors of local newspapers.
- Contact your local newspaper to find out how to submit an opinion article.
- Call in to local talk radio programs when pertinent topics are being discussed.
- Contact local talk radio producers to solicit an invitation to appear on their programs.
- Contact local civic groups to solicit speaking opportunities.
- If you give a speech, contact local news outlets and ask them to cover your presentation.
- Contact local television news producers to explore ways they can cover your issues.

Chapter

12

12 Glossary

12.1 Terms, Abbreviations, and Acronyms

-A-

accident An unfortunate incident that happens unexpectedly and unintentionally, typically resulting in property damage or personal injury.

ACGIH American Conference of Governmental Industrial Hygienists. ACGIH publishes recommended upper limits (Threshold Limit Values – TLVs) for worker exposure to chemicals within the workplace.

acute effect(s) An adverse effect with severe symptoms developing rapidly and coming quickly to a crisis as a result of exposure to heat, overpressure, or toxic material.

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

AFFF Aqueous Film-forming Foam.

AFNOR Association Française de Normalisation.

alcohol(s) Any of a class of organic compounds characterized by the presence of a hydroxyl group covalently bonded to a saturated carbon atom.

alkali metal(s) Group 1A elements in the periodic table.

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.

biodiesel A vegetable oil- or animal fat-based diesel fuel consisting of long-chain alkyl esters. Biodiesel is typically made by chemically reacting lipids (e.g., vegetable oil, animal fat) with an alcohol such as methanol.

BLEVE An acronym for a Boiling Liquid Expanding Vapor Explosion. A hazardous situation exists when a storage tank containing highly flammable gases and liquids (e.g., methanol) under pressure is exposed to direct flames of a fire. Fire making contact with the shell of the tank causes simultaneous loss of strength in the metal and a rapid development of internal pressure in the vapor space above the liquid. If the venting mechanism (pressure relief valve) built into the structure is only sized for normal vapor expansion and not for "fire case," then the inability to vent fumes causes pressure to rapidly accumulate within the tank. The combination of a weakened shell structure and high internal pressure results in an instantaneous tank failure and catastrophic release and ignition of vapor. Use of unmanned firewater monitors is typically recommended in potential BLEVE incidents. BLEVE may occur within 10 to 30 minutes of initial flame contact unless the tank is cooled. A firewater application rate of at least 500 U.S. gallons (approximately 1,900 liters) per minute is required to cool the tank. BLEVEs can cause containers to "rocket" away from the site of the explosion due the force of the explosion.

boiling point or boiling point temperature (B.P.) The temperature at which a liquid phase material changes to a vapor phase. Boiling point is usually expressed in degrees of temperature (centigrade, Celsius, Fahrenheit, Kelvin, or Rankine).

BTU A commonly used abbreviation for British Thermal Unit, a measure of heat. One BTU is equivalent to the heat that is necessary to raise 1 pound of water 1 degree Fahrenheit, specified at the temperature of water's maximum density (39°F or 4°C). One BTU contains 252 calories or 1,055 Joules.

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

-C-

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

CABA Compressed Air Breathing Apparatus.

calorie (cal) The amount of heat required to increase the temperature of 1 gram of water 1 degree Celsius from 14.5°C to 15.5°C.

CANUTEC Canadian Transportation Emergency Center. A national center in Ottawa that is operated by the Department of Transportation. On request, CANUTEC relays pertinent emergency information concerning specific chemicals. CANUTEC has a 24/7 telephone number (613-996-6666).

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

CAS Number Chemical Abstract Service Number. A number assigned by the Chemical Abstracts Service that identifies a specific chemical. The CAS number provides indexing to access information about particular substances.

cc (cubic centimeter) A metric measure of volume equal to one milliliter (ml).

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

CERCLA Comprehensive Emergency Response and Liability Act.

CFR An acronym for the United States Code of Federal Regulations.

chemical family A group of single elements or compounds with a common general name (for example, gasoline, naphtha, kerosene, diesel, etc., and blended cuts of the "hydrocarbon" family).

chemical feedstock A chemical that is used as the starting point for the manufacture of other, more complex chemical substances.

chronic effect An adverse effect on a human or animal body with symptoms that develop slowly over a long period of time.

Class IA The National Fire Protection Agency (NFPA) designation for flammable liquids having flash points temperatures below 73°F (22.78°C) and boiling point temperatures below 100°F (37.78°C). An example of a class IA flammable liquid is *n*-pentane.

Class IB The National Fire Protection Agency (NFPA) designation for flammable liquids with flash point temperatures below 73°F (22.78°C) and boiling point temperatures greater than or equal to 100°F (37.78°C). Examples of Class IB flammable liquids are methanol, benzene, propane gasoline, and acetone.

Class IC The National Fire Protection Agency (NFPA) designation for flammable liquids with flash point temperature(s) greater than or equal to 73°F (22.78°C) and less than 100°F (37.78°C). Examples of Class IC flammable liquids are turpentine and *n*-butyl acetate.

Class II The National Fire Protection Agency (NFPA) designation for combustible liquids having flash point temperatures equal to or greater than 100°F (37.78°C), but less than 140°F (60°C). An example of a Class II combustible liquid is kerosene.

Class IIIA The National Fire Protection Agency (NFPA) designation for combustible liquids that have flash point temperatures equal to or greater than 140°F (60°C) and less than 200°F (93.33°C). Examples of Class IIIA combustible liquids are creosote oils and phenol.

Class IIIB The National Fire Protection Agency (NFPA) designation *for* combustible liquids with flash point temperature equal to or greater than 200°F (93.33°C). Ethylene glycol is an example of a Class IIIB combustible liquid.

CNG Compressed Natural Gas.

coefficient of volumetric thermal expansion The change in the volume of a liquid per degree of change in temperature.

coma A profound state of unconsciousness from which the subject cannot be awakened.

combustible (adj) A substance, solid, liquid, or gas that will burn; a description of flammability of a liquid based on flash point; generally refers to liquids with a flash point greater than or equal to 100°F (37.78°C)

combustible liquid(s) A National Fire Protection Agency (NFPA) designation for liquids having flash point temperatures at or above 100°F (37.78°C). *Combustible liquids* are subdivided into three classes as above based on *flash point temperature*.

combustion A chemical reaction that releases energy as heat and usually light. In everyday usage, it generally indicates something is burning or on fire. Combustion and burning are essentially equivalent terms.

confined space A term used in labor safety that refers to an area with enclosed conditions and limited access.

Contaminant Candidate List (CCL) The primary source of priority contaminants for which the United States EPA conducts research to make decisions about whether regulations are needed. The contaminants on the list are known or anticipated to occur in public water systems; however, they are currently unregulated by existing national primary drinking water regulations. Listing in the CCL is based on a contaminant's potential to occur in public water systems and the potential for public health concern.

Contaminant Reduction Zone (CRZ) The site control zone surrounding the Exclusion Zone. The CRZ holds the only access point for entry of response personnel and equipment, as well as the decontamination corridor for cleaning personnel and equipment exiting the Exclusion Zone.

corrosive (adj) A gas, liquid, or solid that causes irreversible damage to human tissue or containers; defined by the United States Department of Transportation (DOT) as a liquid or solid that causes visible destruction or irreversible alterations in human skin tissue at the site of contact.

Cradle-to-Grave An environmental assessment of the impact of a product or chemical through its entire life cycle, from manufacture to eventual disposal.

CRI Carbon Recycling International.

-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.

density The property of a substance that measures its compactness; the mass of a substance divided by the volume it occupies.

dermal toxicity The adverse effects resulting from skin exposure to a substance; toxicity associated with a substance of chemical that enters the body by absorption of the chemical through the skin.

detonation (explosive detonation) A detonation is caused by a very rapid chemical reaction that passes through the exploding material at speeds of 0.6 to 6.2 miles per second (1 to 10 km/s), well in excess of sonic velocity. High pressures are developed, and the products of combustion move in the same direction as the pressure wave. A detonation is a shock wave accompanied by the chemical reaction that sustains it. Explosives that normally detonate are termed "high explosives" and have high shattering power, even when unconfined. Trinitrotoluene (TNT) is an example of a detonating high explosive.

detonation velocity The velocity at which the shockwave front travels through a detonated explosive.

dilution The process of making a substance less concentrated by adding a solvent, such as water.

DIN Deutsches Institut für Normung E.V.

DMDC Dimethyl dicarbonate.

DME Dimethyl Ether.

DMFC Direct Methanol Fuel Cell.

DMT Dimethyl Teraphthalate.

dose The amount of a poisonous substance that causes adverse health effects.

DOT (USDOT) An acronym for The United States Department of Transportation, a Federal agency that regulates the transportation of chemicals and hazardous materials.

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

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

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

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

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

Drinking Water Advisory A non-regulatory document that analyses the currently available cancer and non-cancer data on a contaminant, as well as studies on its organoleptic (taste and odor) effects.

-E-

EH&S Environmental Health and Safety.

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

enthalpy of combustion (see also *Heat of Combustion)* The exothermic thermal energy that is released by a combustion reaction.

EPA (USEPA) The United States Environmental Protection Agency, a Federal agency that regulates environmental hazards.

EPCRA Emergency Planning and Community Right-to-Know Act.

ER Emergency Response.

ERC Emergency Response Coordinator.

ERP Emergency Response Plan.

EU European Union.

explosion A rapid increase in volume and release of energy in an extreme manner, usually with the generation of high temperatures and the release of gases. An explosion creates a shock wave.

extinguishing materials A substance that prevents the spread of fire and arrests the chemical reaction that allows sustained fire. Ideal extinguishing materials for methanol fires include alcohol-resistant foam, dry powder, carbon dioxide (released from automatically triggered sources), or water in at least a three- to four-fold excess of methanol by volume.

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

-F-

FFFP Film-forming fluoroprotein.

fire monitor (firewater monitor) A stationary, typically unmanned firewater nozzle that can be aimed and left unattended to disperse a stream of water into a predetermined area.

fire point The minimum temperature at which self-sustained combustion occurs.

Fischer-Tropsch process (water gas process) An industrial method of making hydrocarbon fuels from carbon monoxide and hydrogen. Hydrogen and carbon monoxide are mixed in the ratio 2:1 (water gas is used with added hydrogen) and passed at 392°F (200°C) over a nickel or cobalt catalyst. The resulting hydrocarbon mixture can be separated into a higher boiling fraction for diesel engines and a lower boiling fraction gasoline fraction. The process is also used in the manufacture of SNG (Synthetic Natural Gas) from coal.

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

flammable A solid, liquid, or gaseous substance that will ignite easily and burn rapidly, as opposed to a combustible substance that will not ignite as easily or burn as rapidly.

flammable limits Pertaining to ignition of liquids, gases, and vapors in air. Also called the explosive limits. The lower and upper flammable limits define the concentrations outside of which ignition will not occur due to the mixture being too concentrated (rich) or too diluted (lean), respectively. (See *flammable range, LEL, UEL.*)

flammable liquid(s) Generally, liquids do not actually burn in the liquid state. Liquids release vapors that ignite when a flammable mixture with air is attained in the presence of an ignition source.

flammable material(s) Any solid, liquid, vapor, or gaseous materials that ignite easily and burn rapidly when exposed to an ignition source. Examples of flammable materials within this broad definition include certain solvents such as methanol, dusts like flour, certain finely dispersed powders like aluminum, and gases like hydrogen and methane.

flammable range The numerical difference between the upper and lower explosive limits measured as the experimentally determined volumetric concentration of a substance in air above which and below which ignition does not occur.

flash point/flash point temperature The minimum temperature at which a liquid (or solid) gives off a sufficient volume of vapor at atmospheric or near atmospheric pressure to first form an ignitable mixture with air near the surface of the liquid or within the test apparatus. The United States Department of Transportation defines the flash point temperature as the “minimum temperature at which a substance gives off flammable vapor(s) which, in contact with sparks or flame, will ignite.” The term does not ordinarily have meaning or significance when applied to flammable gases or solids.

freezing point temperature The temperature at which the liquid and solid states of a substance coexist at one atmosphere (atm) of pressure.

fuel cell An electrochemical cell that converts chemical energy from a fuel (such as methanol) into electric energy. Electricity is generated from the reaction between the fuel supply and an oxidizing agent. The reactants flow into the cell, and the reaction products flow out of it, while the electrolyte remains within it. Fuel cells can operate continuously as long as the necessary reactant and oxidant flows are maintained.

fuel in vaporized stoichiometric mixture The volume percent of vaporized fuel available to a combustion reaction which occurs at stoichiometric concentration.

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

-G-

g/cm^3 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^3 Grams per cubic meter. A metric unit of concentration measure (weight/volume) expressed in units of grams of weight per cubic meter volume.

gal Gallon. A commonly used abbreviation for both a U.S. and an English (Imperial) unit of volume. A U.S. gallon contains 231 cubic inches (3.8 liters). An Imperial gallon is defined as the volume that contains exactly 10.0 pounds of water at standard temperature and pressure (which is 277.4 cubic inches or 4.56 liters).

gas(es) The phase of matter in which a substance has no definite shape and a volume that is defined only by the size of the container in which the gaseous matter resides.

ground (electrical) A common return path for electric current, or a direct physical connection to the Earth.

GWBB-8 h Grenswaarde beroepsmatige blootstelling (Belgium 1998). A measure of exposure concentration for an eight-hour workplace exposure.

GWK-15 min Grenswaarde kortstondige blootstelling (Belgium 1998). A measure of exposure concentration within the workplace for a time duration of 15 minutes.

-H-

hazard A hazard is a situation that poses a level of threat to life, health, property, or environment. Most hazards are dormant or potential, with only a theoretical risk of harm; however, once a hazard becomes "active," it can create an emergency situation. Hazard and vulnerability interact together to create risk.

HAZCHEM Code Also known as Emergency Action Code (EAC), a code designed to be displayed when hazardous chemicals are transported or stored in bulk. It is used to help the emergency services take action quickly in any accident. The code consists of a number followed by one or two letters. The number indicates the type of substance to be used in treating the accident (e.g., stream of water, fine spray, foam, dry agent). The first letter indicates the type of protective clothing needed, along with information about the possibility of violent reaction on whether the substance should be contained or diluted. The second letter, where it exists, is E, indicating that people have to be evacuated from the proximity of the incident. In the UK, the code is usually displayed as part of a panel, which includes an international UN number for the substance, a telephone number for specialist advice, the company name, and a symbol indicating the danger or hazard posed by the material (e.g., skull and crossbones for toxic substances).

HAZOP (HAZOPS, HAZOP Analysis) An acronym for HAZard and OPerability Study. A safety procedure by which various engineering and administrative safeguards are assessed to identify accidental release scenarios for hazardous materials.

HAZWOPER An acronym for Hazardous Waste Operations and Emergency Response. It refers to five types of hazardous waste operations conducted in the United States under OSHA Standard 1910.120 "Hazardous Waste Operations and Emergency Response." The standard contains the safety requirements employers must meet in order to conduct these operations.

heat capacity *(*see also *Specific Heat or Specific Heat Capacity)* The amount of heat needed to raise either 1 gram of a substance 1 degree Celsius or 1 pound of substance 1 degree Fahrenheit.

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

heating value The theoretical amount of heat that can be released by a combustion reaction if the fuel and oxidants are converted with 100% efficiency to CO_2 and H_2O vapor. Two values are given heat value: a higher heating value (HHV) and a lower heating value (LHV). HHV is used for situations in which all of the heat (heat of reaction, the sensible heat of product gases, and the heat of condensation of water vapor) is recovered and utilized to perform work. HHV is essentially the same as the thermodynamic heat (enthalpy) of combustion. The LHV is used if a portion of the sensible heat of the gases and the heat of condensation of water vapor is not recovered to perform work. The process industries typically use the lower heating value.

hot work Any process that can be a source of ignition when flammable material is present or can be a fire hazard regardless of the presence of flammable material in the workplace. Common hot work processes are welding, soldering, cutting, and brazing. When flammable materials are present, processes such as grinding and drilling become hot work processes.[

-I-

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

IC Incident Command.

ICC International Code Council.

IDLH Immediately Dangerous to Life and Health. Pertaining to measurement of toxicity, the maximum concentration from which one could escape within 30 minutes without experiencing any escape-impairing symptoms or any irreversible adverse health effect. IDLH levels are published for many substances by NIOSH/OSHA *Pocket Guide to Chemical Hazards,* United States Department of Health and Human Services/United States Department of Labor.

IEC International Electrotechnical Commission.

IEEE Institute of Electrical and Electronics Engineers.

ignition The initiation of combustion.

IMPCA International Methanol Producers and Consumers Association.

incident A hazardous situation that has come to pass.

IPCC Intergovernmental Panel on Climate change, a scientific intergovernmental body set up by the World Meteorological Organization (WMO) and by the United Nations Environment Programme (UNEP). It assesses the scientific, technical, and socioeconomic information relevant for the understanding of the risk of human-induced climate change.

IRIS Integrated Risk Information System.

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

ISO International Organization for Standardization.

-J-

joule(s) Symbol j. The SI unit of measure for energy.

-K-

K Kelvin. The degrees of temperature relative to thermodynamic absolute zero.

kg(s) kilogram(s). A commonly used abbreviation for a unit of metric measure for the weight (mass) of a substance: 1,000 g = 1 kg.

kJ kilojoule(s). SI abbreviation for common unit of energy.

kPa kilopascal(s). SI abbreviation of commonly used measure of pressure.

-L-

latent heat of vaporization The energy to transform a given quantity of a material into a gas.

LEL Lower Explosive Limit. Also lower flammability limit. The volumetric concentration of a flammable material in air at 1 atmosphere of pressure, below which the mixture of fuel and air is too lean or dispersed to ignite in the presence of an ignition source with a standard and relative high amount of energy, such as a spark.

Level A Protection Protection used for hazardous work conditions with a high potential for exposure to very high concentrations of chemical splash, immersion, or exposure to chemical vapors. It consists of a fully encapsulated chemical suit with supplied air-breathing apparatus for the highest available level of respiratory protection. It is required for chemical hazards with a high vapor pressure and toxicity through skin absorption or which are carcinogenic.

Level B Protection Level B has the same level of respiratory protection required as in Level A protection; however, it allows for certain areas of exposed skin on the wearer and encapsulating garments that are not “vapor tight.” Used in exposure situations at chemical concentrations below established exposure limits and chemicals that are not vapors or gases that are toxic by skin absorption or are carcinogenic.

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

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

LPG Liquefied Petroleum Gas.

-M-

M.P. Melting point. A commonly used abbreviation for the melting point temperature of a solid material.

M85 A fuel mixture consisting of 85% methanol and 15% gasoline.

MAC Maximale aanvaarde concentratie (the Netherlands 2002). Maximum Occupational Exposure Concentration Limits.

MAC-TGG 8 h Maximale aanvaarde concentratie. Maximum Occupational Exposure Concentration Limits for an eight-hour exposure.

MAK Maximal Arbeitsplatzkonzentrationen (Germany 2001). Maximum Concentrations of Chemical Substances in the Workplace: Occupational exposure concentration limits.

mass burning rate The loss in mass per unit time by materials burning under specified conditions.

methanol (methyl alcohol, wood alcohol) Methanol (CH_3OH) is a colorless, poisonous liquid with essentially no odor and very little taste. Chemically, it is the simplest alcohol and is derived by replacing a hydrogen atom of the methyl group with a hydroxide atom. Methanol is a liquid at room temperature and pressure that is miscible in all proportions with water and with gasoline. Methanol is a polar solvent that disperses readily within the surface environment and is quickly rendered nontoxic by the combined processes of dilution and degradation. Because of its solubility, methanol can be difficult to remove from potable ground water.

mg/m^3 A metric unit of concentration measure (weight/volume) expressed in units of milligrams of weight per cubic meter of volume.

MI Methanol Institute.

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

miscible A liquid that will evenly dissolve in another liquid; 100% miscibility is when two liquids will mix completely in all proportions.

mm Hg Millimeters of mercury. A measure of pressure.

mol(s) A commonly used abbreviation for mole, as in a mole weight of a particular element, chemical, compound, or substance.

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-

NACE National Association of Corrosion Engineers.

NAERG The North American Emergency Response Guidebook, a paperback publication developed jointly by Transport Canada, the United States Department of Transportation, and the Secretariat of Communications and Transportation of Mexico. A free electronic version can be downloaded from the Transport Canada web site at http://www.tc.gc.ca/eng/canutec/guide-ergo-221.htm. The ER Guidebook is a guide for first responders to quickly identify the specific or generic hazards of material involved in a transportation incident. The information assists first responders in protecting themselves and the public from chemical exposure during the initial response phase of the incident.

NEC Acronym for *National Electrical Code* of the United States (NFPA 70).

NFPA An acronym for the National Fire Protections Association. This group classifies substances according to their fire and explosion hazard.

NFPA #30 A National Fire Protection Association code called the *Flammable and Combustible Liquid Code*.

NFPA #30A A National Fire Protection Association called the *Code for Motor Fuel Dispensing Facilities and Repair Garages*.

NIOSH National Institute for Occupational Safety and Health. This United States government agency tests equipment, evaluates and approves respirators, and conducts studies of workplace hazards. NIOSH also proposes workplace exposure standards to OSHA.

NPDWRs National Primary Drinking Water Regulations. Also called primary standards. Legally enforceable standards that apply to public water systems in the United States. Primary standards protect public health by limiting the levels of contaminants in drinking water.

NSDWR National Secondary Drinking Water Regulation.

NTP National Toxicology Program. An entity that tests chemicals and reviews evidence for cancer in the United States.

-O-

OECD Organization for Economic Cooperation and Development.

OES The Occupational Exposure Standards (United Kingdom 2001).

OHSAS Occupational Health and Safety Advisory Services.

organic Of, relating to, or denoting compounds containing carbon (other than simple binary compounds and salts) and chiefly or ultimately of biological origin.

OSHA The Occupational Safety and Health Administration, a United States Federal agency that adopts and enforces health and safety standards within industrial workplaces other than mines and mills (e.g., chemical manufacturing plants, petroleum refineries, oil production fields, merchant liquid air plants, etc.). MSHA (the Mine Safety and Health Agency) is responsible for health and safety standards in mines and mills.

OVA Organic Vapor Analyzer.

-P-

partition coefficient The ratio of concentrations of a compound in the two phases of a mixture of two immiscible solvents at equilibrium. Partition coefficients are a measure of differential solubility of the compound between these two solvents.

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

PEL The Permissible Exposure Limit for a chemical within the workplace. PELs are enforced by OSHA in the United States.

PHA Process Hazard Analysis.

PLC Programmable Logic Controller.

poison A substance that, when introduced into or absorbed by a living organism, causes death or injury, especially one that kills by rapid action even in a small quantity.

PPE Personal Protection Equipment. An ensemble worn by a worker to protect against physical and chemical hazards. It can include head, eye, and hearing protection equipment, gloves, safety shoes, and additional specialized equipment for specific hazardous conditions.

ppm Parts per million. A volumetric unit of measure for the concentration of a substance in air or in a solution.

process safety Refers to the prevention of unintentional releases of chemicals, energy, or other potentially dangerous materials during the course of chemical processes that can have a serious effect to the plant and environment. Process safety involves the prevention of leaks, spills, equipment malfunction, over pressures, over temperatures, corrosion, metal fatigue, and other similar conditions. Process safety programs focus on design and engineering of facilities, maintenance of equipment, effective alarms, effective control points, procedures and training. It is sometimes useful to consider process safety as the *outcome* or *result* of a wide range of technical, management, and operational disciplines coming together in an organized way.

producer gas (air gas) A mixture of carbon monoxide (CO) and nitrogen (N_2) made by passing air over very hot carbon. Usually some steam is added to the air, and the mixture contains hydrogen (H_2). Producer gas is used as a fuel in some industrial processes.

Product Stewardship A principle where environmental protection centers around the product itself, and everyone involved in the lifespan of the product is called upon to take responsibility to reduce its environmental impact. For manufacturers, this includes planning for, and if necessary, paying for the recycling or disposal of the product at the end of its useful life. This may be achieved by redesigning products to use fewer harmful substances; to be more durable, re-useable, and recyclable; and to make products from recycled materials. For retailers and consumers, this means taking an active role in ensuring the proper disposal or recycling of an end-of-life product.

psi (also psig) Pounds per square inch. A measure of pressure; the pounds of force per square inch of surface area, or pounds per square inch of gauge.

psia Pounds per square inch absolute. A measure of pressure in pounds of force exerted per square inch of surface area that includes 14.7 psi of atmospheric pressure experienced at mean sea level; psia = (psi + 14.7).

PSM Process Safety Management.

PSP Product Stewardship Practice.

PSV Process Safety Valve.

-R-

R&D Research and Development.

RCRA Resource Conservation and Recovery Act, a United States Federal law that regulates hazardous waste from generation to final disposal, also referred to as “cradle to grave.”

reactive A solid, liquid, or gas substance that releases energy under certain conditions.

Reid Vapor Pressure (RVP) A commonly used measure of vapor pressure for gasoline and other liquid fuels, defined as the pressure exerted by a liquid at 100°F as determined by the test method ASTM D-323. The test method does not apply to liquefied petroleum gases such as propane.

Responsible Care Ethic An initiative under which companies work together to continuously improve their health, safety, and environmental performance and to communicate with their stakeholders about their products and processes.

Responsible Distribution Ethic An initiative where the principles of the Responsible Care Ethic are extended to all aspects of the distribution of chemicals, chemical products, and chemical services.

risk A situation involving exposure to danger (i.e., when a vulnerability is exposed to a hazard).

Risk Assessment The determination of quantitative or qualitative value of risk related to a concrete situation and a recognized hazard.

Risk Communication The interactive exchange of information and opinions throughout the risk-analysis process concerning hazards and risks, risk-related factors, and risk perceptions among risk assessors, risk managers, consumers, industry, the academic community and other interested parties, including the explanation of risk-assessment findings and the basis of risk-management decisions.

running fire (running liquid fire) A burning liquid that flows away from the point of release and ignition. Running fires are particularly hazardous if allowed to enter sewers, drains, man-ways, or sub-grade structures, such as electrical or pipeline vaults where the burning material can pool and block evacuation routes.

-S-

SCBA Self-Contained Breathing Apparatus. A supplied air tank with a pressure-demand regulator used in high-hazard environments as part of Level A and B protection.

SCC Stress Corrosion Cracking.

SDWR Secondary Drinking Water Regulations. Non-enforceable United States Federal guidelines regarding cosmetic effects (such as tooth or skin discoloration) or aesthetic effects (such as taste, odor, or color) of drinking water.

SIDS Screening Information Data Set.

SNG Synthetic Natural Gas.

solubility The maximum amount of material that will dissolve in a given amount of solvent at a specified temperature to produce a stable solution.

solvent A liquid capable of dissolving other substances. In industrial use, commonly used to mean a chemical capable of dissolving petroleum-based products.

specific electrical conductance (see *Electrical Conductivity*).

specific gravity The mass of a given volume of matter compared to the mass of an equal volume of water.

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

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

STEL Short-Term Exposure Limit. Pertains to inhalation exposure of a toxic aerosol.

stewardship See *Product Stewardship.*

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

Air-to-fuel ratio: A/F = (100/21)(O/F)

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

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

Support Zone The outermost of the site control zones, the SZ is the perimeter used for staging response equipment and the location of the command post and communications center.

Sustainability Practices and processes developed with the intent of improving the quality of human life while living within the carrying capacity of supporting ecosystems. A commonly used definition is to "**meet present needs without compromising the ability of future generations to meet their needs**." A key concept that places sustainability in more familiar business terms is the “three Es” or “triple bottom line” concept of economic, environmental, and (social) equity sustainability.

-T-

TDG Transportation of Dangerous Goods. Canadian regulations with equivalency to the United States 49 Code of Federal Regulations (CFR).

teratogen A substance that causes birth defects by damaging the fetus.

thermal conductivity The ability of a material to conduct heat. Liquids with high thermal conductivity conduct heat more readily than liquids with low thermal conductivity.

TLV Threshold Limit Value. Airborne concentrations of chemical substances that represent conditions under which it is believed that nearly all workers may be repeatedly exposed, day after day, over a working lifetime, without adverse health effects. In the United States, values of the TLV are set by the American Conference of Governmental Industrial Hygienists (ACGIH). TLV is usually expressed as parts per million (ppm) or milligrams per cubic meter (mg/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 2,000 pounds.

tonne The metric unit of weight (mass) equal to 1,000 kilograms (2,204.62 pounds).

tote A portable vessel widely used for containment during shipping and storage of relatively small amounts of bulk liquid chemicals. The so-called JumboBin Tote is a sealed metal box fabricated of 304 stainless steel. The tote is fitted with lifting lugs on the four top corners and short legs on the four bottom corners.

toxic/toxicity The degree to which a substance can damage an organism. Toxicity can refer to the effect on a whole organism, as well as the effect on a substructure of the organism. A central concept of toxicology is that effects are dose-dependent.

TPA Terephthalic acid.

TRI Toxics Release Inventory. A publicly available EPA database that contains information on toxic chemical releases and waste management activities reported annually by certain industries, as well as federal facilities, in the United States.

turnout Also called turnout gear or bunker gear, it is a firefighter’s uniform consisting of overall pants, boots, gloves, a hat or helmet, and often a jacket. The components of turnout gear may vary with agency and geographic zone.

TWA Time Weighted Average.

-U-

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

UEL Upper Explosive Limit (see also *upper flammability limit, flammable range, LEL*). The maximum molar or volumetric concentration of a vapor in air above which ignition does not occur. Fuel concentrations above the upper explosive limit are said to be too rich to burn.

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

UFL Upper Flammability Limit (see also *upper explosive limit).* The maximum molar or volumetric concentration of a vapor in air above which ignition does not occur. Fuel concentrations above the upper explosive limit are said to be too rich to burn.

UN Number or UN IDs Four-digit numbers that identify hazardous substances and articles such as explosives, flammable liquids, and toxic substances for the purpose of international transport.

UNEP United Nations Environment Programme.

USDHHS U.S. Department of Health and Human Services.

-V-

vapor The gaseous form of a substance that is normally a liquid or solid at ordinary temperature and pressures.

vapor pressure The pressure exerted by a vapor that is in equilibrium with the liquid at a given temperature. A measure of how readily a liquid or solid releases a vapor that mixes with air at the surface of the liquid or solid. A higher vapor pressure indicates a higher concentration of vaporized substance in air and, therefore, increases the likelihood of a person's breathing the vapor into his or her lungs while breathing toxic-laden air.

viscosity The quality of resistance to flow.

VLE-15 min Valeurs limites d'Exposition a court terme. (France 1999). Limit value for a short-term exposure of 15-minute duration.

VME-8 h Valeurs limites de Moyenne d'Exposition. Limit value of average exposure for an eight-hour workplace exposure.

VOC Volatile Organic Compound.

vol% or v/v% Volume percent. A measure of concentration that relies on relative volume rather than relative weight (mass).

volatility The tendency of the molecules of a substance to escape from the liquid phase and enter the gas phase. Liquids that have high volatility have high vapor pressure.

-W-

waste stream The complete flow of waste from domestic or industrial areas through to final disposal.

WMO World Meteorological Organization.

Chapter

13

13 References

13.1 List of References

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Appendix

A

A Process Safety Information

A.1 Technology of the Process

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

Process Description	**Operating Parameter Limits**
Feed materials	Pressure, temperature, flow rate
Chemistry	Maximum and minimum safe operating limits
Chemical kinetics (if relevant)	Maximum time at maximum and minimum limits
Intermediate products	Specialized Maintenance Requirements
Reactants/catalysts	
Utility requirements (steam, natural gas, merchant gases, special heat transfer media, etc.)	
Special circumstances (very high pressure, very high temperature, cryogenic temperatures, etc.)	
Potential runaway reactions	
Process Flow Diagram	
Major equipment items (name and item number)	
Heat and material balance	
Typical operating parameters	
Special alloys	
Utility requirements	
Piping specifications	
Pressure vessel specifications	

A.2 Equipment

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

Process Unit Description	Car-Sealed/Chain-Locked Valve List
Name of process unit	Valve number
Block diagram of unit operations	Valve description
Feed material, intermediates, products & intermediate product storage volume	Scenario safe-guarded against
Process Chemistry	Normal position
Strategy for recycling & processing off-spec material	Circumstances for changing position
Piping and instrument diagrams (P&IDs)	Scenario protected against
Piping specifications	Consequences of opening or closing
List of item-numbered equipment (including instrumentation)	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 with hazard classification zones
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 records	Operating procedures
Maintenance procedures	Safety systems (firewater, detectors, etc.)

Appendix

B

B Properties of Methanol/Methyl Alcohol

B.1 Physical Properties

CH_3OH

☐ Color	Colorless
☐ Opacity	Clear
☐ Odor	Faintly sweet, pungent odor like ethyl alcohol
☐ Odor Threshold	Odor threshold is highly variable in air and ranges over several orders of magnitude; 10 ppm to 20000 ppm. [12] 100 ppm to 1500 ppm reported [3] 141 ppm [56] 160 ppm – The range of accepted odor threshold values is quite broad. Caution should be used in relying on odor alone as a warning of potentially hazardous exposures. [48]
☐ Conversion factors	1 ppm = 1.33 mg/m^3; 1 mg/m^3 = 0.76 ppm

B.1.1 Solid

$CH_3OH_{(solid)}$	**$T < -98°C$ (-144°F); P = 1 atm (14.7 psia)**

B.1.2 Liquid

$CH_3OH_{(liquid)}$	**-98°C (-144°F) < T < 65°C (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^3
Vapor pressure @ PTotal=(14.7 psia)	12.3 kPa (96 mm Hg) 1.86 psia @ 20°C (68°F)
Vapor pressure @ PTotal=(760 mm Hg)	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
Electrical conductivity	4.4×10^7 pS/m

Vapor Pressure of Liquid:

P in mmHg	T in °C (°F)	P in mmHg	T in °C (°F)
1	-44.0 (-47)	1520	84.0 (183)
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

$CH_3OH_{(vapor)}$	**65°C (149°F) < T; P = 1 atm (14.7 psia)**
Relative density of vapor saturated air (air = 1)	1.01 @ 20°C (68°F) 1.02 @ 30°C (86°F)
Density of vapor relative to air (air = 1.0)	1.1
Viscosity	9.68 ∝Pa s @ 25°C (77°F) 13.2 ∝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^3/kg-mol
Critical density	0.2715 g/cm^3
Critical compressibility factor	0.224
Accentric factor	0.556
Henry's Law Constant	4.55 x 10^{-6} atm-m^3/g-mol
Airborne Saturation Concentration	166 g/m^3

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^3 @ 25°C (77°F) at 1 atm, 14.7 psia, 760 mm Hg

B.2 Chemical Properties

Chemical Name	Methanol
Chemical family	Aliphatic Alcohol
Chemical formula	CH_3OH
Molecular weight	32.04 grams/mole
Elemental composition by weight	
○ Oxygen	50.0 wt%
○ Carbon	37.5 wt%
○ Hydrogen	12.5 wt%
Solubility CH_3OH (liquid) in Water:	100%; miscible in all proportions
Solvents:	ethanol, ether, benzene, acetone, alcohol, chloroform
pH	7.2
Biological Oxygen Demand:	0.6 to 1.12 lbs/lb in 5 days

B.2.1 Reactivity

Flammable	May explode when exposed to flame
Stability	Stable material
Hazardous polymerization	Will not occur

B.2.2 Decomposition

Excessive heating and/or incomplete combustion will generate carbon dioxide, carbon monoxide, formaldehyde, and possibly unburned methanol.

B.2.3 Incompatibilities

- Methanol-water solutions at 40:60 concentration and methanol:water, 30:70 mixtures can be ignited by a static discharge. [93].
- Air, methanol-air mixtures at 1.81 bar (26.25 psia) and 120°C (248°F) may explode with or without the addition oxygen and water. [8]
- Explosive reaction with chloroform + sodium methoxide and diethyl zinc.
- Reacts violently and uncontrollably with strong reducing agents and dilute solutions of alkyl aluminum salts, diethyl zinc, acetyl bromide, cyanuric chloride.
- Incompatible with beryllium dihydride. Reaction with the ether-containing hydride is violent, even at -196°C (-321°F). [8].
- Reaction with alkali metals (sodium, potassium, magnesium) is vigorous, and often subject to a lengthy induction period. Mixtures with powdered MG or Al are capable of powerful detonation. Reaction with K may lead to an explosion.
- Methanol reacts violently with strong oxidizers (calcium hypochlorite, barium, perchlorates, peroxides, permanganates, chlorates); strong acids (nitric, hydrochloric, sulfuric); and halogen gases (bromine, chlorine, fluorine, and iodine).
- Reacts vigorously and dangerously with oxidizing materials.
- Methylene chloride may become flammable in the presence of small amounts of methanol.
- Reacts violently with liquid phosphorus (III) oxide above 24°C (75°F).
- Reaction of liquid methanol with solid potassium *tert*-Butoxide causes ignition after 2 minutes.

B.3 Corrosivity to Metals, Alloys, Gaskets and Plastic

Corrosivity points immediately to the issue of materials selection, which in turn points directly to application. What type of equipment is in question: pumps, piping, vessels, heat exchangers distillation towers, accumulators, reformer furnaces, strippers, etc.? What are the normal, abnormal, and emergency process conditions? What are maximum, minimum, and typical control parameters: flow, temperature, pressure, composition, impurities, etc.?

Is it a batch process or a continuous process? What is the anticipated inspection and testing schedule, the anticipated maintenance program, the intended service life? Given a particular selection, what are the anticipated failure modes and mechanisms?

All of these considerations enter into materials selection. The process is technically complex and organizationally difficult. The vast array of conditions and circumstances that fall within the purview of materials selection for methanol service means that the most appropriate material is based on the particular details of the specific application.

While issues pertaining to materials selection are fundamental and likely among the most often asked questions, there are no standard or universal answers. Recognizing this, the following guidance is provided as very general in nature. It is the responsibility of those asking the questions to search out the best answers for their particular circumstance.

- Pure anhydrous methanol is mildly corrosive to lead and aluminum alloys and more so to magnesium, and platinum. That is not to say that aluminum alloys are unfit for methanol service, but rather to alert users to the necessity of periodic inspection and nondestructive testing. Positive materials identification, inspection, and nondestructive testing are essential for fitness for continued service. This applies to all pressure boundary materials in all chemical services, including methanol. Rate of attack on aluminum alloys is typically a slow pitting form of corrosion; however, it can be accelerated to the point of compromising integrity of structural components if not anticipated and monitored.

  Methanol-water solutions can be corrosive to some non-ferrous alloys depending on application and environmental circumstances. This caution applies to equipment built with copper alloy, galvanized steel, titanium, aluminum alloy components, and some plastics and composites. Coatings of copper (and copper alloys), zinc (including galvanized steel), and aluminum exhibit corrosive degradation of various types and at various rates depending on circumstances accompanying application. In general, corrosive attack of structural components such as aluminum alloy floating roofs on storage tanks is slow; it requires periodic visual inspection and nondestructive testing to verify “fitness for continued service.” The same can be said for heat exchanger tube materials, pump components, valve trim, and sensing elements in direct contact with methanol.

- Mild steel is usually selected as the construction material, provided moisture is excluded from the system. If moisture and trace amounts of inorganic salts are expected to exist within the system from time to time, then one should consider upgrading from carbon steel to 316 L stainless steel or a titanium or molybdenum stabilized grade of 316 L stainless steel. The issue in the presence of moisture and inorganic salts is corrosion within weld-heat-affected zones. Weld integrity can become an issue.

- Best practice uses molybdenum-stabilized low carbon 300 series stainless steel. Though expensive, this material protects against generalized corrosion, pitting corrosion, stress corrosion cracking, hydrogen induced cracking, and product contamination. Mild steel is widely used for piping. Piping connections are made with welded flanges and methanol compatible gaskets. Threaded connections are not considered suitable in methanol service. Non-ferrous materials should not be used for the construction of permanent pipework. It is recommended that underground storage, buried pipelines, and underground piping be protected with a cathodic protection system and be inspected on a regular basis.

- Many resins, nylons, and rubbers, such as neoprene, nitrile (Buna-N), and ethylene propylene (EPDM), are suitable, though some are more suitable in flowing applications than others. Buna-N is NOT recommended by its manufacturers for dynamic applications (i.e., service in flowing methanol). Buna-N is satisfactory for fluid-static applications; however, it is not considered to be a superior material for methanol service.

- Fluorinated materials such as Teflon are used satisfactorily as equipment components in methanol service. Of these, Teflon offers good dimensional stability and is resistant to attack and degradation.

- Rubber hoses should have an internal wire coil for strength and electrical continuity. Use of hoses should be restricted to temporary applications, such as loading and unloading. Hose material must be compatible with methanol service. All hoses should be clearly labeled for methanol service only. Hose ends must be capped or otherwise protected to avoid contamination during storage. Hoses should be periodically replaced with new hoses, rather than kept in service to the point of failure.

- First-time hose and piping must be washed with water and then methanol to ensure that contaminants are removed before being placed in service.

- Methanex ranks compatibility of gasket and O-ring materials in methanol-fueled truck service in the following table.

Compatibility of Gasket and O-Ring Materials with Methanol[7]		
Gasket/O-Ring Material	**Rating[8] (Compatibility with Methanol Fuel in Truck Service)**	**Recommended[9], [10]**
Natural Rubber	Good	No Recommendation Given
EPDM (ethylene-propylene	Good	Yes, Recommended
Neoprene	Good	Yes, Recommended
Silicone	Good	Yes, Recommended
Kalrez	Good	Yes, Recommended
Teflon	Good	No Recommendation Given
Fluorosilicone	Good	No Recommendation Given
Buna-N	Fair	Not Recommended
Nitrile	Fair	Not Recommended
Polyurethane	Sometimes OK	No Recommendation Given
Butyl Rubber	Poor	No Recommendation Given
Butadiene	No Data	No Recommendation Given
Fluorocarbon	No Data	No Recommendation Given
VITON (most types)	No Ranking Given	Not Recommended

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[7] REFERENCE: efunda- engineering fundamentals; efunda.com; O—Ring Compatibility Guide

[8] Cautionary note regarding Buna-N & Ntrile: These materials may be adequate for static situations such as gloves to protect against methanol contact.These materials are generally not recommended for dynamic situations involving flowing methanol, such as gaskets on pumps and fittings.

[9] Note regarding VITON F: Most VITON types are not recommended for methanol service due to swelling of the material when exposed to methanol. However, VITON F shows only small changes when exposed to methanol. Manufacturers recommend use of VITON F for methanol service.

[10] REFERENCE: Daemar Inc. (daemar.com); Chemical Compatibility Chart

Methanol is one of the few specialized environments that may cause stress corrosion cracking (SCC) in titanium alloys. SCC failures have occurred in dry methanol, methanol/acid, and methanol/halide mixtures. Water is an effective inhibitor and will maintain the passivity of titanium in many environments if present in weight % concentrations. General guidance is provided in the following table.

Titanium Alloy Grade	wt % water Intermittent Exposure[a]	wt % Water Sustained Exposure[b]
1,2,7,11,16,17	1.5	2.0
9, 12	2.0	2.0
28	2.5	3.0
5, 23	3.0	3.0
19, 29, 6-2-4-6	5.0	10.0

[a]Intermittent exposure = short-term, noncontinuous exposure
[b]Sustained exposure = long-term, continuous exposure

B.4 Structure and Properties

☐	Index of refraction, nD	1.328 @ 20°C (68°F)
☐	Dielectric constant, εr	32.66 @ 20°C (68°F)
☐	Bond angle	all 109.5o
☐	Magnetic susceptibility	5.3 x 10-7 cm3/g
☐	Surface tension	22.5 dyn/cm @ 20°C (68°F)
☐	Viscosity	0.808 mPa’s @ 0°C (32°F)
☐		0.690 mPa’s @ 10°C (50°F)
☐		0.593 mPa’s @ 20°C (68°F)
☐		0.449 mPa’s @ 40°C (104°F)
☐		0.349 mPa’s @ 60°C (140°F)

B.5 Combustion and Ignition Properties

☐	Flash Point T at P = 1 atm (14.7 psia)	12°C (54°F) closed cup TCC method
☐		15.6°C (60.1°F) open cup TOC method
☐	Auto-ignition T at P = 1 atm (14.7 psia)	385°C (725°C)[11]
☐	Explosive Limits in air at ambient T and P	6-36 vol%[12],[13]

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[11] Methanex Corporation & Terra Industries among others indicate auto-ignition temperature as 464°C (867^{o}F).

[12] 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.

[13] The Upper Explosive Limit (UEL) of 36 vol% corresponds to a temperature of 41°C (106°F) and a vapor pressure of 274 mm Hg. The explosive range extends over a relatively wide range of temperatures and to a vapor pressure that is over a third of an atmosphere of pressure. Methanol produces an explosive mixture of vapor in air within the explosive range of 6 to 36 vol%. Precautions must be taken to insure that methanol vapors do not come in contact with a potential ignition source at vapor concentrations between 6 and 36 vol %.

☐	Explosive Range	30 vol%
☐	Flame	Non-luminous blue flame
☐		Not visible to naked eye in daylight
☐	Flammable Methanol-Water Mixtures:	Down to 21 vol% (25 wt%) methanol
☐	Stoichiometric air/fuel weight ratio	6.45
☐	CH3OH(vapor) in stoichiometric air/vapor mixture	12.3 vol%

B.5.1 Fire Extinguishing Media

☐ Carbon dioxide

☐ Dry chemical

☐ Alcohol-resistant foam – AR-AFFF with 6% proportioning with water

☐ Water mist or fog[14]

B.6 Thermodynamic Properties[15]

☐	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 ($\Delta_f H^{o}_{gas}$)	-205. ±10. kJ/mol
☐	Standard Enthalpy of Combustion Vapor ($\Delta_c H^{o}_{gas}$)	-763.68 ±0.20 kJ/mol
☐	Standard Enthalpy of Formation Liquid (ΔH^{o}_{liquid})	-238.4 kJ/mol
☐	Standard Enthalpy of Combustion Liquid ($\Delta_c H^{o}_{liquid}$)	-725.7 ±0.1 kJ/mol
☐	Standard Entropy of Liquid Phase (S^{o}_{liquid})	127.19 J/mol K
☐	Standard Entropy of Solid Phase (${}^{S}{}_{osolid, 1 bar}$)	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 (Δ_{fus} S)	12.5 J/mol K @ 176 K
☐	Enthalpy of Phase Transition ($\Delta H_{trs\ Xtline \rightarrow L}$)	3.159 kJ/mol @ 175.4 K
☐	Specific heat	2.51 kJ/kg K; 0.6 Btu/lb-°F
☐	Heat Capacity Ratio, γ = Cp/Cv	1.203 @ 77°C (171°F)
☐	High Heating Value (HHV)	22.7 MJ/kg, 9800 Btu/lb, 726 kJ/mole
☐	Low Heating Value (LHV)	19.937 MJ/kg @ 25 °C

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[14] 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.

[15] Methanex Corporation Web site: www.methanex.com/methanol/techsafetydata.htm; *Lange's Handbook of Chemistry*, 10th Edition, *CRC Handbook of Chemistry and Physics*, 44th Edition; *CRC Handbook of Chemistry and Physics*, 68th Edition; *Perry's Chemical Engineers' Handbook*, 6th Edition; James A. Plambeck, *University Chemistry: Molar Thermodynamic Properties of Pure Substances*, © 1995; Robert D. Goodwin, "Methanol Thermodynamic Properties from 176 to 673 K at Pressures to 700 bar," *Journal of Physical and Chemical Reference Data*, October 1987, Vol. 16, Issue 4, pp. 799-892.

Appendix

C

C Regulatory, Health, and Safety Information for Methanol

C.1 U.S. Regulations and Codes

This table lists the primary United States Federal OSHA, EPA, and DOT regulations that affect the production, storage, packaging, distribution, or use of methanol. This listing is not necessarily inclusive of all relevant regulations and codes. Relevant and applicable state and local codes and regulations for the particular facility should also be consulted.

Regulation/Code	Relevant Section or Part
Occupational Safety and Health, Code of Federal Regulations – 29 CFR	Part 1904 – Recordkeeping
	Section 1910.20 – Access to Exposure and Medical Records
	Section 1910.38 – Employee Emergency Plans and Fire Protection Plans
	Section 1910.119 – Process Safety Management of Highly Hazardous Chemicals
	Section 1910.120 – Hazardous Waste Operations and Emergency Response
	Section 1910.132 to 139 – Personal Protective Equipment
	Section 1910.146 – Confined Space Entry
	Section 1910.147 – Control of Hazardous Energy (Lockout/Tagout)
	Section 1910.151 – First Aid/Medical Service
	Section 1910.331 to 335 – Electrical Safety
	Section 1910.1000 – Air Contaminants (exposure limits)
	Section 1910.1200 – Hazard Communication

Regulation/Code	Relevant Section or Part
Environmental Regulations – 40 CFR	Part 61 – National Emissions Standards for Hazardous Air Pollutants
	Part 68 – 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 international regulations, standards, and guidance that affect the production, storage, packaging, distribution, or use of methanol. This listing is not necessarily inclusive of all relevant international regulations, standards, and guidelines; however, it is noteworthy that there is a growing consensus that hazards identification, risk assessment, and management of risk to tolerable levels is a fundamental requisite to worker safety. If your organization is not already applying principles of risk management, then you may want to make plans to do so in the near future.

Authority	Topic
European Union (EU)/European Commission (EC)	Control of Major-Accident Hazards Involving Dangerous Substances (Directive 96/82/EC)
Organization for Economic Cooperation and Development (OECD)	OECD Guiding Principles for Chemical Accident Prevention, Preparedness, and Response
EU/EC	Personal Protective Equipment Directive (Directive 89/686/EEC)
EU/EC	Health & Safety at Work (Directive 89/391/EEC)
EU/EC	Directive on Indicative Occupational Exposure Limit Values (DIR 2006/15/EC) & Chemical Agents at Work Directive (DIR 98/24/EC)
EU/EC	Dangerous Substances Directive (Directive 67/548/EEC)
EU/EC	Directive on Pollutant Release and Transfer Register (EC/166/2006); Integrated Pollution Prevention and Control (IPPC Directive: 96/61/EC); Management of Quality of Ambient Air (96/62/EC)
EU/EC	Water Framework Directive (Directive 2000/60/EC); Quality of Drinking Water (98/83/EC)
EU/EC	Directive on Waste (2006/12/EC); Controlled Management of Hazardous Waste (91/689/EEC)
EU/EC	Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) (EC/2006/1907)
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)

Authority	Topic
EU/EC	Transport of Dangerous Goods by Road (Directive 94/55/EC)
EU/EC	Transport of Dangerous Goods by Rail (Directive 96/49/EC)
EU/EC	Accidental Marine Pollution (2850/2000/EC); Maritime Safety: Prevention of Pollution from Ships (2002/84/EC); Protection of Groundwater Against Pollution (2006/118/EC)
International Standards Organization (ISO)	ISO 9001:2000 – Quality Management Systems
International Electrotechnical Commissions (IEC)	Functional Safety – Safety Instrumented Systems for the Process Industry Sector IEC 61511-1 • Part 1: Framework, definitions, system, hardware and software requirements • Part 2: Guidelines for the application of IEC 61511-1 • Part 3: Guidance for the determination of the required safety integrity levels
ANSI/AIHA Occupational Health and Safety Management Systems: Z10-2005	Sets a benchmark provision requiring that processes be in place to identify and take steps to prevent or otherwise control hazards and reduce risks associated with new processes or operations at the design stage.
Australian Safety and Compensation Council, Australian Government, 2006	Guidance on the Principles of Safe Design for Work
National Institute for Occupational Safety and Health (NIOSH), 2006	Announced an initiative on prevention through design.
American National Standards Institute (ANSI/PMMI) B155.1-2006	Safety Requirements for Packaging Machinery and Packaging-Related Converting Machinery
Society of Fire Protection Engineers (SFPE), 2006	• Engineering Guide to Application of Risk Assessment in Fire Protection Design • Introduction to Fire Risk Assessment
Occupational Health and Safety Management Systems standard issued by the Canadian Standards Association	CSA Z1000-2006
Industrial Safety and Health Act of Japan, rev. April 2006	Stipulates, without penalty, that employers should make an effort to implement risk assessment.
International Standardization Organization (ISO 14121-1)	Safety of Machinery – Principles for Risk Assessment, 2007

Authority	Topic
National Fire Protection Association (NFPA), 2007	Guidance Document for Incorporating Risk Concepts Into NFPA Codes and Standards
British Standards Institute BS-OHSAS 18001, 2007	Guidelines now read: “The organization shall establish, implement and maintain a procedure(s) for the ongoing hazard identification, risk assessment and determination of necessary controls.” The term *tolerable risk* was replaced by *acceptable risk.*
China’s State Administration of Work Safety, 2008	Published provisional regulations on risk assessment.
U..K. Health and Safety Executive, 2008	Issued five steps to risk assessment: “The law does not expect you to eliminate all risk, but you are required to protect people as far as is ‘reasonably practical.’”
Industry Committee for Emergency Lighting Ltd.	ICEL 1008: Emergency Lighting Risk Assessment
Institute for Research for Safety and Security at Work (Quebec, Canada), 2009	Machine Safety: Prevention of Mechanical Hazards
American Society of Safety Engineers (ASSE), 2009 Technical Report Z790.001	Prevention Through Design: Guidelines for Addressing Occupational Risks in the Design and Redesign Processes
Singapore Standard SS506, 2009	Occupational Safety and Health Management Systems, Part 1: Requirements
ANSI-ITAA GEIA-STD-0010, 2009	Standard Best Practices for System Safety Program Development and Execution
ISO/IEC 31010, 2009	Risk Assessment Techniques
EN ISO 12100-2010	Safety of Machinery: General Principles for Design Risk Assessment and Risk Reduction explicitly requires risk assessments
ANSI B11.0, 2010	Safety of Machinery: General Safety Requirements and Risk Assessments

C.3 Hazardous Material and Health & Safety Information

Hazardous Material Information	
European Inventory of Existing Commercial Substances (EINECS) No. (EU)	200-659-6
UN Number	UN 1230
Dangerous Goods Classification	
○ Primary Classification	3
○ Subsidiary Classification	6.1
○ Packing Group	PG II
ADR Classification (transport by road)	
○ Class	3
○ Packing	II
○ Danger Label Tanks	3+6.1
○ Danger Label Packages	3+6.1
RID Classification (transport by rail)	
○ Class	3
○ Packing	II
○ Danger Label Tanks	3+6.1
○ Danger Label Packages	3+6.1
ADNR Classification (transport by inland waterways)	
○ Class	3
○ Packing	II
○ Danger Label Tanks	3+6.1
○ Danger Label Packages	3+6.1
IMDG Classification (maritime transport)	
○ Class	3
○ Sub Risks	6.1
○ Packing	II
○ MFAG	19
ICAO Classification (air transport)	
Class	3
Sub Risks	6.1
Packing	II

Health & Safety Information	
Exposure Limits	
TLV-TWA	262 mg/m^3
	(200 ppm)
TLV-STEL	328 mg/m^3
	(250 ppm)
OES-LTEL	266 mg/m^3
	(200 ppm)
OES-STEL	333 mg/m^3
	(250 ppm)
MAK	270 mg/m^3
	(200 ppm)
MAC-TGG 8 h	260 mg/m^3
VME-8 h	260 mg/m^3
	(200 ppm)
VLE-15	1,300 mg/m^3
	(1000 ppm)
GWBB-8 h	266 mg/m^3
	(200 ppm)
GWK-15 min.	333 mg/m^3
	250 ppm
EC	260 mg/m^3
	(200 ppm)
NFPA Classification	1B Flammable Liquid
NFPA Hazard Rating	
○ Health	1
○ Flammability	3
○ Reactivity	0

Appendix

D

D Database of Methanol-Related Incidents (1998-2011)

D.1 Methanol Incidents by Sector, Location, and Cause

{Compiled for the Methanol Institute by Alliance Consulting International (8/12/2011)}

Sector	Location	Date	Type of Disaster	Cause	Activity	Damage/Injury/Fatality
Biodiesel	Staten Island, NY	6/3/2005	Fire	Hot work	Maintenance	Explosion, 1 fatality
Biodiesel	Bakersfield, CA	2/17/2006	Fire	Electrical	Maintenance	Burned 9,600 sq. ft. bldg
Biodiesel	Parker, CO	5/7/2006	Fire	Process	Operations	House fire, no injuries
Biodiesel	Canby, OR	6/23/2006	Fire	Spill	Operations	Large fire

Sector	Location	Date	Type of Disaster	Cause	Activity	Damage/Injury/Fatality
Biodiesel	New Plymouth, ID	7/7/2006	Explosion, Fire	Hot work	Maintenance	Large fire, one fatality
Biodiesel	Dayton, TX	7/14/2007	Fire	Unknown	Operations	Fire
Biodiesel	Augusta, GA	8/21/2007	Explosion	Hot work	Maintenance	Explosion, one fatality
Biodiesel	Lenoir, NC	8/25/2007	Fire	Unknown	Operations	Large fire – no injuries
Biodiesel	Princess Ann, MD	5/18/2008	Explosion	hot work	maintenance	Explosion, one fatality
Biodiesel	Decatur, TN	8/15/2008	Fire	Unknown	Unknown	Destroyed idled plant
Biodiesel	York, ND	8/27/2008	Fire	Unknown	Unknown	Processing building and equipment destroyed
Biodiesel	Gasdten, AL	9/15/2008	Explosion	Process	Maintenance	Top of tank blew off
Biodiesel	Clinton, IA	9/30/2008	Fire	Process	Operations	Small fire, one firefighter steam burn
Biodiesel	Houston, TX	2/9/2009	Fire	Process	Maintenance	Fire
Biodiesel	Brewster, MN	5/24/2009	Explosion, fire	Unknown	Unknown	Several tanks burned
Biodiesel	Toledo, OH	6/15/2009	Implosion, fire	Process	Maintenance	Destroyed one production line
Biodiesel	Chicago, IL	7/19/2009	Explosion	Process	Operations	Two workers burned
Biodiesel	St. Cloud, FL	9/24/2009	Explosion, fire	Unknown	Unknown	Destroyed one building and several tanks
Biodiesel	Savannah, GA	10/15/2009	Explosion	Process	Operations	One injury

Sector	Location	Date	Type of Disaster	Cause	Activity	Damage/Injury/Fatality
Biodiesel	Hoquiam, WA	12/2/2009	Explosion	Process	Operations	Tank split open
Biodiesel	Spanish Fork, UT	7/25/2010	Fire	Process	Maintenance	Small fire
Biodiesel	Melbourne, Australia	10/6/2010	Explosion	Hot work	Maintenance	One man seriously burned, tank exploded
Biodiesel	Summitville, TN	7/30/2011	Fire	Electrical	Operations	Biofuel plant destroyed, one minor burn
Commercial	Seattle, WA	7/21/2010	Explosion	Not intended	Not intended	One dead, one hospitalized
Home	Belleville, MO	4/13/2006	Fire	Not intended	Not intended	One juvenile seriously burned
Home	Brisbane, Australia	6/19/2007	Explosion, fire	Not intended	Not intended	Two juveniles seriously burned
Home	Syracuse, NY	9/19/2007	Fire	Not intended	Not intended	Two juveniles seriously burned
Home	Troy, OH	2/14/2011	Fire	Unknown	Unknown	House fire, no injuries
Industrial	Sydney, Australia	7/12/1998	Explosion, fire	Unknown	Unknown	Property damage
Industrial	Southbridge, MA	12/14/1998	Fire	Unknown	Unknown	One worker injured
Industrial	Green River, WY	1/29/2003	Fire	Unknown	Unknown	One injured with burns
Industrial	Buffalo , NY	10/13/2004	Spill	Unknown	Operations	Six employees were hospitalized.
Industrial	Sydney, Australia	5/2/2005	Fire	Unknown	Unknown	Extensive damage, no injuries

Sector	Location	Date	Type of Disaster	Cause	Activity	Damage/Injury/Fatality
Industrial	Angarsk, Russia	10/24/2005	Explosion, fire	Process	Operations	Damage to plant, one fatality
Industrial	Songmaping Town, China	11/10/2005	Explosion	Unknown	Unknown	Two fatalities
Industrial	Kuala Lumpur, Malaysia	2/28/2006	Explosion, fire	Unknown	Maintenance	Three killed, one hospitalized
Industrial	Cleveland, OH	4/20/2006	Explosion	hot work	Maintenance	Five hospitalized
Industrial	Quebec, Canada	8/30/2006	Explosion	Unknown	Unknown	Chemical plant part. destroyed
Industrial	Kuala Lumpur, Malaysia	8/27/2007	Explosion	Unknown	Unknown	Two workers burned
Industrial	Defiance, OH	1/4/2008	Explosion	Electrical	Maintenance	Four injured, plant shut down
Industrial	Kandla, India	2/8/2008	Fire	Unknown	Unknown	Prevented catastrophic fire
Industrial	North County, CA	10/3/2008	Fire	Unknown	Operations	Unknown
Industrial	Lafayette, LA	6/15/2009	Explosion, fire	Hot work	Maintenance	One injured with burns, $500 damage to platform
Industrial	Longview, NC	1/24/2010	Explosion, fire	Unknown	Unknown	Damage to plant, no injuries
Industrial	Kuala Lumpur, Malaysia	2/22/2010	Explosion	Unknown	Unknown	Damage to plant – no injuries
Industrial	Belle, WV	9/21/2010	Spill	Spill	Maintenance	>160,000 lbs MeOH spilled in Kanawha River
Industrial	Erie, PA	10/14/2010	Fire	Unknown	Operations	Unknown

Sector	Location	Date	Type of Disaster	Cause	Activity	Damage/Injury/Fatality
Industrial	Sterling, CO	2/3/2011	Fire	Hot work	Maintenance	1.5 ton truck caught fire – no injured
Industrial	New Iberia, LA	6/14/2011	Explosion, fire	Unknown	Unknown	Plant destroyed, no injuries
Industrial	Bernay, France	7/5/2011	Explosion	Unknown	Unknown	No injuries
Industrial	Pearland, TX	7/18/2011	Fire	Unknown	Unknown	Chemical plant tanks – no injuries
Pipeline	Jal, N.M.	12/7/2000	Fire	Process	Maintenance	Unknown
Pipeline	Prudhoe Bay, AK	2/7/2005	Spill	Process	Maintenance	1,092 gallon methanol-water spill
Pipeline	Deadhorse, AK	10/15/2007	Spill	Process	Operations	1,932 gallon methanol (630 gll neat); water, oil
Pipeline	Lisburne, Alaska	7/16/2011	Spill	Process	Maintenance	4,200 gallon methanol-oil spill on tundra
School	Akron, OH	1/25/2006	Fire	Not intended	Not intended	Six students, one teacher seriously injured
School	Huntsville, TN	10/8/2007	Explosion, fire	Not intended	Not intended	Teacher, two students hospitalized
School	Hudson, OH	1/18/2008	Fire	Not intended	Not intended	Two students seriously burned
Transportation	Kiel, WI	1/17/2000	Spill	Collision	Operations	No injuries
Transportation	Toledo, OH	3/15/2001	Spill	Spill	Operations	Unknown
Transportation	Hoganas, Sweden	10/12/2011	Ship ran aground	Collision	Operations	Hull damaged, but no spill
Transportation	Vercelli, Italy	8/22/2002	Fire	Collision	Operations	Property damage

Sector	Location	Date	Type of Disaster	Cause	Activity	Damage/Injury/Fatality
Transportation	Ontario, Canada	2/13/2003	Spill	Collision	Operations	Unknown
Transportation	Leghorn, Italy	3/22/2003	Explosion, fire	Collision	Operations	Nine people injured
Transportation	Red Wing, Mn	4/5/2003	Spill	Collision	Operations	Derailment with minor spill
Transportation	Uberaba, Brazil	6/13/2003	Fire, Spill		Operations	Property damage
Transportation	Jiangshan City, China	7/13/2003	Explosion, fire		Operations	Property damage
Transportation	Edmonton, Canada	10/8/2005	Spill	Collision	Operations	Unknown
Transportation	Schwerte, Germany	10/22/2005	Derailment	Collision	Operations	No spills or damage
Transportation	Shenyang, China	1/27/2006	Fire	Hot work	Maintenance	Unknown
Transportation	Butler Township , MI	7/30/2006	Explosion	Process	Operations	One fatality
Transportation	Jingjiang City, China	8/15/2006	Explosion, fire	Unknown	Unknown	Damage to barges
Transportation	Devon, Africa	10/9/2006	Collision	Collision	Operations	Five fatalities
Transportation	Johannesburg, South Africa	10/10/2006	Collision, fire	Collision	Operations	Five people incinerated, one burned
Transportation	Albany, NY	1/5/2007	Collision, fire	Collision	Operations	50 home evacuated
Transportation	Wuhan, China	9/2/2007	Fire	Unknown	Unknown	Unknown

Sector	Location	Date	Type of Disaster	Cause	Activity	Damage/Injury/Fatality
Transportation	Bloomfield Hills, MI	12/27/2007	Spill	Collision	Operations	Minor spill
Transportation	Stamford, CT	11/12/2009	Fire	Collision	Maintenance	Tanker burned with 6,800 gll MeOH-no injuries
Transportation	Stamford, CT	6/13/2011	Turnover	Collision	Operations	No spills or damage
Transportation	Beijing-Xinjiang, China	7/4/2011	Fire	Collision	Operations	Two trucks burned-Two fatalities (drivers)
Wastewater Treatment	Daytona Beach, FL	1/11/2006	Explosion	Hot work	Maintenance	Two dead, one severely burned

D.2 Incident Description and Reference or Source

Sector	Location	Date	Incident Description	Reference or Source
Biodiesel	Staten Island, NY	6/2/2001	Grinding on glycerin tank at Environmental Alternatives	http://www.rebelwolf.com/essn/ESSN-Jul2005.pdf
Biodiesel	Bakersfield, CA	2/16/2002	MeOH tote ignited by electricity, fire	http://biodieselmagazine.com/articles/830/fire-destroys-american-biofuels-facility-in-bakersfield-calif.
Biodiesel	Parker, CO	5/6/2002	Home biodiesel maker left heating element on tank	http://www.cdc.gov/mmwr/preview/mmwrhtml/mm5545a3.htm

Sector	Location	Date	Incident Description	Reference or Source
Biodiesel	Canby, OR	6/22/2002	Spill ignited and melted plastic MeOH tanks	Biodiesel Safety White Paper
Biodiesel	New Plymouth, ID	7/6/2002	Welding sparks explosion	http://www.fox12idaho.com/Global/story.asp?S=5162251&nav=menu439_2
Biodiesel	Dayton, TX	7/13/2003	MeOH spill, ignition	Biodiesel Safety White Paper
Biodiesel	Augusta, GA	8/20/2003	Welding on top of tank	Biodiesel Safety White Paper
Biodiesel	Lenoir, NC	8/24/2003	Tanks destroyed after shut down	Biodiesel Safety White Paper
Biodiesel	Princess Ann, MD	5/17/2004	Welding	Biodiesel Safety White Paper
Biodiesel	Decatur, TN	8/14/2004	Unknown	Biodiesel Safety White Paper
Biodiesel	York, ND	8/26/2004	Unknown	Biodiesel Safety White Paper
Biodiesel	Gasdten, AL	9/14/2004	Faulty heating element of biodiesel equipment	Biodiesel Safety White Paper
Biodiesel	Clinton, IA	9/29/2004	Small fire in primary biodiesel recovery column	Biodiesel Safety White Paper
Biodiesel	Houston, TX	2/8/2005	Circulation pump mechanical seal failure	Biodiesel Safety White Paper
Biodiesel	Brewster, MN	5/23/2005	Unknown	Biodiesel Safety White Paper

Sector	Location	Date	Incident Description	Reference or Source
Biodiesel	Toledo, OH	6/14/2005	Faulty vacuum control safety valve ignited biodiesel	Biodiesel Safety White Paper
Biodiesel	Chicago, IL	7/18/2005	Mixing glycerin and sulfuric acid-Columbus Food Co.	http://www.chitowndailynews.org/Chicago_news/OSHA_launches_investigation_at_plant_that_exploded,30103
Biodiesel	St. Cloud, FL	9/23/2005	Unknown, possibly lightning	Biodiesel Safety White Paper
Biodiesel	Savannah, GA	10/14/2005	Reactor used to store biodiesel	Biodiesel Safety White Paper
Biodiesel	Hoquiam, WA	12/1/2005	Glycerin tank overpressurization	Biodiesel Safety White Paper
Biodiesel	Spanish Fork, UT	7/24/2006	MeOh transfer line failure	Biodiesel Safety White Paper
Biodiesel	Melbourne, Australia	10/5/2006	Welding on top of tank	http://www.heraldsun.com.au/news/victoria/man-critical-after-factory-explosion/story-e6frf7kx-1225934873475
Biodiesel	Summitville, TN	7/29/2007	Motor sparked methanol tank	http://www.wkrn.com/story/15181803/bio-diesel-plant-destroyed-in-fire?clienttype=printable
Commercial	Seattle, WA	7/20/2006	Intentional ignition while riding a barrel with MeOH	http://www.komonews.com/news/local/98960929.html
Home	Belleville, MO	4/12/2002	MeOH fuel for toy caused fire	http://www.evesun.com/printedition/pdfs/2007-09-19.pdf
Home	Brisbane, Australia	6/18/2003	Playing with MeOH and fire; explosion	Eos Environmental
Home	Syracuse, NY	9/18/2003	MeOH mixture caught fire, traced back to fuel	Eos Environmental

Sector	Location	Date	Incident Description	Reference or Source
Home	Troy, OH	2/13/2007	Unknown-150 gll MeOH for racecars in garage	http://www.whiotv.com/news/26854632/detail.html
Industrial	Sydney, Australia	7/11/1994	Chemicals involved included ethanol, methanol and white spirits – unknown	http://www.fireworld.com/incident_logs/incident_log2.php?table=incidents&cmd=search&mode=normal&month=08&year=2011&submit=List
Industrial	Southbridge, MA	12/13/1994	Methanol fire at a plant specializing in fiber optics – unknown	http://www.fireworld.com/incident_logs/incident_log2.php?table=incidents&cmd=search&mode=normal&month=08&year=2011&submit=List
Industrial	Green River, WY	1/28/1999	Unknown – Flash fire on well site	http://www.fireworld.com/incident_logs/incident_log2.php?table=incidents&cmd=search&mode=normal&month=08&year=2011&submit=List
Industrial	Buffalo , NY	10/12/2000	A mixture of acetonitrile and methanol spilled at a medical supply manufacturing company	http://www.fireworld.com/incident_logs/incident_log2.php?table=incidents&cmd=search&mode=normal&month=08&year=2011&submit=List
Industrial	Sydney, Australia	5/1/2001	Unknown - gas furnace with methanol	http://ctif-hazmat.gasilci.org/modules/news/article.php?storyid=36
Industrial	Angarsk, Russia	10/23/2001	Angarsk Petrochemical-process upset	http://www.icis.com/Articles/2005/10/24/1015565/russias-angarsk-methanol-plant-hit-by-explosion.html
Industrial	Songmaping Town, China	11/9/2001	Unknown	http://www.fireworld.com/incident_logs/incident_log2.php?table=incidents&cmd=search&mode=normal&month=08&year=2011&submit=List
Industrial	Kuala Lumpur, Malaysia	2/27/2002	MeOH tank exploded during maintenance	Eos Environmental

Sector	Location	Date	Incident Description	Reference or Source
Industrial	Cleveland, OH	4/19/2002	Hot work on catwalk over MeOH tank sparked explosion	Eos Environmental
Industrial	Quebec, Canada	8/29/2002	Spark caused explosion, fire – unknown	Eos Environmental
Industrial	Kuala Lumpur, Malaysia	8/26/2003	Unknown-Petronas Methanol plant	http://www.koreanpress.net/news/view.asp?msection=1&ssection=2&idx=598
Industrial	Defiance, OH	1/3/2004	MeOH vapors ignited in warehouse from garage opener	Eos Environmental
Industrial	Kandla, India	2/7/2004	Unknown – methanol tank caught fire-dowsed with seawater	Eos Environmental
Industrial	North County, CA	10/2/2004	Small quantity of methanol caught fire in an oven at medical diagnostic equipment facility – unknown	http://www.fireworld.com/incident_logs/incident_log2.php?table=incidents&cmd=search&mode=normal&month=08&year=2011&submit=List
Industrial	Lafayette, LA	6/14/2005	Welding on offshore platform tank-Mariner Energy	http://blog.chron.com/newswatchenergy/2010/09/mariner-involved-in-13-gulf-accidents-since-06-seven-with-violations/
Industrial	Longview, NC	1/23/2006	Tailored Chemicals – unknown origin – stores MeOH and ethanol	http://firenews.net/index.php/news/news_article/20100126_news_four_alarm_fire_at_local_catawba_plant/
Industrial	Kuala Lumpur, Malaysia	2/21/2006	Unknown – Petronas Methanol plant	http://uk.reuters.com/article/2010/02/22/petronas-fire-idUKSGE61L0E520100222

Sector	Location	Date	Incident Description	Reference or Source
Industrial	Belle, WV	9/20/2006	Leaking equipment	http://www.newsandsentinel.com/page/content.detail/id/118720/W-Va--DEP-investigates-methanol-spill-in-river-.html?isap=1&nav=5071
Industrial	Erie, PA	10/13/2006	Methanol fumes ignited and flared out a vent stack at a foundry	http://www.fireworld.com/incident_logs/incident_log2.php?table=incidents&cmd=search&mode=normal&month=08&year=2011&submit=List
Industrial	Sterling, CO	2/2/2007	Using torch to remove bolts from water-methanol tank	http://www.journal-advocate.com/sterling-local_news/ci_17283330
Industrial	New Iberia, LA	6/13/2007	Multichem plant with MeOH, xylene, toluene – unknown	http://www.nola.com/business/index.ssf/2011/06/firefighting_crews_enter_new_i.html
Industrial	Bernay, France	7/4/2007	Unknown cause for methanol solvent tank at Ceisa Packaging	http://www.saunalahti.fi/ility/PI1127.htm
Industrial	Pearland, TX	7/17/2007	Unknown – tanks with methanol-mineral oil	http://www.yourhoustonnews.com/pearland/news/article_c2b4f932-615c-5066-92d5-56efd0921d0b.html
Pipeline	Jal, N.M.	12/6/1996	NG pipeline ruptured and burst into flames, igniting two tanks filled with methanol and glycol at a gasoline refinery	http://www.fireworld.com/incident_logs/incident_log2.php?table=incidents&cmd=search&mode=normal&month=08&year=2011&submit=List
Pipeline	Prudhoe Bay, AK	2/6/2001	Corrosion of DS 11 injection line, lack of isolation	http://www.dec.state.ak.us/spar/perp/response/sum_fy05/050217301/050217301_index.htm
Pipeline	Deadhorse, AK	10/14/2003	Strike punctured DS-16 flowline D	http://www.dec.state.ak.us/spar/perp/response/sum_fy08/071015301/071015301_index.htm

Sector	Location	Date	Incident Description	Reference or Source
Pipeline	Lisburne, Alaska	7/15/2007	BP pipeline failed during valve pressure test for maintenance	http://www.msnbc.msn.com/id/43795063/ns/us_news-environment/t/methanol-spill-reported-bp-alaska-oil-field/
School	Akron, OH	1/24/2002	MeOH vapor ignition	http://www.ohio.com/news/students-burned-in-lab-fire-settle-1.87719
School	Huntsville, TN	10/7/2003	MeOH demonstration caused beaker explosion, fire	Eos Environmental
School	Hudson, OH	1/17/2004	HS Chemistry expt; fire	Eos Environmental
Transportation	Kiel, WI	1/16/1996	Spill after railroad tanker car derailed and overturned	http://www.fireworld.com/incident_logs/incident_log2.php?table=incidents&cmd=search&mode=normal&month=08&year=2011&submit=List
Transportation	Toledo, OH	3/14/1997	Small amount of methanol leaking into rail yard from a tank car	http://www.fireworld.com/incident_logs/incident_log2.php?table=incidents&cmd=search&mode=normal&month=08&year=2011&submit=List
Transportation	Hoganas, Sweden	10/11/1997	Ship with 3,000 T MeOH ran aground in heavy fog	http://info.tse.fi/dagob/documents/Dangerous%20Goods%20Related%20Incidents%20and%20Accidents%20in%20the%20Baltic%20Sea%20Region%20PDF%20final.pdf
Transportation	Vercelli, Italy	8/21/1998	Freight train containing methanol derailed, ruptured and burned	http://www.fireworld.com/incident_logs/incident_log2.php?table=incidents&cmd=search&mode=normal&month=08&year=2011&submit=List
Transportation	Ontario, Canada	2/12/1999	Freight cars carrying methanol gas and styrene derailed and leaked	http://www.fireworld.com/incident_logs/incident_log2.php?table=incidents&cmd=search&mode=normal&month=08&year=2011&submit=List

Sector	Location	Date	Incident Description	Reference or Source
Transportation	Leghorn, Italy	3/21/1999	Ship bumped up against the dock while being towed	http://www.fireworld.com/incident_logs/incident_log2.php?table=incidents&cmd=search&mode=normal&month=08&year=2011&submit=List
Transportation	Red Wing, Mn	4/4/1999	Train carrying methanol derailed	http://www.fireworld.com/incident_logs/incident_log2.php?table=incidents&cmd=search&mode=normal&month=08&year=2011&submit=List
Transportation	Uberaba, Brazil	6/12/1999	Train derailment into a river and igniting a large fire. Methanol leaked into the river	http://www.fireworld.com/incident_logs/incident_log2.php?table=incidents&cmd=search&mode=normal&month=08&year=2011&submit=List
Transportation	Jiangshan City, China	7/12/1999	Collision involving a truck loaded with coal and a train carrying methanol	http://www.fireworld.com/incident_logs/incident_log2.php?table=incidents&cmd=search&mode=normal&month=08&year=2011&submit=List
Transportation	Edmonton, Canada	10/7/2001	A tanker truck making u-turn and punctured a tank, releasing methanol	http://www.fireworld.com/incident_logs/incident_log2.php?table=incidents&cmd=search&mode=normal&month=08&year=2011&submit=List
Transportation	Schwerte, Germany	10/21/2001	Three methanol rail tank cars derailed	http://info.tse.fi/dagob/documents/Dangerous%20Goods%20Related%20Incidents%20and%20Accidents%20in%20the%20Baltic%20Sea%20Region%20PDF%20final.pdf
Transportation	Shenyang, China	1/26/2002	Methanol truck caught fire after the driver was heating a frozen valve at a warehouse	http://www.fireworld.com/incident_logs/incident_log2.php?table=incidents&cmd=search&mode=normal&month=08&year=2011&submit=List
Transportation	Butler Township , MI	7/29/2002	A worker pouring methanol sparked caused an explosion	http://www.fireworld.com/incident_logs/incident_log2.php?table=incidents&cmd=search&mode=normal&month=08&year=2011&submit=List

Sector	Location	Date	Incident Description	Reference or Source
Transportation	Jingjiang City, China	8/14/2002	Unknown – two barges loaded with methanol caught fire	http://www.fireworld.com/incident_logs/incident_log2.php?table=incidents&cmd=search&mode=normal&month=08&year=2011&submit=List
Transportation	Devon, Africa	10/8/2002	Car collided with methanol truck	http://www.fireworld.com/incident_logs/incident_log2.php?table=incidents&cmd=search&mode=normal&month=08&year=2011&submit=List
Transportation	Johannesburg, South Africa	10/9/2002	MeOH tanker collides w/vehicle and catches fire	Eos Environmental
Transportation	Albany, NY	1/4/2003	CSX MeOH railcar caught fire	Eos Environmental
Transportation	Wuhan, China	9/1/2003	Unknown – fire spread through four vessels carrying methanol at a pier	http://www.fireworld.com/incident_logs/incident_log2.php?table=incidents&cmd=search&mode=normal&month=08&year=2011&submit=List
Transportation	Bloomfield Hills, MI	12/26/2003	A tanker carrying methanol overturned, causing a small spill	http://www.fireworld.com/incident_logs/incident_log2.php?table=incidents&cmd=search&mode=normal&month=08&year=2011&submit=List
Transportation	Stamford, CT	11/11/2005	Tanker truck caught fire from tire malfunction	http://www.local830.org/index.cfm?zone=/unionactive/view_article.cfm&HomeID=144049&page=200920Incident20Archive
Transportation	Stamford, CT	6/12/2007	Tanker truck overturned with 8,000 gll MeOH	http://www.wtnh.com/dpp/news/fairfield_cty/tanker-carrying-methanol-closes-i-95-northbound-in-stamford
Transportation	Beijing-Xinjiang, China	7/3/2007	Truck collision with 30-ton MeOH truck	http://www.globaltimes.cn/NEWS/tabid/99/articleType/ArticleView/articleId/664422/2-truckers-killed-in-fiery-crash.aspx
Wastewater Treatment	Daytona Beach, FL	1/10/2002	Hot-work ignited MeOH vapors	Eos Environmental

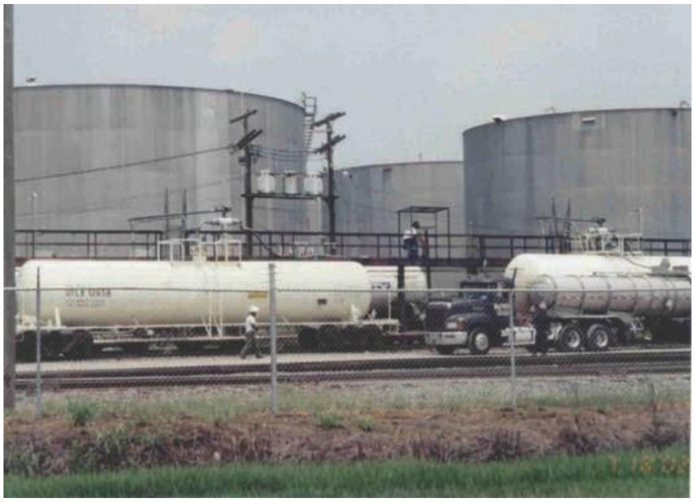
E Technical Bulletins

Methanol Safe Handling

TECHNICAL BULLETIN

Methanol Institute

Precautions for Loading, Unloading, Transport and Storage of Methanol



Methanol requires that handlers pay particular attention to two specific hazards in order to avoid accidental release and ignition of methanol and methanol mixtures: 1.) accidental combustion hazard, and 2.) accelerated corrosion of common containment alloys.

Hazards associated with loading, unloading, rail and road transport, and tank storage of methanol are essentially the same regardless of intended use. The severity of the hazards varies depending on circumstances and ambient conditions. For example, accidental release of methanol from pressurized piping causes immediate liquid flashing and vapor generation. Accidental release of methanol from a gravity transfer system results in liquid pooling and substantially less vapor generation. Combustion and corrosion hazards are always present to a greater or lesser extent when handling methanol.

BEST PRACTICE

Best practice for loading, unloading, transporting, and storing methanol is determined by inherent hazards of methanol, and by circumstances associated with blending and handling, and by considerations whih accompany potential accidental release. In order to prevent fire, practices for loading, unloading, transporting, and storing methanol should consider taking the following precautions:

1) Avoid accumulation and subsequent discharge of static electricity within low methanol concentration blends which may result from turbulence:

   a) Control flow rate into and out of containers to minimize turbulence and avoid accumulation of static electricity within the flowing liquid;[1]

   b) Discharge through a liquid seal dip leg pipe rather by free-falling through air to prevent air entrainment,

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[1] Methanol is not a static accumulator. This is recognized by the American Petroleum Institute (API) in recommended Practice 2003 (API-RP-2003) Protection Against Ignitions Arising out of Static, Lightning and Stray Currents which states in part that in most situations when water-soluble liquids (such as alcohols) are handled in grounded conductive equipment they “do not accumulate electrostatic charges because of their relatively high electrical conductivity (greater than 50 picosiemens per meter)”. API-RP-2003 also states that the necessary precautions for prevent build-up of static charge “do not apply to the loading of water-soluble products such as alcohols. These materials do not accumulate hazardous static charge.” The APRP-2003 stipulates that the accumulation of electric charge is likely if the electrical conductivity of the liquid is below 50 picosiemens per meter. However, the electrical conductivity of methanol is considerably greater than 50 picosiemens per meter. A value for pure methanol has been reported as 150,000 picosiemens per meter (Commercial Solvents Corporation). Values measured for commercial grade methanol have been in the range of 2 X 106 to 2 X 107 picosiemens per meter (Methanex).

absorption of moisture, and accumulation of static electricity in the falling liquid;, Bond and ground tanks, vessels, containers, and associated piping,

c) Avoid switch loading with gasoline, diesel, and other petroleum products that have bulk electrical conductivities less than 50 picosiemens per meter.

2) Isolate liquid and vapors from recognizable ignition sources (electrically-caused sparking, electrically-generated hot spots, welding, brazing, grinding, oxy-acetylene cutting, air-arc gouging, internal combustion engines, space heaters, etc.) to a radial distance of 50 feet.

OR

3) Prevent contact with air (oxygen) by padding free board in vessels tanks and containers with inert gas (e.g., nitrogen). International Maritime Organization (IMO) regulations make padding a requirement for individual vessel tanks 3000 m^3 or larger. Consider using a combination of gravity and pressure transfer using nitrogen rather than pump transfer.

4) Cordon the area surrounding transfer to a radial distance of 50 feet and use caution tape and signage indicating presence of a flammable hazard.

5) Seal drains and sewers to a distance of 50 feet or more as appropriate. Methanol spills may create flammable mixtures of vapor in air as they run down hill and pool.

6) Use appropriate personal protection equipment.

Physical properties of methanol are available in Appendix B of the Methanol Institute's *Methanol Safe Handling Manual.*

COMBUSTION

Combustion is the most widely recognized hazard associated with methanol. Ignition and sustained combustion occur in the vapor phase immediately above a liquid surface: vapors burn; liquids do not. Conditions capable of supporting combustion are determined by the partial pressure of methanol vapor above a liquid, and the relative molar concentration of methanol vapor in surrounding air. Methanol vapor/air mixtures with concentrations between the flammability limits will burn in a sustained manner if ignited. Ignition energy of methanol is similar to that for gasoline boiling-range fuels.

A uniform mixture of methanol and air at ambient temperature and pressure, and above the upper flammability limit is too rich to burn because there is insufficient oxygen to support combustion. Similarly, if the methanol vapor in air is below the lower flammability limit, then combustion cannot be sustained because there is insufficient fuel. In this case the mixture is too lean to burn. If the concentration of methanol vapor in air is within the flammability range, then ignition and sustained combustion are expected to occur in the presence of a sufficiently energetic ignition source.

It is particularly important to understand the principles of hazard control for methanol because methanol, a weakly polar flammable chemical, is 100% miscible in water. The attraction between water vapor and methanol liquid is so great that methanol is an effective desiccant for removing moisture from air.

Precautions for Loading, Unloading, Transport and Storage of Methanol *(Continued)*

The affinity between water and methanol requires special fire fighting techniques when responding to methanol fires. Because the partial pressure of methanol vapor is high compared to that of water vapor in methanol/water solutions , these solutions will burn at concentrations which are 70% water. Water may or may not act as an effective extinguishing medium for methanol fires, depending on circumstances. For example, a mist or fine spray generated by a loading rack spray curtain may knock methanol molecules out of the air above a pool fire, reducing the further spread of flames. Application of water as a pressurized stream from a nozzle or water cannon may create “running fires” in methanol gasoline blends, which may be doubly hazardous because methanol flames are difficult to see in bright sunlight, and because uncontrolled addition of water may cause a fire to spread rapidly and unpredictably.

CORROSION

Corrosion is a second hazard resulting from the affinity between methanol and water. Air-absorbed moisture in the presence of inorganic salts causes methanol to be unexpectedly corrosive to carbon steel alloys which are commonly used for containment. Methanol containment systems require special provisions for corrosion monitoring, crack detection around high stress welded joints, and nondestructive inspection of anomalous conditions which are subject to crevice and pitting-types of corrosion. This is true for storage, transport and piping systems. Pipelines may also be subject to accelerated localized corrosion if used to transport methanol or methanol/gasoline blends.

Methanol Safe Handling
TECHNICAL BULLETIN

Atmospheric Above Ground Tank Storage of Methanol

INTRODUCTION

Guidelines for designing, fabricating, constructing, repairing, and safeguarding above-ground methanol storage tanks is essentially the same as that for liquid transportation fuels such as ethanol and gasoline, and flammable liquid feed stocks such as benzene, acetone, and toluene. However, physical and chemical properties of methanol are unique to methanol and are not the same as those of other bulk-stored flammable liquids. Some considerations of tank storage are unique to methanol.

One important consideration is flammability range. Because the upper flammability limit of methanol is 36 percent by volume (vol%) compared to that of gasoline which is 6-7 vol%, methanol vapor can ignite and burn inside tank vapor space.

Corrosion is another consideration. Methanol is a conductive polar solvent; gasoline is a non-conductive, non-polar solvent. Galvanic and dissimilar metal corrosion in methanol service may be high if incompatible materials are placed in electrical contact with one another. Cathodic protection, and regulator inspection of methanol storage tanks and trim hardware is vitally important to avoid corrosion failure.

Principal considerations of tank storage of methanol are siting, liquid and vapor containment, electrical grounding, cathodic protection, protection from stray currents, in-tank vapor control, vapor space fire suppression, and management of inhalation, ingestion, and dermal contact.

Methanol Institute recommends that users familiarize themselves with relevant codes and standards, and devise and implement a disciplined layers of protection program to prevent spills, accidental release, overpressure, ignition, and fire suppression. It is essential that fire detection, alarm, response, and suppression be rapid and effective.

Guidance for design, fabrication, construction, and tank safety are available in American Petroleum Institute (API) publications:

- API Standard 620, *Design and Construction of Large, Welded, Low-Pressure Storage Tanks*
- API Standard 653, *Tank Inspection, Repair, Alteration, and Reconstruction.*

Provisions for siting, electrical grounding, berming, and safeguarding above ground storage tanks containing flammable liquids are given by the International Code Council (ICC) and the National Fire Protection Agency (NFPA). Guidelines are available in:

- NFPA 1 *Uniform Fire Code*
- NFPA 30, *Flammable and Combustible Liquids Code.*

Considerations not addressed in the above-sited references are specific to methanol storage, namely,

- Materials selection
- Purity protection
- Fire prevention, suppression and spill containment.

TANK MATERIALS OF CONSTRUCTION & TRIM MATERIALS COMPATIBILITY

Methanol is classified by the International Code Council and the National Fire Protection Agency as a class IB flammable liquid. Other IB liquids are ethanol, hydrocarbon fuels such as gasoline and kerosene, and reactants such as benzene, acetone, and toluene. No. 1 diesel, No. 2 diesel, and biodiesel are classified as combustible motor fuels, and are also handled and stored in above ground atmospheric storage tanks.

Methanol gasoline fuel blends are subject to phase separation in the presence of water. Methanol and water, two polar compounds, form a mixture which separates from gasoline, a non-polar mixture of C_4 thru C_{12} hydrocarbons. Methanol boils at 149 °F; gasoline boils over a range of temperatures extending from < 140 to 390 °F.

Methanol tanks can be constructed of either carbon steel or 300 series austenitic stainless steel. Carbon steel has the advantage of lower capital cost, but the disadvantage of higher life cycle cost due to increased maintenance and costs associated with corrosion protection. Because methanol is a polar solvent, galvanic corrosion is more prevalent with methanol than with other commonly-used motor fuels.

Because of its very high affinity to form mixtures with water, methanol is hygroscopic and extracts moisture from ambient air that enters tank vapor space during normal liquid level cycling. In the presence of neat or technical grade methanol, the small amount of water added by desiccation of atmospheric air does not substantially increase the rate of general corrosion. Never-the-less, because of the relatively high conductivity of liquid methanol, corrosion induced failures of carbon steel tanks have been reported. Efforts to coat interior tank surfaces with epoxy resin have met with limited success. Typical coating life is less than seven years, and the coatings tend to form an electrically non-conductive barrier between the methanol and the tank, thereby complicating bonding and grounding. Recent reports indicate progress is being made in developing more suitable electrically conductive spray-on tank liner coatings.

Galvanic corrosion of dissimilar trim materials may be accelerated in methanol service, particularly trim materials of aluminum, lead, magnesium, copper, zinc and platinum alloys. An example of this resulted in a methanol tank fire when the aluminum alloy flame_arrester corroded to the point of being non-functional. “The Chemical Safety Board concluded that the flame arrester did not prevent the fire outside the tank from igniting the tank contents. Routine inspections would have detected the corrosion in the flame_arrester that occurred over 12 years. The use of an aluminum flame arrester in methanol service coupled with the lack of inspection and maintenance allowed the flame arrester to corrode to the point that it no longer functioned.”

Galvanized steel is not suitable for methanol service.

If the methanol-water mixture forms within a gasoline-methanol blend and separates from the gasoline as a separate phase, then localized corrosion may be accelerated. If the water phase accumulates chloride salts due to proximity to a coastal environment, then under-deposit corrosion, localized pitting corrosion, and crevice corrosion may be accelerated. In extreme cases, stress corrosion cracking (SCC) of high carbon, non-molybdenum stabilized austenitic stainless steel weld heat- affected zones may result due to localized exposure to water containing high concentrations of chlorides.

Atmospheric Above Ground Tank Storage of Methanol *(Continued)*

Methanol is one of the few specialized environments, which may cause 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 alloys in some environments.

Titanium Alloy Grade	**%water- Intermittent exposure**[1]	**% 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

[1] Intermittent exposure is short term non-continuous contact; sustained exposure is long term continuous contact.

Where-as, SCC has been observed in ethanol tanks, this phenomenon has not been reported for methanol service. Never-the-less, good practice for analysis of failed components should include consideration of phenomena observed in ethanol service.

Plastics are generally not recommended for storage purposes due to long-term deterioration of plasticizers, loss of mechanical integrity, and risk of methanol contamination. Many resins, nylons and rubbers, particularly nitrile (Buna-N), ethylene-propylene, Teflon and neoprene are used satisfactorily as components of equipment in methanol service.

METHANOL PURITY PROTECTION

Carbon steel is more likely to corrode and cause methanol contamination than stainless steel, particularly in the presence of moist air and/or water in coastal environments. This can be mitigated by padding tank free-board space with dry inert gas such as nitrogen.

Stainless steel has higher capital cost than carbon steel, but offers the advantage of lower life cycle maintenance cost, and reduced likelihood of methanol contamination. Three-hundred series stainless steel alloys are recommended. Alloy selection and welding procedures should avoid sensitization of weld heat-affected zones. The American Welding Society (AWS) and the American Society of Metals (ASM) offer guidelines for preventing heat-affected zone sensitization.

The National Association of Corrosion Engineers (NACE) offers guidance for cathodic protection of above ground storage tanks.

Methanol absorbs moisture from air. If tank liquid level cycles through large volumes on frequent intervals, then moisture-laden ambient air may be pulled into the tank. This may be particularly harmful in a coastal environment where moisture laden air carries dissolved chloride salts. If the facility is in a region that has characteristically high relative humidity, then methanol will dry the air in the vapor space of the tank and thereby self-contaminate the contained methanol.

If purity is an important consideration, then inert gas padding and stainless steel tanks may be economically justified as product quality and risk reduction measures. Be certain to pay equal attention to selecting compatible trim materials.

Water absorption can be eliminated by padding tank vapor space with an inert gas such as argon or nitrogen, or by padding the vapor space with dry natural gas. If natural gas is used, then measures to eliminate ignition must be thorough, consistent, and rigorously enforced. Methane is a lighter-than-air gas and is expected to float up and away from the tank vent when expelled. Never-the-less, precaution should be taken to avoid accidental ignition of expelled methane by controlling potential ignition sources near and above the tank. Hot work above unpadded and methane-padded methanol tanks must be managed and controlled.

Inert gas padding reduces the need for controlling ignition sources, providing methanol vapor and/or condensed vapors do not leave the tank by way of a gravity drain that discharges alongside the tank. Inert padding protects against contamination, accidental ignition, and exposure to airborne toxic vapor.

Incidentally, tank vapor space inerting may be required in order to obtain a variance regarding setback distances. Refer to International Fire Code (IFC) -2000 Sections 911.1 and 3404.2.9.5.1 for guidelines regarding variances in setback distance.

FIRE PREVENTION

The U.S. Department of Transportation (DOT) classifies methanol as a “Primary Class” 3.2 flammable liquid and a “Secondary Class” 6.1 toxic substance. Protective safeguards should be developed for both hazards which may be present near tanks and within spill impoundment areas. This includes protection of workers during normal operation and maintenance, and safeguarding fire fighters and first responders during accidental releases.

The International Code Council (ICC) and the National Fire Protection Association (NFPA) designate methanol as a Class IB *flammable liquid.* Class IB liquids are characterized by flash points below 73 °F and boiling points at or above 100 °F. Gasoline is another example of a commonly-used Class IB liquid, but with important differences due to the polarity of methanol, and the non-polarity of gasoline.

Practically speaking, the vapor pressure of Class IB liquids under commonly-expected conditions of outside tank storage is high during warm portions of the year. The vapor phase is the most hazardous physical state of methanol; airborne methanol vapors are mobile, and are readily ignited and readily enter the body by way of the lungs. Hazard management is especially important when the temperature of the liquid phase rises above flash point temperature. The fact that flash point temperature of methanol is low indicates substantial amounts of vapor are present immediately above the liquid surface and within the vapor space of the tank. Liquids with vapor pressure greater than 10 mm Hg are considered flammability-explosion hazards. The vapor pressure of methanol is several times this value at commonly encountered ambient storage temperatures. Ignition may occur both within and outside the tank, and may be accompanied by tank liquid contents roll-over due to external heating and subsequent Boiling Liquid Expanding Vapor Explosion (BLEVE).

Depending on liquid temperature, vapor may be capable of supporting combustion if the vapor-air composition is within the flammable range, and if vapors are exposed to a sufficiently energetic ignition source. The flammable range of methanol is much broader (6 vol% to 36 vol %) than that of gasoline (1.4 v% to 7 v%). Ignition energy of methanol is 0.14 millijoules (mJ) compared to that of gasoline at 0.20 mJ. These values are essentially the same as those for most motor fuels, and therefore not a major factor in assessing ease of ignition. Flash point temperature, vapor pressure (or Reid vapor pressure), upper and lower flammability limits, autoignition temperature, and heat of combustion are more important parameters when assessing the relative ease of ignition and hazard severity of methanol and gasoline.

Methanol fires are more likely to occur than gasoline fires within tank freeboard space when liquid temperature is near or above the methanol flash point temperature (52 °F). The vapor pressure of methanol is 90 mm Hg at 68 °F and that of gasoline is 190 mm Hg at 68 °F. The volumetric concentration of gasoline vapor is much higher at a given temperature than that of methanol. This may cause vapor concentration of gasoline to exceed the 7 v% upper flammable limit, but not the concentration of 36 v% of the upper flammability limit of methanol. Safeguards for gasoline tank fires are not necessarily sufficient to prevent methanol tank fires.

During tank filling, methanol vapor is displaced through tank vents to atmosphere thereby creating potential flammability and toxicity hazards in the ambient air which surrounds the tank. These hazards can be controlled using either of two strategies:

- Eliminating ignition sources and recognizing toxicity hazards in the proximity of the tank by classifying the area surrounding the tank as a hazardous location.
- Excluding air from tank vapor space by inerting or gas blanketing.

Tank storage of methanol requires strict and rigorously-enforced provisions to prevent over filling and tank overflow. Tank maximum allowable working volume must always allow additional volume for liquid expansion. The volumetric coefficient of thermal expansion for methanol (0.00066 /°F) is greater than that of gasoline (0.00056 /°F). A general rule of thumb is to allow 20% of tank working volume for liquid expansion.

Guidelines for sizing the volume of a methanol tank containment dike are not the same as for fuels such as gasoline and diesel. Spill containment must allow extra capacity for the substantial volume of fire water (greater than 5 parts water to 1 part methanol) necessary to dilute methanol to a non-flammable concentration. This consideration is discussed in detail under the heading of “Spill Containment.”

Provisions for controlling potential ignition sources near methanol liquid storage tanks are more or less the same as those for gasoline. The lower flammable limit of gasoline vapor is 1.4 v% compared to 7 v% for methanol. The relative density of gasoline vapor is 3 to 4, compared to that of methanol which is 1.1. Gasoline vapor will travel further along the ground without being diluted below the lower flammability limit and will ignite at much lower concentration than methanol vapor. Generally speaking, the hazard zone for ignition of methanol vapor is less restrictive than that of gasoline. The perimeter of hazard zones for methanol must consider both the toxicity and the flammability of methanol. Refer to the following for information on classifying, designating, and safeguarding hazardous locations:

- A.W. Cox, F.P. Lees, and M.L. Ang: *Classification of Hazardous Locations,* Published by Institution of Chemical Engineers, Davis Building, 165-171 Railway Terrace, Rugby, Warwickshire, CV21 3HQ, England, © 1990, ISBN 0 85295 258 9
- NFPA 70E, *Standard for Electrical Safety Requirements for Employee Work Places.*
- NFPA 70, *National Electrical Code.*

The United States Occupational Safety and Health Administration (OSHA) among others, provides guidance for permitting, testing, entering, and safeguarding employees during performance of hot work within hazardous locations and confined spaces. The applicable sections of Title 29 of the Code of Federal Regulations (CFR) are:

- 29CFR1910.106, *Flammable and Combustible Liquids*

- 29CFR1910.146, *Confined Space Entry*
- 29CFR1910.252, *Fire Protection and Prevention*
- 29CFR1910.253, *Oxygen Fuel Gas Welding and Cutting*
- 29CFR1910.254, *Arch Welding and Cutting*
- 29CFR1910.255, *Resistance Welding*
- 29CFR1917.152, *Marine Terminals Welding, Cutting, and Hot Work*
- 29CFR1910.301, *Electrical Safety*

Other applicable references include:

- API Publication 2201, *Procedures for Welding or Hot Tapping on Equipment Containing Flammables*
- NFPA 51-B, *Fire Prevention During Welding, Cutting, and Other Hot Work*
- Association of Energy Services Companies (AESC) *Hot Work*
- American National Standards Institute (ANSI) Z49.1-67, *Safety in Welding and Cutting*
- American Welding Society (AWS) Z49.1-88, *Safety in Welding and Cutting and Applied Processes.*

FIRE SUPPRESSION

Fire suppression may use any of several media:

- alcohol resistant fire-fighting, fire-extinguishing foam (AR-AFFF)
- dry chemical extinguishers (for small fires)
- CO2
- Water mist spray.

Guidelines for foam extinguishing systems with optimum application rates are provided in NFPA 11.

Fixed fire monitors may be used to cool tank walls and to extinguish flames provided at least five parts water is added for every one part of methanol: i.e., methanol concentration is diluted to less than 15%. Water-methanol solutions are flammable to compositions of about ≈ 80 v% water.

Some facilities equip methanol tanks with an internal foam delivery system combined with an internal floating roof. Care must be taken to coat the internal floating roof if it is constructed of aluminum or aluminum/magnesium alloy. Methanol is mildly corrosive to aluminum-magnesium, aluminum-copper, and copper-zinc alloys.

TANK SPILL CONTAINMENT

General guidance for liquid hydrocarbon (gasoline, kerosene, and diesel) spill containment is to size the containment volume to at least 110% of the working volume of the largest tank within a tank battery. This volume accommodates a worst case, full tank breech when precipitated moisture is present within the containment without overflowing containment dikes. Guidelines for spill containment are provided in NFPA 1, NFPA 30, and federal regulations for spill prevention: 40CFR110 and 112.

Atmospheric Above Ground Tank Storage of Methanol *(Continued)*

Because methanol is highly soluble in water, and because flammability of water-methanol solutions is persistent to high proportions of water, it is suggested that the containment volume for methanol tank spills be enlarged accordingly if water is to be used as an extinguishing medium. The additional containment volume must be sufficient to allow responders to use water as a suppressant without overflowing the tank impoundment dike. If alcohol resistant foam is used, then less volume is required for spill containment. Provisions must insure that a sufficient amount of AR-AFFF suppressant is onsite and available to extinguish worst case fire scenarios.

Methanol Drum Transport, Handling, and Storage

INTRODUCTION

Totes, drums (55 gallon), and cans (5 gallon, and 1 gallon) are used to transport, store, and dispense methanol in a wide variety of circumstances by low volume users. Non-bulk transport and storage of hazardous material are regulated activities in the U.S. and some other countries. Failure to adhere to applicable regulations may be punishable by fines and imprisonment. Requirements are specific to the country and the circumstances; however requirements will generally consist of the following; shipping papers, container labeling, transport vehicle placarding, driver training and licensing, and availability of emergency repines equipment. If you are not a designated hazardous materials carrier, then it may be against the law to transport methanol in totes, drums, and cans.

Do not transport methanol in your personal vehicle. Do not store methanol totes, drums, or cans indoors or in your home. Storage requires precautions for flammable loading, fire-safe storage, ventilation, spill containment, spill cleanup, and fire suppression.

Never use mouth suction to siphon-transfer methanol. Methanol liquid and vapor are toxic to humans. Exposure is cumulative and may result in harm if vapor or liquid are inhaled, ingested, or contacted with skin for extended periods of time.

Methanol (CAS: 67-56-1, NIOSH: PC-1400000, DOT: 1230, UN-1230, NA-1230) is classified by the International Code Council (ICC) and the National Fire Protection Agency (NFPA) under the *Uniform Fire Code* as a “IB Flammable Liquid” and by the United Nations as a “1993 Class 3 Flammable Liquid.” NFPA and Department of Transportation (DOT) rank Flammability as a 3 primary hazard, and toxicity, as a 6.1 ranked secondary hazard. Guidelines for handling IB flammable liquids are provided by codes and standards published by ICC, NFPA, and the International Fire Code.

ICC and NFPA guidelines are recommended as ‘best practices,’ but are not mandatory unless deemed so by national, or local authority. Within the United States, local authority generally rests with the local Fire Marshal. Mandatory regulations have been developed within the United States by the Occupational Safety and Health Administration (OSHA), an agency of the federal government. Specific safe handling practices are given under three separate regulations for various industries, circumstances, and work environments:

- General Industry: 29 Code of Federal Regulations (CFR) 1910.106
- Construction Industry: 29CFR1926.152
- Shipyard Industry: 29CFR1915.36).

Guidelines for international transportation of flammable liquids are available from the following bodies:

- International Maritime Organization, *International Maritime Dangerous Goods (IMDG) Code* (volumes, 1, 2, and Supplement)
- International Air Transport Association (IATA), *Dangerous Goods Regulations*
- Intergovernmental Organization for International Carriage by Rail, *Regulations concerning the International Carriage of Dangerous Goods by Rail.*

Transportation within the United States is governed by the Department of Transportation (DOT), an agency of the federal government. DOT regulations are available in 49CFR which can be accessed on the internet or purchased in book format at a nominal cost over the internet.

Drums, totes, and cans are transported, stored, and handled by the vast majority of methanol users. This discussion focuses on 5-gallon and 55-gallon quantities packaged in metal containers.

Plastic containers are not recommended for long-time storage or shipment of methanol because the solvent properties of methanol may degrade the plastic, causing the containers to lose structural integrity.

STORAGE OF METHANOL-CONTAINING TOTES, DRUMS, AND CANS

Guidance for safe storage of methanol is provided by ICC, NFPA, and the International Fire Code. ICC and NFPA guidelines are available in:

- NFPA 1, *Uniform Fire Code.*
- NFPA 30, *Flammable and Combustible Liquids Code.*

Methanol storage areas should be curbed with a compatible material such as concrete, ventilated to prevent accumulation of vapors, and drained to a safe location which is remote from the storage area. Storage areas should be equipped with vapor, and heat detector/alarms. Because methanol burns with a transparent, non-luminous blue flame, combustion will likely not be detected by standard smoke detectors, and luminous-type flame detectors. Carbon monoxide and carbon dioxide detectors may serve in place of smoke detectors and luminous flame detectors. First responders use infra-red detection methods to determine if combustion is occurring. It is recommended that this type of detector be installed and alarmed to monitor methanol tote, drum, and can storage areas. Detection should be redundant with detectors positioned at right angles to one another.

If more than several drums are stored, then consideration should be given to automatic fire suppression using either fine water mist spray, or alcohol resistant fire-fighting foam (AR-FFF). Storage of multiple containers is subject to limitations on stacking height, and container density loading. Refer to the listed codes to obtain guidance, which is specific to your circumstance.

Tote and drum containers must be stored outside, not within a structure, unless placed in a liquid storage room or warehouse meeting the requirements for flammable liquids storage buildings. Five-gallon and 1-gallon containers may be stored within a building provided they are contained in a fire-safe cabinet which is grounded, and vented to an outside safe location which includes an explosion suppression devise.

SHIPMENT OF TOTES, DRUMS, 5-GALLON CANS, AND 1-GALLON CONTAINERS

Guidance for shipment of methanol via the U.S. Postal Service is contained in United States Postal Service Publication 52, *343 Flammable and Combustible Liquids (Hazard Class 3).*

Transportation of drum quantities (8 to 119 gallon quantities of methanol) is regulated by multiple agencies and organizations. The regulatory authority depends on:

- Method of transport (truck, rail, air, or sea-going vessel).
- Capacity of individual containers, the number of containers which comprise a single shipment.
- Whether shipment is domestic within U.S.-controlled territory or outside of U.S. controlled territory.

Shipping oversight is the responsibility of the following regulatory bodies:

- Within the United States, the U.S. Department of Transportation (DOT), *Hazardous Material Regulations 49 CFR 100-199 and Emergency Response Guide Book*
- United Nations Location Codes (UN/LOCODES), *UN Recommendations on Transport of Dangerous Goods (i.e., the so-called UN-Orange Book)*
- International Maritime Organization (IMO), *International Maritime Dangerous Goods Code (IMDG),* Volumes 1 and 2, plus a supplement
- International Civil Aviation Organization (ICAO): *Technical Instructions for the Safe Transport of Dangerous Goods by Air*
- International Air Transportation Association (IATA), *Dangerous Goods Regulations (DGR) 3.3.*

Road, rail, airborne, and water transport of hazardous materials is controlled by DOT for goods shipped within the United States. Regulatory revisions are made almost continuously; verify that you are using current versions of the regulations.

DOT restricts aircraft transportation of Class 3 flammables (e.g., methanol) to a maximum of 1 liter on passenger aircraft and 60 liters on cargo aircraft, irrespective of the shipping company: Fed-X, UPS, etc. Drum quantities are not considered to be air transportable. Refer to 49CFR172.101, "Hazardous Materials Table" for specific information regarding shipment of methanol. Refer to 49CFR173.202 for non-bulk packaging requirements on passenger and cargo aircraft.

CONTAINER SPECIFICATIONS FOR TRANSPORTING AND STORING METHANOL

Class IB Flammable Liquids are equivalent to DOT-designated PG II Flammable Liquids. Non-bulk volumes of PG II Flammable Liquids between 8 and 119 gallons are required to be packaged in DOT performance-oriented packaging identified using the United Nations identification system. Specifications for drums are established and published by Oak Ridge National Laboratory. A copy of these specifications can be obtained by contacting Oak Ridge National Laboratory, Packaging Operations Manager, Bldg. 7001, MS 6288 P.O. Box 2008, 1 Bethel Valley Road Oak Ridge, Tennessee 37831-6288. Totes, drums, and cans are available which just meet, and which exceed published specifications. Those which exceed specifications offer the potential cost-benefit of testing and re-using the containers.

Methanol Drum Transport, Handling, and Storage *(Continued)*

Standards for DOT designated packaging requirements for drum drop, stacking, and vibration testing are as follows:

- Drop
    - American Society of Testing and Materials (ASTM) D-5276, *Standard Test Method for Drop Test of Loaded Containers by Free Fall*
    - International Organization for Standardization (ISO) 2248, *Packaging – Complete, Filled Transport Packages – Vertical Impact Test By Dropping*
- Stacking
    - ASTM D-4577, *Standard Test Method for Compression Resistance of a Container Under Constant Load*
    - ISO 2234, *Packaging – Complete, Filled Transport Packages – Stacking Tests using Static Load*
- Vibration
    - ASTM D-999, *Standard Test Method for Vibration Testing of Shipping Containers*
    - ISO 2247, *Packaging – Complete, Filled transport Packages – Vibration Test at Fixed Low Frequency*

Packaging may be re-used provided it is cleaned, refurbished, re-tested, and found to be compliant.

SHIPPING REGULATIONS

Shipping requirements for hazardous materials are rigorous and complex. Failure to comply with DOT regulations can result in civil penalties consisting of monetary fines of $50,000 per occurrence and criminal penalties of 5-years' imprisonment.

If you are not comfortable interpreting regulations for identifying, labeling, packaging, and shipping hazardous materials, then consider obtaining professional guidance from a qualified professional who is knowledgeable about your specific circumstances.

It is unsafe to transport drum or even 5-gallon cans of methanol in the trunk of a car, even if the trunk remains open. Transportation of methanol requires special hazard and incident response training. Transporting vehicles must be placarded, and drivers must have government required papers authorizing transport.

CONTROLLING STATIC ACCUMULATION AND SPARK DISCHARGE

Liquids which have conductivity less than 50 picosiemens per meter are charge accumulators; that is, these liquids tend to accumulate static charge as a result of fluid handling in un-bonded and un-grounded fuel containment systems. Liquids which have electrical conductivity greater than 50 picosiemens per meter are not considered to be charge accumulators. The conductivity of gasoline is less than 500 picosiemens; the conductivity of methanol is substantially greater than 50 picosiemens.

Methanol is a polar material; gasoline, and most other common transportation fuels are non-polar materials. The flash temperature, ignition energy, and lower flammability limit of methanol compared to gasoline cause methanol to be less easily ignited than gasoline in many commonly-encountered circumstances. This is also true for ignition resulting from accumulation and subsequent discharge of static electricity. Charge accumulation and discharge is less likely for methanol than for gasoline, Jet, kerosene, low sulfur diesel, and other low sulfur distillates. Electrical conductivity of gasoline is 25 picosiemens per meter, which is typical for petroleum derived distillate fuels. Gasoline accumulates static electricity.

By comparison, the electrical conductivity of methanol is 7 x 10^6 picosiemens per meter, and that of good quality drinking water (also a polar compound) is 5 x 10^8 picosiemens per meter. Neither methanol nor water are charge accumulators. However, methanol may accumulate static charge under abnormal circumstances. Always make provisions to bond and ground methanol containers with electrical resistance less than 10 ohms ($R_{\text{bond or ground}} \leq 10$ ohms). Neat (pure) methanol does not normally have a high risk of charge accumulation, static discharge, and static spark ignition. Possible exceptions to this occur when large transient ground currents are present due to lightning strikes, nearby high voltage power lines, and other sources of ground current.

As a matter of good practice, bonding, grounding and turbulence quelling, and liquid stilling during handling procedures should be followed in the event the methanol is a blended fuel, or is contaminated with hydrocarbon and therefore has an unexpectedly low electrical conductivity. Methanol burns with a non-luminous flame which may be difficult to detect during daytime hours, and methanol vapor has a very wide flammability range (7 v% to 36 v%).

DRUM HANDLING AND LIQUID TRANSFER

The difficulty of drum handling increases proportionally to the size and weight of the drum. Five gallon cans are relatively easy to handle without mechanical assistance, provided the cans are moved and handled one-at-a-time.

Fifty-five gallon drums contain less than 55 gallons of liquid in order to allow space for fluid volume expansion. A 55 gallon drum filled to 80% capacity with methanol weights approximately 300 lbs. In order to move a full drum, it is necessary to use a mechanical means such as a barrel hoist or fork lift. If no mechanical means is available, then individual drums can be moved by tipping the drum on its side, and rolling it to a designated curbed storage area.

If it is necessary to remove a measured quantity of methanol from the drum without using mechanical means such as low pressure inerting, or a siphon, then it is possible to lay the drum on its side, and roll the drum into a slanted position with some form of a prop such as a short section of board under the bunged end of the drum. Position the drum with the small bung in a 12 o'clock position, and verify that the drum is chocked in a stable position. The drum and the receiving container must be bonded and grounded.

In the 12 o'clock position, the small bung is now in the vapor space of the drum. Replace the bung with a threaded, alcohol compatible hose. Be careful not to breathe the escaping vapors, which are toxic, and may be flammable. Methanol can be removed from the drum in a controlled manner by carefully rolling the drum to the side so the small bung is in the 1 o'clock position, slightly below the liquid level within the drum. Methanol will now flow out of the drum in a controlled manner. Flow can be terminated by returning the drum to the 12 o'clock position. Replace the transfer hose with the bung, and return the drum to an upright position. Extreme care must be taken to not drop or otherwise damage totes, drums, cans, and 1-gallon containers during handling.

Methanol is toxic, especially when breathed or ingested. Siphon transfer of methanol must never be started by mouth-suction. Ingestion of tea-spoon-sized quantities are known to cause blindness. Inhalation of methanol vapor, even in small amounts over short periods of time, is known to produce acute health effects in some individuals. Methanol is toxic. Do not breathe the vapor, ingest the liquid, or allow bare skin to contact the liquid.

Using Physical and Chemical Properties to Manage Flammable Liquid Hazards

Part 1-A: How to Use the Technical Bulletin[1]

INTRODUCTION

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

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

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

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

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

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

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

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[1] This three-part Technical Bulletin was written by Mr. Robert R. Roberts of Roberts & Roberts Risk & Reliability Engineering and edited by Alliance Consulting International, San Diego, California under contract to the Methanol Institute..

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

SELECTED FUELS

The fuels include Hydrogen gas (H_2), compressed natural gas, propane (a liquefied gas), three Class IB Flammable Liquids (methanol, ethanol, and gasoline), and two Class 2 combustible liquids (No. 2 diesel, and biodiesel). Parameters listed for methanol and ethanol are for neat (i.e., pure) materials, not for fuel blends. Parameters for fuel blends must be determined for each specific blend.

SOURCES OF INFORMATION

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

GLOSSARY OF TERMS AND ACRONYMS

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

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

API- American Petroleum Institute

ASME- American Society of Mechanical Engineers

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

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

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

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

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

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

Using Physical and Chemical Properties to Manage Flammable Liquid Hazards

Part 1-A: How to Use the Technical Bulletin

DOT- U.S. Department of Transportation

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

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

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

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

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

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

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

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

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

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

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

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

Using Physical and Chemical Properties to Manage Flammable Liquid Hazards

Part 1-A: How to Use the Technical Bulletin

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

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

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

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

Heating Value- The theoretical amount of heat that can be released by a combustion reaction if the fuel and oxidants are converted with 100% efficiency to CO_2 and H_2O vapor. Two values are given heat value: a higher heating value (HHV) and a lower heating value (LHV). HHV is used for situations in which all of the heat (heat of reaction, the sensible heat of product gases, and the heat of condensation of water vapor) is recovered and utilized to perform work. HHV is essentially the same as the thermodynamic heat (enthalpy) of combustion. The LHV is used if a portion of the sensible heat of the gases and the heat of condensation of water vapor is not recovered to perform work. The process industries typically use the lower heating value.(1,8)

ICC- International Code Council

IEEE- Institute of Electrical and Electronics Engineers

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

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

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

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

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

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

NACE- National Association of Corrosion Engineers

NEC- National Electrical Code

NFPA- National Fire Protection Association

OSHA- U.S. Occupational Safety and Health Administration

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

Reid Vapor Pressure (RVP)- A commonly used measure of vapor pressure for gasoline, defined as the absolute vapor pressure exerted by a liquid at 100ºF as determined by the test method ASTM D-323. The test method does not apply to liquefied petroleum gases such as propane. RVP is the absolute vapor pressure. True Vapor Pressure (TVP) is the partial vapor pressure.(10)

Specific Electrical Conductance (see *Electrical Conductivity*)

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

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

Specific Heat Capacity (see *Specific Heat or Heat Capacity*)

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

Stoichiometric Air to Fuel Ratio- The ratio of the theoretical amount of air (expressed as moles or mass) to the amount of fuel expressed in the same units which contains sufficient oxygen to allow full and complete combustion of 100% of the hydrogen and carbon contained within the fuel.(1)

Oxygen-to-fuel ratio: oxygen/Fuel = (1 + x/4) where x = H/C of the fuel
Air-to-fuel ratio" A/F =)100/21)(O/F)

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

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

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

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

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

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

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

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

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Using Physical and Chemical Properties to Manage Flammable Liquid Hazards

Part 1-B: Physical & Chemical Properties of Selected Fuels

SECTION 1: GENERAL INFORMATION

Property/Information	Hydrogen H_2 (gas)	CNG CH_4 83-99%; C_2H_6 1-13% (gas)	Propane C3 (liquid)	Methanol CH_3OH (liquid)	Ethanol C_2H_5OH (liquid)	Gasoline C_4-C_{12} (liquid)	No. 2 Diesel C_8-C_{25} (liquid)	B100 Biodiesel C_{12}-C_{22} (liquid)
DOT Number	UN 1049 UN 1966	UN 1971	UN 1075 UN 1978	UN 1230	UN 1170	UN 1203	UN 1202 NA 1993	-
DOT Hazard Class or Division	2.1 flammable gas	2.1 flammable gas	2.1 flammable gas	3.6.1 flammable liquid	3 flammable liquid	3 flammable liquid	3 flammable liquid	3 flammable liquid
DOT Guide Number	22	17	22	28	26	27	128	-
CAS Number	1333-74-0	74-82-8	74-98-6	65-56-1	64-17-5	8006-61-9	68476-34-6	67784-80-9
STCC Number	4905746	4905755	4905781	4909230	-	4908178	-	-
ICC, OSHA, NFPA Liquid Flammability Class	-	-	-	IB flammable liquid	IB flammable liquid	IB flammable liquid	2 combustible liquid	2 combustible liquid
DOT Packing Group	-	-	-	PG II	PG II	PG II	PG III	PG III
DOT Packaging (non-bulk/bulk)	302/302	302/302	304/314	202/242	202/242	202/242	203/242	203/242
Types of Shipping Containers	Pressurized cylinders & tank cars	Pressurized cylinders	pressurized cylinders, tank trucks, tank cars,	NON-BULK: 1-119 gal DOT PG-II performance-oriented containers BULK: tank cars, tank trucks	NON-BULK: 1-119 gal DOT PG-II performance-oriented containers BULK: tank cars, tank trucks	BULK: pipelines, tank cars, tank trucks	BULK: pipelines, tank cars, tank trucks	BULK: pipelines, tank cars, tank trucks

Using Physical and Chemical Properties to Manage Flammable Liquid Hazards

Part 1-B: Physical & Chemical Properties of Selected Fuels

SECTION 1: GENERAL INFORMATION (CONT.)

Property/Information	Hydrogen H_2 (gas)	CNG CH_4 83-99%; C_2H_6 1-13% (gas)	Propane C3 (liquid)	Methanol CH_3OH (liquid)	Ethanol C_2H_5OH (liquid)	Gasoline C_4-C_{12} (liquid)	No. 2 Diesel C_8-C_{25} (liquid)	B100 Biodiesel C_{12}-C_{22} (liquid)
Shipping Container Hazards	rupture, BLEVE: containers may fragment & rocket in fire	rupture, BLEVE: containers may fragment & rocket in fire	rupture, BLEVE: containers may fragment & rocket in fire	rupture, BLEVE: containers may fragment & rocket in fire	rupture, BLEVE: containers may fragment & rocket in fire	rupture, BLEVE: containers may fragment & rocket in fire	rupture, BLEVE: containers may fragment & rocket in fire	rupture, BLEVE: containers may fragment & rocket in fire
Special Fire Hazards	blue flame invisible in daylight; flame flashes back from ignition source to leak point; accumulated vapor may explode if ignited in confined or in unconfined area	yellow luminous flame visible in daylight; flame flashes back from ignition source to leak point; accumulated vapor may explode if ignited in confined area or deflagrate as a buoyant radiant fireball in unconfined area	yellow luminous flame visible in daylight; flame flashes back from ignition source to leak point; accumulated vapor may explode if ignited in confined area or deflagrate as a non-buoyant radiant fire ball in unconfined area	blue flame invisible in daylight; flame flashes back from ignition source to leak point; accumulated vapor may explode if ignited in confined area or deflagrate as a near- neutral-buoyancy radiant fire ball in unconfined poorly ventilated area	blue flame invisible in daylight; flame flashes back from ignition source to leak point; accumulated vapor may explode if ignited in confined area, or deflagrate as a near-neutral-buoyancy fire ball in unconfined poorly ventilated area	yellow luminous flame visible in daylight; flame flashes back from ignition source to leak point; accumulated vapor may explode if ignited in confined area or deflagrate as a non-buoyant radiant fire ball in unconfined area	yellow luminous flame visible in daylight; dense black smoke	yellow luminous flame visible in daylight; dense black smoke

Using Physical and Chemical Properties to Manage Flammable Liquid Hazards

Part 1-B: Physical & Chemical Properties of Selected Fuels

SECTION 1: GENERAL INFORMATION (CONT.)

Property/Information	Hydrogen H_2 (gas)	CNG CH_4 83-99%; C_2H_6 1-13% (gas)	Propane C3 (liquid)	Methanol CH_3OH (liquid)	Ethanol C_2H_5OH (liquid)	Gasoline C_4-C_{12} (liquid)	No. 2 Diesel C_8-C_{25} (liquid)	B100 Biodiesel C_{12}-C_{22} (liquid)
Other Information	H_2 gas release is very buoyant and invisible	CNG gas release is buoyant and invisible, natural gas has characteristic odor	liquid floats & boils on water; heavier-than-air visible vapor cloud	liquid floats & mixes with water; near neutral vapor buoyancy	liquid floats & mixes with water; near neutral vapor buoyancy	liquid floats on water; high vapor pressure, expected to form negative buoyancy vapor cloud	liquid floats on water; low vapor pressure, formation of vapor cloud not expected	liquid floats on water; low vapor pressure, formation of vapor cloud not expected
Molecular Weight	2.02 (2)	16.04 (2)	44.1 (2)	32.04 (1,2)	46.07 (1,2)	100-105 (1,2)	~200 (1,2)	~292 (2)
Chemical Composition								
Carbon (w/w%)	0 (2)	75 (2)	82 (2)	37.5 (2)	52.2 (2)	85-88 (2)	87 (2)	77 (2)
Hydrogen (w/w%)	100 (2)	25 (2)	18 (2)	12.6 (2)	13.1 (2)	12-15 (2)	13 (2)	12 (2)
Oxygen (w/w%)	0 (2)	-	-	49.9 (2)	34.7 (2)	0	0 (2)	11 (2)

Using Physical and Chemical Properties to Manage Flammable Liquid Hazards

Part 1-B: Physical & Chemical Properties of Selected Fuels

SECTION 2: LIQUID PROPERTIES

Property/Information	Hydrogen H_2 (gas)	CNG CH_4 83-99%; C_2H_6 1-13% (gas)	Propane C3 (liquid)	Methanol CH_3OH (liquid)	Ethanol C_2H_5OH (liquid)	Gasoline C_4-C_{12} (liquid)	No. 2 Diesel C_8-C_{25} (liquid)	B100 Biodiesel C_{12}-C_{22} (liquid)
Freezing Point Temp. (°F)	-435 (2)	-296 (2)	-305.8 (2)	-143.5 (1,2)	-173.2 (1,2)	-40 (1,2)	-40 to -30 (1,2)	26-66 (2)
Specific Gravity (@ 60 °F/60 °F)	0.07 (2)	0.424 (2)	0.508 (2)	0.796 (1)	0.794 (1)	0.72-0.78 (2)	0.85 (2)	0.88 (2)
Density (lb/gal @ 60 °F)	-	1.07 (2)	4.22 (2)	6.63 (1,2)	6.61 (1,2)	6.0 – 6.5 (1,2)	6.7 – 7.4 (1) 7.079 (2)	7.328 (2)
Viscosity								
@ -4 °F (centipoises / mm2/s)	-	-	-	1.15 (1) 1.345 (2)	2.84 (1) 3.435 (2)	0.6-.77 (1) 0.8 - 1.0 (2)	9.7-17.6 (1) 9.0 - 24.0 (2)	-
@ 68 °F (centipoises / mm2/s)	-	-	-	0.59 (1) 0.74 (2)	1.19 (1) 1.50 (2)	0.37–0.44 (1) 0.5 – 0.6 (2)	2.6-4.1 (1) 2.8 – 5.0 (2)	-
@ 104 °F (centipoises / mm2/s)	- -	- -	- -	- -	- -	- -	- 1.3 – 4.1 (2)	4.0 – 6.0 (2)
Specific Heat (C_p, Btu/lb-°F)	-	-	-	0.60 (1,2)	0.57 (1,2)	0.48 (1,2)	0.43 (1,2)	-
Thermal Conductivity (Btu/hr-ft-°F)	0.097 (4)	0.17 (4)	0.075 (6)	0.12 (3)	0.099 (3)	0.087 (4)	0.081-0.087 (5,6)	0.09-0.12 (7)
Coefficient of Thermal Volume Expansion (@ 60 °F & 1 atm)	-	-	-	0.00067 (1)	0.00062 (1)	0.00067 (1)	0.00046 (1)	-
Electrical Conductivity								
Neat or without additives	-	-	-	4.4 x 10^7 pS/m (1,26,32)	1.35 x 10^5 pS/m (1,26,32)	25 pS/m (7)	5 pS/m (7)	-

Using Physical and Chemical Properties to Manage Flammable Liquid Hazards

Part 1-B: Physical & Chemical Properties of Selected Fuels

SECTION 2: LIQUID PROPERTIES (CONT.)

Property/Information	Hydrogen H_2 (gas)	CNG CH_4 83-99%; C_2H_6 1-13% (gas)	Propane C3 (liquid)	Methanol CH_3OH (liquid)	Ethanol C_2H_5OH (liquid)	Gasoline C_4-C_{12} (liquid)	No. 2 Diesel C_8-C_{25} (liquid)	B100 Biodiesel C_{12}-C_{22} (liquid)
Electrical Conductivity Cont.								
Industrial use	-	-	-	30 μS/m (28)	-	-	-	-
Fuel specification	-	-	-	< 1000 μS/m (32)	< 500 μS/m(27)	-	< 250 pS/m(28)	-
Latent Heat of Vaporization								
(Btu/gal @ 60 °F)	-	-	775 (2)	3,340 (1,2)	2,378 (1,2)	≈900 (1,2)	≈710 (1,2)	-
(Btu/lb @ 60 °F)	192.1 (2)	219 (2)	193.1 (2)	506 (1,2)	396 (1,2)	≈150 (1,2)	≈100 (1,2)	-
Heating Value (a)								
Lower [liquid fuel combusted to water as vapor] (Btu/gal @ 60 °F)(1)	-	-	- 84250 (2)	56800 (1) 57250 (2)	76000 (1) 76330 (2)	109000-119000 (1) 116090 (2)	126000-130800 (1) 128450 (2)	- 119,550 (2)
Lower [liquid fuel combusted to water as vapor] (Btu/lb)	- 52217 (2)	- 20263 (2)	- 19900 (2)	8570 (1) 8637 (2)	11500 (1) 11585 (2)	18000-19000 (1) 18676 (2)	18000-19000 (1) 18394 (2)	16,131 (2)
Higher [liquid fuel combusted to liquid water] (Btu/gal)	-	-	91420 (2)	65200 (2)	84530 (2)	124340 (2)	137380 (2)	127960 (2)
Higher [liquid fuel combusted to liquid water] (Btu/lb)	- 59806 (2)	- 22449 (2)	21594 (2)	9750 (1) 9837 (2)	12800 (1) 12830 (2)	18800-20400 (1) 20004 (2)	19200-20000 (1) 19673 (2)	17266 (2)

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[a] The higher heating value (HHV) and heat of combustion are cited for completeness only. No vehicles currently in use or under development for future use have engines capable of recovering heat of condensation from water of combustion. Use the lower heating value (LHV) for practical comparison between fuels which combust accidentally as a result of a spill or containment failure.

Using Physical and Chemical Properties to Manage Flammable Liquid Hazards

Part 1-B: Physical & Chemical Properties of Selected Fuels

SECTION 2: LIQUID PROPERTIES (CONT.)

Property/Information	Hydrogen H_2 (gas)	CNG CH_4 83-99%; C_2H_6 1-13% (gas)	Propane C3 (liquid)	Methanol CH_3OH (liquid)	Ethanol C_2H_5OH (liquid)	Gasoline C_4-C_{12} (liquid)	No. 2 Diesel C_8-C_{25} (liquid)	B100 Biodiesel C_{12}-C_{22} (liquid)
Heat of Combustion $[\Delta H_c^0]$ [liquid fuel combusted to liquid water] (Btu/lb)	60000 (30,31) 61000 (34)	23000 (30,31)	21500 (30,31) 21000 (34)	9900 (30,31) 9378 (35)	12900 (30,31) 12000 (34) 12764 (36)	20000 (30,31, 34)	20700 (30,31) 19300 (34)	≈18,145 (30,31)
Equilibrium Vapor Pressure								
Reid [RVP] (psi @ 100 °F)	-	2400 (2)	208 (2)	4.6 (1,2)	2.3 (1,2)	8 – 15 (1,2)	<0.2 (1,2)	<0.04 (2)
True Vapor Pressure [TVP] (mm Hg @ 68 °F)	-	-	6257.7 (13)	92 (10) 104 (11)	43 (9)	258-775 (15) (@ 100 °F)	0.4 (14)	-
Boiling Pt. Temperature (°F)	-423 (2)	-263.2 – 126.4 (2)	-44 (2)	149 (1,2)	172 (1,2)	80 – 437 (2)	356–644 (2)	599 – 662 (2)
Water Solubility @ 70 °F								
Fuel in Water (v/v %)	-	Negligible (2)	Negligible (2)	100 (1,2)	100 (1,2)	Negligible (1,2)	Negligible (1,2)	-
Water in Fuel (v/v %)	-	-	-	100 (1,2)	100 (1,2)	Negligible (1,2)	Negligible (1,2)	-
Vapor Specific Heat (Btu/lb/°F)	3.42 (16)	0.59 (16)	0.39 (16)	0.38 (18)	0.45 (19)	0.38 (33)(b)	-	-

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[b] This value of C_p for an ideal gas at STP (60 °F and 1 atm of pressure) uses the heat capacity of heptane (C_7H_{16}) as a surrogate for gasoline vapor.

Using Physical and Chemical Properties to Manage Flammable Liquid Hazards

Part 1-B: Physical & Chemical Properties of Selected Fuels

SECTION 2: LIQUID PROPERTIES (CONT.)

Property/Information	Hydrogen H_2 (gas)	CNG CH_4 83-99%; C_2H_6 1-13% (gas)	Propane C3 (liquid)	Methanol CH_3OH (liquid)	Ethanol C_2H_5OH (liquid)	Gasoline C_4-C_{12} (liquid)	No. 2 Diesel C_8-C_{25} (liquid)	B100 Biodiesel C_{12}-C_{22} (liquid)
Equilibrium Vapor Pressure (c)								
Reid (psi @ 100 °F)	-	2400 (2)	208 (2)	4.6 (1,2)	2.3 (1,2)	8 – 15 (1,2)	<0.2 (1,2)	<0.04 (2)
True Vapor Pressure (mm Hg @ 68 °F)	-	-	6257.7 (13)	92 (10) 104 (11)	43 (9)	258-775 (15) (@ 100 °F)	0.4 (14)	-
Vapor Density (air=1)	0.07 (24, calc'd)	0.55-0.69 (25, calc'd)	1.5 (12)	1.1 (23)	1.6 (11)	3 – 4 (15)	>3(14)	-
Vapor Heat of Combustion								
Lower [gaseous fuel combusted to water as vapor] (Btu/lb @ 60 °F)	-	-	-	9080 (1)	11900 (1)	19000-19300 (1)	-	-

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[c] True Vapor Pressure is the partial pressure of fuel vapor in air, compared to Reid Vapor Pressure which is the total pressure of fuel vapor, and air contained in the small volume of laboratory test apparatus. Reid Vapor Pressure (RVP) is determined experimentally, and is typically used in reference to hydrocarbon mixtures such as natural gas, Liquid Petroleum Gas (LPG), propane, butane, gasoline, kerosene, diesel, and fuel oil. RVP is expressed as differential pressure in pounds per square inch (psi); true vapor pressure is expressed as absolute pressure in millimeters of mercury (mmHg) or pounds per square inch absolute (psia). One atmosphere of pressure is equivalent to 0.0 psi of differential pressure, and 14.7 psia or 760 mmHg of absolute pressure.

Using Physical and Chemical Properties to Manage Flammable Liquid Hazards

Part 1-B: Physical & Chemical Properties of Selected Fuels

SECTION 4: FLAMMABILITY PROPERTIES

Property/Information	Hydrogen H_2 (gas)	CNG CH_4 83-99%; C_2H_6 1-13% (gas)	Propane C3 (liquid)	Methanol CH_3OH (liquid)	Ethanol C_2H_5OH (liquid)	Gasoline C_4-C_{12} (liquid)	No. 2 Diesel C_8-C_{25} (liquid)	B100 Biodiesel C_{12}-C_{22} (liquid)
Flash Point Temperature								
Closed Cup (°F)	-	-300 (2)	-156 (1)	52 (1)	55 (1)	-45 (2)	140 - 176 (2)	212 - 338 (2)
Open Cup (°F)	-	-	-	-	-	-	-	-
Autoignition Temperature (°F)	932 (2)	900 – 1170 (2)	842 (2)	867 (1,2)	793 (1,2)	495 (1,2)	≈600 (1,2)	-
Flammability Limits								
Lower (v/v %)	4.1 (2)	5.3 (2)	2.2 (2)	7.3 (1,2)	4.3 (1,2)	1.4 (1,2)	1.0 (1,2)	-
Upper (v/v%)	74 (2)	15.0 (2)	9.5 (2)	36.0 (1,2)	19.0 (1,2)	7.6 (1,2)	6.0 (1,2)	-
Flammability Range (v/v %)	69.9 (calc by diff)	9.7 (calc by diff)	7.3 (calc by diff)	28.7 (calc by diff)	14.7 (calc by diff)	6.2 (calc by diff)	5 (calc by diff)	-
Stoichiometric air/fuel ratio (w/w)	34.3 (2)	17.2 (2)	15.7 (2)	6.45 (1,2)	9.00 (1,2)	14.7 (1,2)	14.7 (1,2)	13.8 (2)
Fuel in Vaporized Stoichiometric Mixture (v/v%)	-	-	-	12.3 (2)	6.5 (2)	2.0 (2)	-	-
Stoichiometric Flame Speed (ft/s)	10.63 –14.44 (20)	1.48 (20)	1.48 (20)	1.41 (20)	-	1.12 (20)	-	-
Minimum Ignition Energy (mJ)	0.017 (20)	0.30 (20)	0.26 (20)	0.14 (20)	-	0.29 (20)	0.23 (21)	-
Adiabatic Flame Temperature (°F)	3807 (21)	3542 (21)	3610 (21)	3470 (21)	3281 (21)	3525 (21)	-	-
Flame Temperature (°F)	3722 (20)	3542 (20)	3497 (20)	3,398 (20)	3,488 (20)	3,686 (20)	-	-
Mass Burning Rate (lb/ft^2)	-	-	-	0.083(29)	-	0.27(29)	0.22(29)	-

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Using Physical and Chemical Properties to Manage Flammable Liquid Hazards

Part 1-B: Physical & Chemical Properties of Selected Fuels

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Using Physical and Chemical Properties to Manage Flammable Liquid Hazards Part Two of a Three Part Series[1]

INTRODUCTION

This is part two of the three-part Technical Bulletin, which provides guidance for using physical, chemical, thermal, and electrical properties to identify and control hazards of flammable liquids. Properties and characteristic parameters of eight fuels [hydrogen, compressed natural gas (CNG), propane, methanol, ethanol, gasoline, No. 2 diesel, and biodiesel] are listed in part 1B of the Technical Bulletin.[2] This bulletin compares various properties for gasoline and methanol.

Chemical and physical properties data may be difficult to locate and even more difficult to interpret and verify. Flame speed is an example of this difficulty. Some sources indicate the flame speed of methanol is greater than that for unleaded gasoline; others sources state the reverse. Still others report that small additions of methanol increase the flame speed of gasoline. All may be correct, depending on the temperature, pressure, mixing, and stoichiometry at which combustion occurs and how flame temperature is determined.

Flame speeds of methanol and gasoline have similar values (1.12 and 1.41 feet per second [ft/s] for gasoline and methanol, respectively). Therefore, there may be overlap of flame speed parameters depending on whether measurements were made at lean, rich, or stoichiometric fuel/air ratios. Flame speed data used in this three-part bulletin series are characteristic of stoichiometric combustion of a vapor at NTP (Normal Temperature = 68°F and Normal Pressure = 14.7 psia or 760 mmHg).

Differences between the published values of flame speed for methanol and gasoline do not have a large effect on first order estimates for explosive overpressure and fire radiant heat flux, and are not of major concern. The approximately tenfold difference between the flame speed of hydrogen (≈12 ft/s)[3] and those of gasoline and methanol have a very large difference on overpressure and heat flux.

The purpose of collecting and comparing data for different fuels is to determine and compare the severity of potential consequences: fires, explosions, and toxic plumes for particular circumstances. Consequence analysis[4] has been in widespread use for about 25 years, but remains an inexact mixture of science and art borne of experience. Results of modeling may be generally correct, but are typically inexact and non-specific. Nevertheless, modeling results are highly useful in estimating order-of-magnitude consequence severity.[5]

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[1] This three-part Technical Bulletin was written by Mr. Robert R. Roberts of Roberts & Roberts Risk & Reliability Engineering and edited by Alliance Consulting International, San Diego, California under contract to the Methanol Institute.

[2] Information and data are collected from a variety of published and internet sources, though different sources may contain conflicting data regarding the same information. Effort has been made to use reliable sources; however, no responsibility is taken for correctness, accuracy, or errors in information.

[3] Refer to Part 1B of Methanol Institute Technical Bulletin on Using Physical and Chemical Properties to Manage Flammable Liquid Hazards.

[4] Center for Chemical Process Safety: *Guidelines for Chemical Process Quantitative Risk Analysis*, 2nd edition, © 2000, American Institute of Chemical Engineers, ISBN 0-8169-0720-X

[5] A.J. Roos, The Director-General of Labour, Committee for the Prevention of Disasters caused by Dangerous Substances, and The Netherlands Organisation of Applied Scientific Research (TNO): *The Green Book, CPR 16E, Methods for the Determination of Possible Damage to People and objects Resulting from Releases of Hazardous Materials,* December 1989, 1st edition 1992, ISBN 90 5307 052 4.

Using Physical and Chemical Properties to Manage Flammable Liquid Hazards

Part Two of a Three Part Series

Gasoline and methanol are NFPA class IB flammable liquids. Both are known to BLEVE in non-bulk and bulk transport containers, in pressure vessels, and storage tanks in 'roll-over' situations. Vapors of both fuels form plumes and may accumulate in unventilated areas, and both are considered to present an explosion hazard in confined spaces. Beyond this point, the behavior of gasoline and methanol begin to diverge.

The vapor density and equilibrium of gasoline and methanol vapors show marked differences. Gasoline vapor is heavier than air, while methanol vapor is near neutral in buoyancy. Gasoline has an equilibrium true vapor pressure (TVP) two to three times greater than that of methanol. The flammability range of gasoline is 1.4 to 7.6 v/v % versus 7.3 to 36 v/v % for methanol; flash point temperature of gasoline is minus (-) 45 °F versus 52 °F for methanol. Finally, the lower heating value of gasoline is over twice that of methanol; the mass burn rate of gasoline is over three times that of methanol; minimum ignition energy and stoichiometric flame velocity are approximately the same for both.

When comparing the hazardous characteristics of these vapors, it is apparent that gasoline vapor accumulates in low-lying areas and is capable of traveling long distances. Gasoline is also more easily ignited, ignites at lower concentrations, burns faster, and releases more radiant heat than methanol. As a result, gasoline vapor is more likely to concentrate and explode. Gasoline fires produce a much greater radiant heat flux hazard, and as much or more shock wave over pressure. The sum of these characteristics has caused gasoline to be replaced with methanol in high performance race cars where collision, tank rupture, fuel spillage, ignition, fire and explosion are expected to occur.

If consequence severity must be determined beyond a first order level, then users should verify that data contained in the Technical Bulletin's Part 1-B Physical and Chemical Properties tables is appropriate for the desired level of precision in determining the radius of overpressure and radiant heat flux hazard zones. Second order consequences can be readily determined using proprietary consequence modeling software (a variety of software packages can either be purchased or leased). Each software package uses parameter values and calculation techniques, which are judged by the software providers to be appropriate for the algorithms used in their particular model. Therefore, parameter values in the Physical and Chemical Properties tables in Part 1-B of this Technical Bulletin may not correspond to the values used by third-party software.

In order to establish whether the software is appropriate for your specific needs, it is recommended to compare software modeling results to results of actual fire and explosion incidents. Additionally, it is good practice to confirm software modeling results with hand calculations to verify that results provided by the software are reasonable. [6,7,8,9]

A word of caution regarding the use of chemical and physical properties parameters is appropriate. Values of parameters presented in the Physical and Chemical Properties tables are determined in a laboratory environment, and therefore characterize a narrow range of standardized, controlled, and repeatable conditions. Test results for pure materials are not representative of fuel blends, contaminated materials, complications associated with switch loading, and substance property parameters at elevated temperature and pressure. Values presented in the Physical and Chemical Properties tables may or may not typify your conditions of usage or process environments.

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[6] Institution of Chemical Engineers: *Explosions in the Process Industries,* 2nd edition, © 1994 by Institution of Chemical Engineers, pp. 74, ISBN 0 85295 315 1

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FLAMMABLE LIQUIDS

ICC, NFPA, and OSHA classify liquids as flammable or combustible. Each of these designations is divided into sub-classes based on values of selected physical and chemical parameters. These parameters indicate conditions at which vaporization, piloted ignition, and combustion are likely to occur. Liquids are assigned to classes based on the values of identifiable and measurable properties (boiling point temperature and flash point temperature); each flammability class contains materials whose properties fall within a specified range of values. For example, class IA flammable liquids have flash point temperatures below 73ºF and boiling point temperatures below 100ºF (e.g., *n*-pentane). Class IA substances have substantial equilibrium vapor pressure at NTP, and are known to ignite in air at temperatures below normal ambient temperature in the presence of a sufficiently energetic ignition source. Class IB flammable liquids are defined as having flash point temperatures less than 73ºF and boiling point temperatures at or above 100ºF (e.g., methanol, ethanol, and unleaded gasoline). Class IC flammable liquids have flash point temperatures at or above 73 ºF, and boiling point temperatures below 100ºF (e.g., turpentine). Guidance provided in this Technical Bulletin series focuses on IB flammable liquids. This flammability class contains three widely-used motor fuels which are transported, handled, and stored in large volumes by persons and organizations highly experienced in safe handling, as well as in small volumes by users who are less familiar with and practiced in safe handling requirements and procedures.

To an extent, fire hazards that characterize a particular flammability class are common to all of the materials within that class. Class IB flammable liquids include motor fuels, solvents, reactants, and feed stocks. Benzene, toluene, acetone and alcohols are examples of class IB solvents and feed stocks. Notice from the “General Information, Section 1,” of the Physical and Chemical Properties tables that NFPA uses a different classification system than that used by the United Nations (UN) and the United States Department of Transportation (DOT). The latter do not distinguish between Class IA, IB, and IC flammable liquids, and class 2 combustible liquids. Substances in all four of these classifications are grouped together as class 3 flammable liquids by the UN and DOT.

Knowing that a liquid is labeled by UN and DOT as flammable for purposes of transportation and shipping, or falls within a particular NFPA flammability class for storage and handling is useful. However, it is insufficient information to adequately control material hazards and implement effective safe handling programs, though NFPA has published guidance specific to handling each class of flammable and combustible liquids.[10]

In order to implement an effective program, it is necessary to recognize and appreciate differences in the hazards posed by specific hydrocarbons[11] and chemical compounds within each flammability class. Hazards of one material may be different from hazards of another material even though both materials are categorized within the same NFPA flammability class.

Hazard severity is assessed within the context of the properties of the liquid, the circumstances in which the liquid is being used, and the manner in which the chemical is packaged, transported, stored, and handled (blended and processed).

Generalized statements such as “handle and store methanol in a manner similar to the way in which gasoline is handled and stored” are useful only to the extent they establish general expectations of what sorts of safety issues must be addressed. However, guidance based solely on flammability class seldom goes far enough or is specific enough to allow selection of a suite of overlapping safety measures which provide multiple independent layers of protection. Depending on the circumstances, between three and eight levels of protection should be established for

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[10] NFPA 30, 2008 edition

[11] Hydrocarbons are understood to be liquids that boil over a range of temperatures; chemical compounds are understood to boil at a single characteristic boiling temperature.

each hazard. Some levels of protection will safeguard multiple hazards while additional provisions may be necessary to adequately control and protect against a particular hazard in a particular set of circumstances.

Electrical conductivity is an example. 'Specific electrical conductance,' or the electrical conductivity of gasoline is so low that gasoline and other similar hydrocarbons such as kerosene, jet, diesel, and fuel oil are considered to be dielectrics (non-conductors or insulators). By comparison, specific conductance of methanol is several orders of magnitude greater than that of gasoline. Depending on the circumstances, precautions for bonding and grounding may be the same for gasoline and methanol. However, precautions for methanol may necessarily exceed those for gasoline if, for example, methanol containers are coated with a non-conducting spray-on material for corrosion protection. Because of its high conductivity, containers holding methanol are more susceptible to galvanic corrosion than containers holding gasoline. Additionally, methanol is a solvent, and is compatible with only selected plastics and rubbers. Plastic containers commonly used for gasoline may lose structural integrity when used to hold methanol.[12]

No two hydrocarbons, fuels, or chemicals have identical properties. It is essential that users implement safeguards based on properties specific to their materials, to their specific circumstances, and to their particular use. Guidance provided by NFPA, ASME, API, NEC, NACE, ISA, IEEE, and other groups are 'generally-accepted good engineering practices.' Protective measures provided by these organizations stipulate a minimum standard of care. Depending on users' circumstances and aversion to the consequences of fire and explosion, additional measures beyond those indicated in codes, standards, recommended practices, and regulations may be deemed appropriate, necessary, and cost effective over the long term.

Despite the existence of commercial and industrial guidance, it must be emphasized that little or no specific guidance has been published for the personal use of methanol for 'backyard' batch-type manufacture of biodiesel. Guidance must be extracted from more generalized information published by organizations such as NFPA. First time or relatively inexperienced methanol users are advised to thoroughly research and become familiar with the hazards associated with the material and the use of that material prior to bringing it home. This is true for those manufacturing fuel for personal consumption or making a fuel blend.

Within the context of hazardous materials transport, storage and use, it is important to consider what might happen in addition to what one expects to happen. For example, there are very good reasons why transporting five-gallon cans of methanol in the trunk of a car or even in the bed of a pickup truck, is considered a dangerous activity.

- What if the can leaks?
- What if you are rear-ended by another vehicle?
- What if you suffer a seizure or heart attack while driving from the supplier to your home?

Not all of these events are likely, but all do have a chance of occurring. Guidance and regulations such as those for vehicular transport and storage of five- and 55-gallon containers of methanol, ethanol, gasoline, diesel, and biodiesel may be obtained from local fire authorities. Be certain that you have assessed the potential consequences of actions which may jeopardize your safety and the safety of those around you.

The necessity of using material-specific parameters to assess and control hazards is illustrated by three examples. The examples are selected to characterize the range of methanol users from private individuals making biodiesel in 25- to 50-gallon batches to those who transport, store and use large quantities of methanol (e.g., oil refineries, chemical manufacturers, shipping companies, terminal operators, and transport companies).

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[12] Refer to Methanol Institute Technical Bulletins "Above Ground Tank Storage of Methanol," and "Methanol Drum Transport, Storage and Handling."

1. BOUTIQUE-USERS: HANDLING AND TRANSFER OF GASOLINE/METHANOL IN NON-BULK CONTAINERS:

Gasoline is classified as an irritant; methanol is classified as a toxic material. The consequences of inhaling gasoline vapor when mouth-siphoning liquid from one container to another are unpleasant and may cause acute health effects; however, these are mild compared to consequences of swallowing liquid methanol or inhaling methanol vapor.

Methanol may be toxic to some individuals in teaspoon-sized amounts. Toxic effects of methanol vapor are cumulative within the body. An exposure that does not result in a health effect after the first instance may cause serious health effects on the second or third occasion. Avoid ingesting, inhaling, and contacting methanol and methanol-containing fuel blends. If siphoning transfer of methanol is warranted, then use a siphon pump constructed of a methanol-compatible material, wear personal protection equipment (PPE), bond and ground the siphon, and provide containment in the event of a spill. NEVER transfer methanol by sucking on an improvised siphon hose to start liquid flow.

Static accumulation is another situation to consider when siphoning, pouring, and performing other forms of container-to-container transfer of flammable liquids. The electrical conductivity of gasoline is 25 pS/m (pico Siemens per meter), and that of low sulfur diesel fuel is 5 pS/m.[13] Conductivity of gasoline and diesel are so low that these fuels can accumulate static charge during pumping, filtering, and splash transfer operations. Grounding and bonding during liquid transfer is a necessary protection against static discharge when handling all flammable liquids. This is especially true for liquids that have conductivities less than 50 pS/m, and for practical purposes, 100 pS/m. Liquids with conductivity less than 50 pS/m accumulate static charge.[14] Low conductivity hydrocarbon fuels such as gasoline, kerosene, and low sulfur No. 2 diesel are liquid dielectrics (i.e., insulators).[15,16] Transfer rate must be carefully controlled,[17] and containers, hoses, and piping must be bonded and grounded so that electrical resistance of the connection to ground is no greater than 106 ohm for static dissipation and 1-2 ohms for lightning and stray current protection.[18]

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[13] Refer to the Physical and Chemical Properties Tables of this Technical Bulletin

[14] http://www.ntsb.gov/recs/letters/1987/M87_23_25.pdf; Marine Accident Report "Explosion Aboard Tank Barge TTT 103, Pascagoula, Mississippi, July 31, 1986" (NTSB/MAR-87/06)

[15] Fuel oils (kerosene, diesel, fuel oil, and residual fuel oil in the USA; fuel oil and residual fuel oil in Europe) and gasoline are dielectric liquids. Dielectric liquids are defined as having electrical conductivity < 10^{-6} S/m or 1 µS/m. [http://www.mbhes.com/conductivity_measurement.htm; http://www.dispersion.com/non-aqueous-conductivity.html]

[16] A.I. Belousov, I.V. Rozhkov, and E.M. Bushueva: *Measurement of Bulk Conductivity of Hydrocarbon Liquids*, © 1983 Plenum Publishing Corporation, UDC 665.7:543, p. 474.

[17] Pipe maximum velocity = 23 ft/s and maximum air drop velocity = 3 ft/s until fill pipe is submerged at which time velocity may be increased to between 15 and 20 ft/s. [American Petroleum Institute: "Precautions Against Electrostatic Ignition During Loading of Tank Motor Vehicles," 1975, NFPA 70, and http://resource.invensys.com/instrumentation/documentation/eib/ti/ti_027-072.pdf]

[18] API Recommended Practice 2003, 6th edition, September 1998, "Protection Against Ignitions Arising Out of Static, Lightning, and Stray Currents"

By comparison, the electrical conductivity of neat methanol is 44 x10^6 pS/m[19] (44 µS/m) and that of industrial grade methanol is 30 µS/m[20]. The specification for electrical conductance of fuel grade methanol varies by manufacturer, but it is given by PCC Morava Chemicals as less than 1000 µS/m.[21]

Like water, methanol is a polar material and has a relatively high conductivity compared to non-polar hydrocarbon dielectrics such as gasoline and diesel fuel (conductivities less than 1 x 10^4 pS/m). Liquid fuels which have specific conductivity greater than 50 pS/m are not exempt from the necessity of bonding and grounding. The relatively high conductivity of methanol indicates that accumulation of static charge within the liquid is less likely and is not expected under normal circumstances. However, static accumulation, static discharge, and vapor ignition are known to occur in abnormal circumstances more often than might be supposed. The risk of not taking appropriate bonding and grounding measures is that an abnormal circumstance may exist, but can go unrecognized.

Two examples of the consequences of failing to adequately bond and ground when unrecognized abnormal circumstances existed during methanol transfer are described below.

- 2006, California. Green Star Products, Inc., of Bakersfield, California reported a serious "fire incident" late last month at the site of ABF's biodiesel plant. According to GSPI, the accident occurred outside of the plant building when, during a transfer of methanol, a small spill ignited. While the ignition source remains unknown, GSPI expects it was likely caused by static electricity. ABF suffered a total loss of the building and equipment. No plant personnel were injured during the blaze.[22]
- 2008, Canada. During abnormal transfer of methanol from one tanker truck to a second tanker truck, the methanol ignited causing one fatality, destroying the trucks, and damaging a load out facility. Investigators suggested the source of ignition was static discharge resulting from a damaged transfer hose which interfered with grounding and bonding.[23]

Never transport methanol or gasoline in the trunk of a car, even if the trunk lid is open. Vehicular transport must be placarded, and transport within the US must comply with other DOT requirements including provisions for manifest papers, driver emergency response training, emergency response equipment, and emergency notification capability. Always store gasoline and methanol outside, under cover, and in a well-ventilated location. It is not normal practice to store and use 55-gallon quantities or even five-gallon quantities of methanol in urban and suburban housing environments. Contact your local fire marshal before bringing 55-gallon and even five-gallon quantities of flammable liquid to your residence. DO NOT store flammable liquids of any kind, including gasoline and methanol, in your house, garage, patio, or basement, or immediately adjacent to your house, garage, or car port.

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[19] Laurence G. Britton: *Avoiding Static Ignition Hazards in Chemical Operations*: © 1999 by American Institute of Chemical Engineers, ISBN 0-8169-0800-1, pp. 282

20 http://baltchemtrade.com/site/files/metanol-en.pdf and http://n-azot.ru/download/product/product_337.pdf

21 http://www.pccmorava-chem.cz/ttw/mch.nsf/id/EN_Methanol

22 Joseph LaStella, GSPI: "Methanol Spill at CA Biodiesel Plant Ignites Devastating Fire," *Alternate Transportation Fuels Today*, March 3, 2006; http://www.allbusiness.com/operations/shipping/870584-1.html as of March 2011.

23 Fires & Explosions in the Canadian Upstream Oil & Gas Industry: Incident #23-Methanol Spill Ignited While Preparing to Repair Tank Truck Leak; http://www.firesandexplosions.ca/case_studies/case_details.php?id=27.

2. REFINERIES AND BIODIESEL MANUFACTURERS: HOT WORK AND FLAMMABLE LIQUID VAPOR CONTROL

Gasoline floats on water while methanol is fully miscible with water, though methanol floats during methanol-water mixing. Methanol-water mixtures burn at high water concentrations (ratios of 3:1 to 4:1 water:methanol v/v). [24]If floating methanol is ignited, it continues to burn as it mixes with water and the methanol-water solution burns when mixing has occurred. In this situation, addition of water may increase the volume of flammable liquid.

Gasoline TVP is 190 mmHg and the TVP of methanol is 90 mmHg. The partial pressure of gasoline vapor over liquid gasoline is twice that of methanol vapor over methanol liquid, which is to say that, volume for volume, gasoline emits twice as much vapor as does methanol. The amount of heat required to vaporize a pound of gasoline is about a third of that necessary to generate a pound of methanol vapor. The flammability range for gasoline is 1.4 to 7.6 v/v %, compared to 6.0 to 36.5 v/v % for methanol. Gasoline vapor is within its flammable range at 30% of the concentration of methanol under identical circumstances, but passes out of the flammability range much more quickly than methanol as liquid temperature increases.

Ignition energies of gasoline and methanol are similar (0.2 mJ and 0.14 mJ respectively). An ignition source with sufficient energy to ignite gasoline will also ignite methanol and *vice versa*. Gasoline vapor is heavier than air and tends to flow along the ground and accumulate in low-lying areas. Methanol vapor is near neutral buoyancy and responds more readily to dilution and dissipation caused by natural convection currents and forced ventilation. Non-bulk and bulk storage of both gasoline and methanol must be grounded, bonded, and well ventilated. Storage areas should be equipped with vapor detectors. Detectors for gasoline must be positioned to detect gasoline as a dense vapor, while positioning of methanol vapor detectors may be different from that of gasoline vapor detectors because of the difference in relative density of gasoline and methanol vapors. The sensitivity of methanol detectors may need to be greater than that for gasoline.

Vapor density of methanol is 1.1 relative to that of air while the vapor density of gasoline is 3 to 4. Vapors of both gasoline and methanol may be explosive in confined spaces. It is recommended that storage areas be ventilated, that storage containers be clearly labeled, bonded and grounded, that protective restricted-access hazard zones be declared around storage areas, and that sources of ignition be eliminated within designated zones.

A shipping terminal may decide to use inert gas to pad storage tanks for both gasoline and methanol, but for different reasons. The purpose in padding gasoline storage may be for fire protection because of the relatively low concentration of the lower flammability limit. If ambient temperature of the liquid is sufficiently low that vapor pressure causes concentration within the freeboard volume of the tank to be within the flammable range, then it may be desirable to use inert gas padding to avoid piloted ignition within the tank.

The purpose of padding methanol may serve multiple purposes:

1) Fire protection due to the wide flammability range of methanol
2) To maintain methanol purity. Facilities which are located in areas that have characteristically high humidity, and/or which have airborne salts, run the risk of contaminating neat methanol as ambient air is sucked into and out of tanks during tank level fluctuations during normal operations.

At normal liquid storage temperatures, the concentration of gasoline vapor within the vapor space for gasoline storage quickly exceeds the upper flammability limit of 7.6 v/v %. The upper flammability limit of methanol is 36%,

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[24] Methanex: "Technical Information & Safe Handling Guide for Methanol, version 3.0, September 2006.

and methanol has a much lower equilibrium vapor pressure than gasoline. Vapor concentration within methanol storage tanks may be in the flammable range when vapor concentration in a gasoline storage tank is outside the flammable range and *vice versa*.

3. ALL USERS: NON-BULK AND BULK STORAGE FIRE PROTECTION AND RESPONSE:

Fire response for a methanol fire is different than that for a gasoline fire.

- Gasoline fires produce copious amounts of luminous combustion products that make gasoline flames readily visible during daytime and bright sunlight. Methanol flames are non-luminous and are difficult to detect visually in daytime, particularly in bright sunlight. In order to effectively fight a liquid fire, it is necessary to identify the location of the fire. Hand held infrared sensors are available to assist fire fighters responding to methanol fires. As good practice, methanol users should have at least one sensor on site and available to first responders. Sensors should be calibrated and functional. Local fire response should also have infrared sensors.
- Gasoline floats on water and application of water spray, particularly as a cohesive stream from a fire monitor may cause the fire to spread. By comparison, methanol floats on and rapidly mixes with water. Methanol-water mixtures will burn at very high water concentrations. Water is most effective as a suppressant when applied as a spray mist or as a fog. Both gasoline and methanol may form running fires if fire-suppressive water is not physically contained by dikes, berms, and curbs. Propagation of methanol fires may not be immediately noticed by responders.
- Methanol is more toxic than gasoline, even to skin contact. Responders to a methanol fire must wear PPE that protects against chemical exposure as well as exposure to radiant heat. Turnouts provide heat protection but not chemical protection. Inhalation protection is also required.
- Given identical circumstances, vapor cloud explosions may be more likely to occur from spilled gasoline than from a methanol spill. This is especially true in confined areas. The specific gravity of gasoline vapor is 3-4 times heavier than that of methanol vapor. Gasoline vapor has higher tendency to accumulate in low lying and poorly ventilated areas than does methanol vapor, and will flow along ground surface in a downhill or downwind direction over long distances. Gasoline has a lower flammability range, lower flash point temperature, and lower autoignition temperature than methanol. Ignition of vapor within a confined space may cause an explosion with either gasoline or methanol.
- Non-bulk and bulk shipping containers holding gasoline are marginally more likely to BLEVE in a fire than those containing methanol. Gasoline has higher vapor pressure, lower specific heat, and lower latent heat of vaporization than methanol (i.e., less heat is required to cause evaporation of gasoline than of methanol). Pressures within gasoline containers will increase more rapidly than within methanol containers when exposed to the same radiant heat flux. The lower heating value of methanol is 9,080 Btu/lb compared to 19,000 Btu/lb for gasoline. Radiant heat released by a gasoline BLEVE will be twice that of methanol. The stoichiometric laminar flame speed of methanol is only marginally higher than that of gasoline, so differences in overpressure due to differences in flame speed is not a consideration. Flame temperature of gasoline is marginally greater than that of methanol. Differences in flame speed and explosive overpressure are likely offset by the much higher heat release of gasoline.
- Fire suppression foam used to fight gasoline fires is not suitable for use on methanol fires, as methanol fires require alcohol-resistant foam. Good practice consists of inventorying alcohol-resistant foam both on a user’s property and at the location of first responders. It is also good practice to periodically perform response exercises for various scenarios. Table-top exercises may also be useful. Verify that fire suppression foam is of the correct type and that its suppression capability does not degrade as a result of time in storage, or storage temperature variability if the facility is in a hot or cold climate. Verify that fire suppression effectiveness is not compromised by freezing, or exposure to temperatures over 100^{o}F.

In summary, gasoline may be more or less hazardous than methanol depending on the particular set of circumstances.

A tragic example of this involving a race car driver and his chief mechanic occurred in 2010. The driver and mechanic were celebrating winning an important race in the parking lot of their automobile repair shop. In their excitement they decided to ride a lighted drum of methanol across the parking lot of their garage facility. They poured four gallons of methanol racing fuel into an empty drum, tipped the drum over, positioned the bung in an easy-to-reach position, sat atop the drum like it were a horse, and lit the drum. Their expectation was that the drum would slide across the parking lot like a rocket. Instead, the drum exploded. One man died and the other was critically injured.[25]

Methanol, which had increased their survivability in the high stakes sport of automobile racing hours earlier, caused serious injury and death under a different set of circumstances. Though it is unlikely, this may have been a near miss incident had the drum in this instance contained gasoline instead of methanol because of differences between the properties of the two materials. The high vapor pressure, heavier-than-air vapor, small flammability range, and low value of the upper flammability limit for gasoline may have created a fuel-rich atmosphere within the drum that was incapable of igniting. Had this in fact been the case, the men would have been unsuccessful at lighting the drum and the catastrophe would have been avoided. Whereas the men would have possibly recognized the hazards had they used gasoline, it is likely they did not appreciate a potentially greater hazard posed by methanol in this highly abnormal situation.

This tragic example illustrates the importance of understanding the physical and chemical properties of the specific material with which you work and how they apply to your specific circumstances, in order to be able to recognize unique hazardous conditions and establish appropriate measures to manage flammable liquids safely.

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[25] Internet web page as of March 2011: http://www.komonews.com/news/local/98960929.html

Methanol Safe Handling

TECHNICAL BULLETIN

Methanol Institute

Using Physical and Chemical Properties to Manage Flammable Liquid Hazards Part Three of a Three Part Series[1]

INTRODUCTION

This is the last section of the three-part Technical Bulletin, which provides guidance for using physical, chemical, thermal, and electrical properties to identify and control hazards of flammable liquids. Eight fuels [hydrogen, compressed natural gas, propane (a compressed gas), methanol, ethanol, gasoline, No. 2 diesel, and biodiesel] are used as examples. The table in Part 1-B lists the physical and chemical properties of these materials.[2]

PRINCIPLES OF IGNITION AND COMBUSTION

Combustion is a chemical oxidation process that requires formation of chemical radicals by transfer of electrons between an oxidizing agent (21 v% oxygen in air) and reducing agents (flammable liquids). Three conditions are necessary for ignition to occur. A fourth condition is necessary for combustion to occur, and a fifth condition is necessary for fire propagation.

1) A fuel must be present (e.g., methanol)
2) An oxidizer must be present (21 v% oxygen as air)
3) A source of ignition must be present with sufficient energy to initiate formation of chemical radicals
4) A chemical chain reaction must occur which generates an exponentially increasing number of chemical radicals which sustain the combustion process and cause the fire to release increasing amounts of heat.
5) Heat released by the exothermic combustion reaction must be sufficient to pre-heat and ignite surrounding material.

Vapors burn, while liquids do not. Flammable and combustible liquids must be heated to a temperature at which sufficient vapor is generated at the liquid surface to enable ignition and then support combustion. The temperature at which ignition occurs is the *flash point temperature*. Flash point temperature is determined in the laboratory by standardized experimental testing. Fuels ignite but do not combust at their flash point temperature.

1) Flammable liquids must have sufficient energy (measured as temperature) to release a sufficient amount of vaporized fuel (vapor in equilibrium with the liquid) to support combustion. This temperature is termed the flame point temperature of the liquid. In practical terms, flash point temperature is used instead of flame point temperature to assess likelihood of ignition. Flame point temperature is typically 10–15 ^{o}F higher than the flash temperature for most flammable liquids. The flash point temperature is the minimum temperature at which ignition can occur, but does not generate sufficient vapor to support combustion

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[1] This three-part Technical Bulletin was written by Mr. Robert R. Roberts of Roberts & Roberts Risk & Reliability Engineering and edited by Alliance Consulting International, San Diego, California under contract to the Methanol Institute.

[2] Information and data are collected from a variety of published and internet sources, though different sources may contain conflicting data regarding the same information. Effort has been made to use reliable sources; however, no responsibility is taken for correctness, accuracy, or errors in information.

Using Physical and Chemical Properties to Manage Flammable Liquid Hazards

Part Three of a Three Part Series

2) The molar or volumetric concentration of flammable vapor in air must be within the flammable range of that specific liquid

3) Fuel molecules must be mixed and have intimate contact with oxygen molecules within the surrounding air

4) An ignition source must be active and transfer sufficient energy to the vapor/air mixture to initiate a chain reaction. Alternately, the fuel/air mixture must be in contact with a surface above the autoignition temperature of the fuel

5) The exothermic combustion chain reaction must release sufficient heat to propagate ignition, thereby sustaining combustion

The energy source that causes ignition can be *auto-ignition* (e.g., a hot surface or hot air), or *induced* or *piloted* ignition (e.g., a spark, an electric arc, or an open flame). Regardless of whether ignition is auto- or induced, the ignition source must be sufficiently energetic to raise the temperature of an infinitesimally small mixture of fuel and air to the fuel's *ignition temperature*. The *ignition temperature* is the temperature at which covalently-bonded molecules of fuel and oxygen begin to spontaneously transform into positively and negatively charged radicals which then recombine as combustion products (e.g., CO, CO_2 and H_2O), thereby releasing heat.

If an ignition source is sufficiently energetic to drive the rate of formation of free chemical radicals to the point at which the exothermic heat of reaction of combustion products generates a sustainable, exponentially accelerating number of positively and negatively-charged radicals, then combustion has occurred, flames and heat are generated, and a fire begins to burn. If the chain reaction continues unchecked, then combustion occurs and the fire gets larger. Once combustion occurs, flames spread and grow in size as a kinetic process characteristic of exponential chain reactions. Fire propagation will continue as long as there is unburned fuel, or until the fire is extinguished by external intervention. The rate at which fuel is converted (burned) is termed the "mass burning rate." If the mass burning rate, the surface area of the pool, and the lower heating value (LHV) of the fuel are known, then it is possible to estimate the rate of radiant heat flux from the fire.

TYPES OF FIRES AND FIRE HAZARDS

Fires are generally classified as belonging to one of four categories:

1) Pool fires- resulting from spills, leaks, and condensation of vapor from pressure flashing liquids

2) Jet fires- resulting from a pressurized containment vessel or pipe into free air

3) Flash fires- occurs when a cloud of flammable gas is ignited

4) Fireball- fireballs occur when a quantity of flammable liquid or gas suddenly releases from pressurized containment and is immediately ignited as in boiling liquid expanding vapor explosions (BLEVEs)

Behavior of pool fire flames is entirely under the influence of their own buoyancy; flames are easily displaced by wind and can change shape rapidly and unexpectedly. Jet fires typically have a long flame which is unaffected by wind. Fire duration is dependent on release rate and pressure of the exiting fluid at the point of release. The shape of flash fires is determined by the shape of the flammable cloud and the position of the cloud relative to the location of the ignition source. Flash fires are usually short in duration and are known to flash back to the source of fuel vapor, be that a pool, or a jet release. When flame speed and fire propagation are slow then deflagration occurs and overpressure is small. When flame speed is high, approaching sonic velocity (1,126 ft/s @ NTP) the deflagration transitions to an explosion, and overpressure becomes an additional consideration for life safety and damage. Overpressure estimation should be performed by someone who is trained in that subject matter. The hazard of pool, jet, flash, and fireball fires is primarily exposure to radiant heat flux. Exposure to 37.5 kW/m^2 will result in instantaneous death. Safe exposure levels are typically around 5 kw/m^2. Phani K. Raj provides a summary of radiant heat exposure criteria in a 2007 article in *Journal of Hazardous Materials*.[3] A brief summary of overpressure effects on humans is summarized by The Institution of Chemical Engineers.[4]

POINT SOURCE MODEL FOR ESTIMATING RADIANT HEAT FLUX

A point source model can be used as a quick and simple method of estimating thermal radiation. The point source model assumes heat of combustion radiates in all directions equally from a single point. The total heat available for transfer by radiation is calculated as the product of the fuel mass burn rate (a characteristic parameter of each particular fuel), the surface area of burning fuel (not the surface area of the flames), and the LHV for the fuel (preferably the heat release rate of vapor reacting to form non-condensable gaseous combustion products and water vapor).

Incident radiant heat flux (I) at any distance from a pool fire is determined as

$$I = \frac{f\,(\text{LHV as Btu/lb})}{4\pi d^2}$$

where *f* is the fraction of the heat which is released (use *f* = 1 to determine an upper bound), LHV is the heat released when a pound of fuel vapor is converted to gas and vapor combustion products, and d (in feet) is the radius at which one wishes to estimate incident heat flux. A disadvantage of the point source model is that it underestimates incident radiation levels for distances within two diameters of the fire. More refined point source methods are also available.[5]

Behavior of liquid pool fires can be useful in first order estimation of heat flux from large fireballs since both pool fires and fireballs are buoyancy dominated. Fireballs with maximum diameter of 30 to 35 feet have measured surface emissive power of 185 to 224 kW/m^2. Larger fireballs can be approximated using values of surface emissive power between 250 and 300 kW/m^2. Calculating incident radiation levels for fireballs is complicated and depends heavily on the value selected for the emissive power of the fireball. It is recommended that users enlist the assistance of a qualified consultant if second order results are required for radiant heat flux from fireballs.

In small fires, heat is released by conduction, convection, and radiant heat transfer processes. Heat release in large fires (> 1-2 feet diameter) is primarily by radiant heat transfer. Radiant heat flux determines the radius of the hazard zone for a fire. The radius of the hazard zone for overpressure must be determined separately.

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[3] Article by Pani K. Raj, " A Review of Criteria for People Exposure to Radian Heat Flux from Fires," available on http://cms.totalsafety.nl/uploads/Criteria%20for%20people%20exposure%20to%20radiant%20heat%20flux.pdf as of March 2011

[4] Institution of Chemical Engineers: *The Effects of Explosions in the Process Industries, Overpressure Monograph, First paper of the Major Hazards Assessment Panel – Overpressure working party*,© 1989 by The Institution of Chemical Engineers, p. 8, ISBN 0 85295 235 X.

[5] Institution of Chemical Engineers: *Calculation of the Intensity of Thermal Radiation from Large Fires, Thermal Radiation Monograph, First Report of the Major Hazards Assessment Panel – Thermal Radiation Working Group*, © 1989, by The Institution of Chemical Engineers, 22pp., ISBN 0 85295 236 8.

HEAT OF COMBUSTION

The exothermic combustion reactions of fuel in air release heat and are typically characterized by four parameters: two for the liquid to gaseous-plus-liquid phase and two for the liquid to gaseous-plus-vapor phase:

- Gross or High Heating Value (HHV) of a unit volume of liquid
- Net or LHV of a unit volume of liquid
- Gross or HHV of a unit weight of flammable vapor
- Net or LHV of a unit weight of flammable vapor

An additional value, which is more useful for first order consequent modeling, can be determined which takes fuel from the vapor state to combustion products in the gaseous-plus-vapor state. This value is also a LHV, but is more representative of conditions for consequence modeling in that released heat is determined as the heat of combustion of fuel vapor-to-gaseous products plus water vapor. This parameter appears in the table for flammability parameters in Part 1-B of this Technical Bulletin.

Gross or HHV is the amount of heat produced by complete combustion of a unit quantity of fuel (measured either as units of volume or weight) determined as energy released by an exothermic combustion reaction when all combustion products are cooled to the temperature which existed before combustion (e.g., 60 °F), including the energy released as heat by cooling and condensing combustion-derived water vapor. The HHV is essentially the heat of combustion. This is a thermodynamic parameter, which represents theoretically available heat when a pound or gallon of fuel is burned.

Net or LHV is the amount of energy released as heat when all combustion products are cooled to the temperature which existed before combustion, excluding heat associated with cooling and condensing combustion-derived water vapor.

When assessing consequences of fire events, it is appropriate to use the heat of combustion or HHV to determine the theoretical upper limit of radiant heat flux. The LHV should be used if a more realistic value for heat flux is desired. It is preferable to use the LHV of fuel vapor to combustion product vapor when this value is available.

IGNITION

Ignition is a time-dependent process of starting a fire that begins with reactants and evolves over time to combustion: i.e., a steadily burning flame,[6] combustion products, and heat release. *Induced ignition* is initiated by a spark or flame; *autoignition* is a result of temperature. Generally speaking, fuels which ignite easily also grow quickly with rapid flame propagation. Fuels with high heat capacity (the ability to absorb large amounts of heat without increasing liquid temperature) and high thermal conductivity (the ability to readily transfer heat) may be more difficult to ignite than fuels with low heat capacity and low thermal conductivity. Temperature near the source of heat rises rapidly in the latter.

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[6] Ignition processes are always time dependent.

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A list of commonly encountered ignition sources and their respective energy is shown in the table below.

Theoretical/Ideal/Approximate Temperatures of Potential Ignition Sources[7]

Potential Ignition Source Item	Environmental Conditions	Approximate Temperature (°F)
Fluorescent Light	ambient air @ room temperature	140 - 176
Incandescent Light	ambient air @ room temperature	212 - 572
Lighted Cigarette	unventilated ambient air @ room temperature	550
Lighted Cigarette	ventilated ambient air @ room temperature	752 - 1,436
Lighted Cigarette	insulated & smoldering in ambient air @ room temperature	950 - 1,150
Hot Electric Stove Element	ambient air @ room temperature	> 1,026
Burning Match Flame	ambient air @ room temperature	1,112 - 1,472
Tungsten Halogen Light	ambient air @ room temperature	1,112 - 1,652
Burning Candle Flame	ambient air @ room temperature	1,112 - 2,552
Electrical Spark	ambient air @ room temperature	2,400
Electrical Arcing	ambient air @ room temperature	< 6,782
Lighted Bunsen Burner Flame	ambient air @ room temperature	2,858
Methanol Flame	ambient air @ room temperature	3,470
Methane Flame	ambient air @ room temperature	3,488 - 3,540
Plasma Torch	ambient air @ room temperature	≈ 8,492
Lightning Strike	ambient air @ room temperature	54,032

FIRE PREVENTION

Fires can be prevented using several strategies:

1) Declare areas surrounding fuel storage and handling as hazardous locations. Remove potential ignition sources to a safe distance (i.e., a distance beyond the farthest expected concentration of the lower flammability limit) from the area in which fuel vapor may be present

2) Suppress formation of fuel vapor below the lower flammability limit (e.g., reduce liquid temperature, or prevent liquid temperature from rising above a predetermined set point

3) Isolate the fuel from contact with air using natural gas or inert gas padding and/or internal and external floating roof tanks as appropriate

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[7] "Approximate Temperatures of Potential Ignition Sources"; http://www.derose.net/steve/resources/engtables/flametemp.html

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FIRE SUPPRESSION

Fires can be extinguished using several combinations of strategies and tactics:

1) Allow the fire to consume all available fuel and burn itself out

2) Remove the heat of combustion by spraying the fire with water fog and fine water droplets. The heat of vaporization of the water droplets removes heat from the fire and slows the rate of the combustion reaction, thereby reducing the amount of heat available for fire propagation

3) Exclude air from contact with the fuel (CO_2 deluge at loading racks, solid fire extinguishers for small isolated fires, and fire suppressing foam for large fires)

4) Interrupt the chain reaction with fire suppressant extinguishing media (i.e., foam)

FUEL PROPERTIES

The severity of a liquid flammability hazard is determined by the following properties:

- Availability of vapor which is determined by the following properties:
    - Liquid temperature determines the partial pressure of a vapor in equilibrium with its liquid
    - Flash point temperature and flame point temperature determine the minimum temperature at which ignition can occur
    - Boiling point temperature is the temperature at which the partial pressure of the vapor equals atmospheric pressure
- Availability of air (air is 21 v% oxygen)
- Ignition source with sufficient energy or temperature to start an oxidation reaction determined by:
    - Minimum ignition energy
    - Autoignition temperature
- A fuel/air mixture that is capable of burning which is determined by:
    - Upper and lower flammability limits
    - Stoichiometric air-to-fuel ratio
- Sufficient exothermic heat of reaction to sustain combustion which is determined by:
    - Exothermic heat of reaction or net heating value
    - Rate at which energy in the form of heat is conducted away from the fuel

Combustion of fuels with higher heats of combustion release more heat, propagate more quickly, and may be more difficult to extinguish than fuels with lower heats of combustion.

Liquid vapor pressure and therefore evaporation rate increase as temperature of the liquid increases. Typically, if flammable liquid evaporation rate ≥ 0.047 lb/ft^2 ($2\ g/m^2$), then sufficient vapor is available to support combustion.

If the lower flammability limit is comparatively small, such as that for gasoline, then combustion can occur at a relatively low vapor pressure and therefore at relatively low temperature. If the upper flammability limit is close to the lower flammability limit, then the temperature range capable of supporting combustion is relatively small.

Conversely, if the difference between the flammability limits is large, such as the upper and lower limits of methanol, then the temperature range capable of supporting combustion is large, and ignition can occur at high vapor concentrations. The upper flammability limit of gasoline is the same as the lower flammability limit for methanol. This has implications for the flammability limits of gas/methanol blends.

Boiling point is another consideration. Gasoline boils over a range of temperatures, and methanol boils at a single temperature. Depending on the composition of the gasoline, substantial amounts of vapor may be released at relatively low temperature. Typically Reid vapor pressure is used as an indication of initial boiling point and boiling point range. If Reid vapor pressure is high, then true vapor pressure is high at low temperatures. If Reid vapor pressure is low, then true vapor pressure is low at high temperatures.

If a liquid has a low flash point temperature, low minimum ignition energy, and large LHV, then ignition occurs more easily, and fire propagation is rapid. If a large amount of energy is required for ignition, then the vapor is less likely to contact a sufficiently energetic ignition source and ignition is less likely to occur. If LHV is low, then fire propagation is slower. Flame speed and heat release rate should also be considered when assessing flame flash back, and the rate of flame front propagation.

LIQUID PROPERTIES, SOURCE TERMS, AND WORST-CASE CONSEQUENCES

First order worst-case consequences[8] of spills and accidental releases can be estimated using parameters listed in the table in Part 1-B of this Technical Bulletin.

Confined space explosions, BLEVEs, and unconfined vapor cloud explosions (deflagrations) present two hazards: overpressure and radiant heat flux. Severity of fire/explosion damage is greater for fuels with higher flame speed such as hydrogen, higher flame temperature, and higher specific energy than for materials with lower flame speed, lower flame temperature, and lower specific energy. Over-pressure hazard severity increases as flame speed increases. Pressure and temperature also increase flame speed. Within the perimeter of the blast zone, people are subject to serious injury, and the range and severity of damage to plant equipment is greater.

Worst-case process accidents are those involving large amounts of flammable liquid with high vapor pressure, high flame speed, high flame temperature, high specific energy, high heating value, and large mobile vapor plumes. When liquid flammability hazards are combined with process safety hazards (e.g., operating temperature and pressure), consequences may be catastrophic, involving multiple fatalities, extensive destruction and damage to equipment, and forced outage for extended periods of time.

An elevated process temperature creates high vapor pressure and a high rate of vaporization; large and abrupt pressure letdown promotes vapor flashing and conversion of large amounts of escaping liquid to vapor and aerosol. Initial release rate for letdown pressures ≥ 110 psig occurs at speeds approaching sonic velocity. Vapor flashing causes turbulence at the point of release, which increases air entrainment and mixing within the vapor cloud. Kinetic energy supplied by an escaping jet may launch the vapor cloud, causing the plume to travel further than a plume released from a pool fire.

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[8] injuries, fatalities, physical damage and destruction of equipment, business interruption, and environmental remediation costs attributable to accidental release events: toxics, flammable liquids, and explosive vapors and aerosols

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Once formed, vapor clouds may float upward, remain more or less stationary, flow down slope, or move downwind away from the breech point. Moving vapor clouds are more likely to encounter an ignition source than non-moving clouds. Combustion may flash back to the point of breach and forward to the outside edge of the vapor cloud. Vapor concentrations at the surface of the vapor cloud form a steep concentration gradient with ambient air and are almost certain to form a zone that is within the flammable limits.

According to an article on the causes of industrial fires, "Fire and explosion accidents are of major concern to the owners and operators of refineries and petrochemical plants, gas processing plants, terminals, and offshore facilities. Statistics have shown that the majority of monetary loss in these types of complexes is due to fire and explosion. According to recent statistics, 77 percent of the monetary loss in refinery and petrochemical complexes is due to fire and explosion. The breakout of accidents due to fire and explosion is 65 percent vessel failure and vapor cloud explosion and 35 percent fire. The causes of these accidents are mostly attributed to mechanical issues, process upset, and operator error."[9]

Unconfined and confined vapor cloud explosions (UVCEs and VCEs) pose the greatest hazard. BLEVEs, UVCE's, and VCEs, jet fires, and pool fires are credible worst-case scenarios when handling flammable liquids.

PREVENTING FIRES AND EXPLOSIONS

Avoiding worst-case accidents involving flammable liquids requires diligence in establishing and maintaining multiple levels of protection. A facility's 'levels of protection' strategy evolves directly from fundamental operational practices. A list of suggested objectives may be to:

1. Establish a clear understanding of the design intent and performance expectations of
    - The plant
    - Process units that comprise the facility
    - Equipment items that comprise the process units
2. Preserve the engineering design basis (documentation, equipment configuration) through a rigorous management of change program
3. Identify and control hazards
4. Seek out and apply best practices, and generally accepted good engineering practices (be familiar with applicable codes, standards, regulations, and recommended practices and the underlying rational)
5. Preserve equipment mechanical integrity and fitness for purpose
6. Develop job skills and establish standards and responsibilities for job performance of operations and maintenance functions
7. Recognize and learn from mistakes (your own and those of others)
8. Anticipate, prepare for, and practice recovery from abnormal operations and hazardous material release events

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[9] Reza Pourdarvish, Shahryar Khajehnajafi, and Chris Cowles: "The Many Faces of Fire Hazards in Industrial Settings" *OH&S Magazine,* Dec 01, 2010. http://ohsonline.com/Articles/2010/12/01/The-Many-Faces-of-Fire-Hazards-in-Industrial-Settings.aspx

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Ever-occurring incidents involving flammable and combustible liquids at facilities worldwide are testimony to the difficulty of transforming the above objectives into an effective and disciplined management system. The following lists a few of the many reported flammable and combustible liquid accidents during 2010:

- Three hurt in fire and explosion at Sparks, Nevada biodiesel clean fuels plant
- Fire and explosion at Khark, Iran petrochemical complex
- Taiwan's biggest oil refinery complex catches fire for the third time in six months, second time in July
- More trouble for one of Taiwan's largest companies. Formosa Petrochemicals Corp has had another fire in one of its factories
- One person critically injured in an explosion and fire at a refinery in San Antonio, Texas. "Immediate cause of the fire appears to have been an explosion on one of the trucks loading a light hydrocarbon from the AGE loading rack." AGE facility is a refiner of jet fuel and diesel products that refines 13,500 barrels a day and has tank farm storage capacity of 208,000 barrels. The explosion/fire is the second that has occurred since 2008
- TESORO (Anacortes, Washington) Anacortes refinery fire. The blast was the largest fatal refinery accident since a 2005 explosion at a BP American refinery in Texas killed 15 people and injured 170.
- Burning taxi pulled into a gas station in Baltimore, Maryland
- Car Fire explosion in Detroit, Michigan broke firefighter’s legs

CONCLUSIONS

Flammable liquids can be handled safely if they are handled properly. Flammable liquids are dangerous when mishandled.

Each of the hundreds of OSHA and NFPA IA, IB, and IC flammable liquids has characteristic physical, chemical, thermal and electrical properties which are useful in identifying and judging the severity of specific hazards. Use these properties to identify hazards and to devise strategies for controlling those hazards.

Consider using at least three, and in high hazard situations, as many as eight independent protective control measures. Learn to anticipate, prevent, recognize, and respond to abnormal operating conditions.

Users do not deliberately cause fires and explosions. On most occasions, users are unaware of the severity of the hazards. Mishandling is typically the result of a lack of knowledge, not willful destructive intent.

It is users’ responsibility to continuously strive to be better informed, and more adept at identifying and controlling hazards