

Final DRAFT

California Dimethyl Ether Multimedia Evaluation

Tier I

Prepared

By

**The University of California, Davis
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Executive Summary

Dimethyl ether (DME) is a new fuel that could help address environmental and fuel security issues. DME can be produced from a variety of feedstocks, including natural gas or bio-methane. Current production is focusing on methane-containing feedstocks, but gasification of any suitable organic source can lead to the syngas chemistry products with DME as one of the more energy efficient options. DME is a gas under ambient conditions with properties similar to those of LPG and can thus be stored as a liquid under moderate pressure. DME produced from bio-methane (from landfill gas or the decomposition of manure, for example) would be a non-fossil, renewable fuel.

Since DME is a new fuel, the California Air Resources Board (CARB) must provide a “multimedia risk assessment” before adopting new fuel specifications (as required by California Health and Safety Code, Section 43830.8). Further, existing law states that the “California Air Resources Board cannot adopt any regulation establishing a motor vehicle fuel specification unless a multimedia evaluation is conducted to determine whether the regulation will cause a significant adverse impact on the public health or environment” (California Senate Bill 140, 2007). The purpose of this multimedia risk assessment is to provide the State of California information that will allow an informed decision as to the relative health and environmental impacts to the State’s resources, human health and environment posed by the use DME as a transportation fuel.

As a result, the California Environmental Protection Agency (Cal-EPA) has initiated a program to assess the multimedia life-cycle impacts of DME use in California. The risk posed by DME as a diesel alternative is assessed as a relative risk compared to ultra low sulfur California diesel currently in use.

This Tier I report is the first step in a three-tier process evaluating the cumulative health and ecological impacts from releases to air, surface water, groundwater and soil at all stages of the DME life-cycle: production, storage and distribution, and use.

The goal of this Tier I report is to identify what is currently known about DME along with a discussion of key uncertainties and data gaps, including:

- Physical, and chemical and environmental toxicity characteristics of the reference fuel, candidate fuel and additive components,
- Summary of all potential production, distribution, storage, and use release scenarios including a discussion of the most likely release scenarios,
- Summary of the expected environmental behavior (transport and fate conceptual models associated with release scenarios) of proposed fuel or fuel components that may be released, and

- Comparison of physical, chemical, and toxic properties of the fuel or additive components to appropriate agreed upon control fuel or fuel components.

This report excludes the direct and indirect environmental, ecological, and health impacts associated with biomass production such as changes in land use and the possible net gain in carbon emissions due to feedstock production.

During Tier II activities, a plan of action is developed to address these uncertainties and data gaps and conduct a life-cycle based assessment of the potential impacts DME may have to the State's resources, human health and environment. During Tier III activities, the life-cycle based assessment is performed and the results reported to California Environmental Policy Council.

Summary of Tier I Findings on the Potential Impacts of DME

Production of DME

DME can be produced through three different production pathways: a two-step, a one-step, and a liquid-one-step process called bireforming. DME is typically produced through a two-step process using syngas as a feedstock. The syngas is converted to methanol, which is then converted to DME. DME can be produced from any methane-containing feedstock, including pipeline natural gas, biogas, landfill and waste water treatment gas, and stranded natural gas. Water resource requirements and wastewater generation are expected to be minimal.

The Oberon Fuels methane-gas-to-DME small scale production plant process consists of three major steps: syngas production, methanol synthesis, and simultaneous DME synthesis and separation via catalytic distillation. While the first two process steps are common in large scale industrial applications, further development of these processes for small scale applications is open for improvement and implementation. Catalytic synthesis of DME coupled with purification is a well-researched topic that is both promising and feasible but has not been industrially implemented to date. Any needed fuel additives are introduced after the final DME product is produced, ideally prior to transport of the product.

Storage and Distribution of DME

DME is stored, handled, and transferred as a liquefied gas under pressure. LPG infrastructures are widespread in the United States, and basic components of LPG storage and handling technology can be used for the storage and handling of DME. All production and storage, including piping, tanks, and valves, will only be above ground.

To address the lack of existing DME fueling infrastructure, DME producers are likely to initially adopt a hub and spoke model for fuel distribution. DME is centrally produced and delivered to customers as needed on a daily, weekly, or monthly basis. Early adopters are likely to be fleets involved in local and regional haul that drive in and out of the same terminal daily and refuel at this base site.

While handling of DME is similar to propane, pumps, valves, and seals on DME tanks and DME infrastructure must be made of specific materials since there is a risk of seal and gasket failures with some materials. ASTM specification D7901 provides limited guidance on safety and handling of DME, including elastomer selection for gaskets and seals.

Substantial swelling of a variety of incompatible seal and gasket elastomers was observed with DME. Materials used in the storage, handling, and transfer of DME have to be compatible with, and unaffected by, DME, and materials compatibility is a key issue for the tanks, pipes, and valves used for DME storage and distribution. The following materials have been found to be compatible with DME: Nitrile (NBR, BUNA-N), Hydrogenated NBR (HNBR), Silicone (VMQ), Fluorosilicone (FVMQ), Perfluoroelastomer (FFKM), polytetrafluoroethylene (PTFE), and stainless steel. This material compatibility information has been generated by commercial DME handlers, as a general reference, and listed in ASTM D7901.

Use of DME as a Transportation Fuel

There are a number of DME characteristics that require consideration before its wide-spread use as a diesel equivalent fuel in California. Roughly 1.8 Liter (L) of pure DME is equivalent to 1.0 L of diesel fuel, on a lower heating value (LHV) basis. Viscosity of DME is 1/20 of diesel fuel.

Compression ignition engines running on DME do not need diesel particulate filters (DPFs) in order to meet California emission standards for particulate matter. This after-treatment filter is costly and adds weight to trucks whose delivery capabilities are then decreased. Conventional diesel engines require modifications to fuel storage and delivery system to use DME as a fuel. The conversion of seals for fuel pumps and injectors is necessary for conventional diesel injection engines to DME injection engines.

California law requires that all fuel sold or distributed within the State have a fuel specification established by a consensus organization, such as ASTM or SAE. Therefore, development of an ASTM Standard Specification for DME is an important step towards the legal use of DME as a fuel in California. In January 2014, an ASTM specification for DME as a transportation fuel was published as D7901. Since its initial release, the DME specification has been updated to include a lubricity warning and was published in July 2014 as D7901-14a. This specification provides guidance for DME producers, infrastructure developers, and OEMs on the fuel quality required.

It is anticipated that DME will require a lubricity additive due to its low inherent lubricity. To protect engine fuel injection equipment, there are industry recommendations to add a lubricity additive at about 100 parts per million (ppm) to maintain the lubricity of the fuel equal to that of diesel fuel. Further it is anticipated that original equipment manufacturers (OEMs) may specify an engine-cleaning additive or that local jurisdictions will require an odorant such as ethyl mercaptan.

There is also a potential need for an additive to increase flame luminescence. There is not a standard for flame luminosity for DME, but there has been consideration of additives or blending

agents for creating luminosity for fuels that have a non-luminous flames such as methanol and hydrogen. However, information on specific concentrations of each of these additives has not been made available by OEMs at this point in the development of DME as a fuel.

DME Environmental Transport and Fate

A multimedia transport, fate and exposure assessment synthesizes information about partitioning, reaction, and multimedia-transport properties of a chemical in a representative or generic environment with information about exposed humans or wildlife to assess impacts, such as health risk. DME may enter the environment through leakage or spillage during production, transport, storage, and usage. DME will exist primarily in the gas phase when it is released to the atmosphere. Summarized below are the key finding regarding DME releases and the associated environmental fate and transport leading to human and environmental exposures.

Bulk DME release to surface and subsurface soils

It is anticipated that bulk DME will be stored in above ground storage tanks, and any associated pipes and valves will also be above ground. Because of its high volatility, a bulk DME release on to the soil surface would rapidly transition into the vapor phase. This volatilization can occur so rapidly that explosive forces may be generated. Nearby equipment or soil particulates may be displaced by these forces.

Due to rapid DME evaporation, it may be expected that a bulk release to the soil surface would result in localized, shallow, soil freezing rendering the soil impermeable to deeper transport until thawing occurs. DME is chemically inert and chemical interaction with soil particulates or organic materials coating the particulates is unlikely. DME is not expected to sorb to sediments or suspended particles in water, or to hydrolyze in groundwater. As a result, DME has a high potential for mobility in vadose zone soils and groundwater, but DME impact to the subsurface could be confined to the shallow subsurface environment unless DME is dissolved into groundwater that reaches the water table. If water spray is used to knock-down DME vapors, the transport of DME to subsurface waters is a remote possibility with minimal impact. Residual taste and odor issues for DME in drinking water resources have not been tested.

The DME that enters subsurface environment has a slow rate of biotic or abiotic degradation. Since DME is a good solvent, it is possible that organic material associated with the soil matrix may be mobilized and displaced. Any DME vapors trapped in the subsurface soils could eventually disperse to the atmosphere due to vadose zone barometric pumping.

Bulk DME release to surface waters

As with a DME release to soils, a release to a body of surface water would result in rapid, possibly explosive, volatilization of DME. A cold vapor cloud could form on the surface of the water. Wind direction and speed will play an important role in the transport of the cold vapor cloud.

The solubility of DME vapor changes with pressure and temperature. At 100 kPa and 18°C water can hold 7 percent by weight and at 500 kPa and 23.5°C water can hold 35 percent by weight.

DME is expected to quickly volatilize from the water. DME is not expected to hydrolyze, bioconcentrate in aquatic organisms, or directly photolyze, when it is released to surface waters. Estimated half-lives in a model flowing river and model lake are 2.4 hours and 2.8 days, respectively. Moreover, it is not expected that DME reacts with hydroxyl radicals produced from photochemical processes in the water, and DME has a slow process of biodegradation in water. DME has a strong, unpleasant, slightly sweet smell, and residual taste and odor issues for DME in drinking water resources have not been tested.

A DME release into surface waters during the use of watercraft is anticipated to be minimal since the near-term use of DME in marine diesel engines is not planned in California.

Fate of DME in the atmosphere

DME will only exist as a gas if it is released to the atmosphere. The main transport mechanism in the atmosphere will be dispersion. Since DME is heavier than air, during a bulk DME release, it is possible that a cold DME vapor cloud, denser than air, could form and settle into low lying surface features such as basements, storm drains, creek beds, or drainage ditches. If these vapors reach an ignition source, a significant explosion could occur.

Direct photolysis of DME is not expected to be an important process. DME is not regarded as a greenhouse gas. Atmospheric dispersed DME decomposes to carbon dioxide and water via a reaction with photochemically produced hydroxyl radicals during the day and during the night-time by nitrate radicals in the atmosphere. DME degradation in the atmosphere occurs by reaction with hydroxyl and nitrate radicals with estimated half-lives of 5.4 and 123 days, respectively.

Atmospheric partitioning of DME into rainwater can be expected to be low as atmospheric concentrations of DME are expected to be low. On the other hand, if rainfall occurs through a DME vapor cloud that has settled into low-lying area, this rain could adsorb DME and percolate to groundwaters.

DME Combustion emissions

In addition leaks and spills of DME from production and transportation, the combustion of DME in vehicles gives rise to emissions of combustion products. Fossil fuel combustion for transportation has been associated with a number of criteria pollutants such as NO_x, SO_x, ozone, CO, particulate matter (PM); hydrocarbon (HC) emissions that lead to secondary PM and some hazardous air pollutants such as benzene, aldehydes, and polycyclic aromatic hydrocarbons. Preliminary assessments from the California Energy Commission (CEC) report that well-to-wheels (WTW) emissions of the criteria air pollutants NO_x, CO and PM10 from DME derived from natural gas are comparable and somewhat lower when compared on an energy basis to CA ultra low sulfur diesel (ULSD). The CEC WTW analysis indicated that, WTW emissions of hazardous air pollutants from natural-gas-derived DME are lower than ULSD, but there are concerns about higher levels of formaldehyde from DME use compared to ULSD. Similar to LPG, the CEC WTW modeling showed that DME fuel derived from natural gas could have VOC emmissions

higher than ULSD, but these VOC emissions can be controlled. These preliminary WTW estimates need confirmation using engine technology designed for DME.

DME Safety

DME is required to be stored in accordance with all current regulations and standards. Above ground storage tanks (ASTs) holding large quantities of DME are subject to local siting approval and generally should not be located near heavily populated areas. DME is a volatile organic compound that is stable but is extremely flammable and may form potentially explosive mixtures with air. Because the relative gas density of DME is heavier than air, vapors may collect in low lying areas such as ditches, sewers, basements, and can ignite at distances far from the source and flash back.

Unodorized DME has a strong, unpleasant, slightly sweet smell. There remains a need to explore consideration of whether there would be benefit to have DME possess an odor that is readily detectable but unique from natural gas and propane odorants.

Researchers have described the DME flame as nonluminous in cool flames, moderately luminous pale blue with low brightness, or luminous dark-blue in hotter flames. However, when a lubricant is added to improve lubricity, a rather strong, luminous flame might be detected. A flame that is not readily visible poses a safety problem for DME production plant workers, fire-fighters and first responders if an ignited leak occurs. During the evaluation of the luminosity of DME flames, a key issue will be what level of luminosity is required.

DME Toxicity

The current literature provides sufficient information to assess the potential impacts of DME to human and ecological receptors. Dimethyl ether has a low order of toxicity on both an acute and chronic basis. The main physiological action of DME is that of “weak anesthesia” when inhaled at high levels. DME is extremely stable chemically and is essentially an inert chemical substance. Because DME was developed as an aerosol propellant that touches the human body directly, the safety of DME has been evaluated in detail.

Fossil fuel combustion for transportation has been associated with a number of criteria pollutants such as NO_x, SO_x, ozone, CO, particulate matter PM; hydrocarbon (HC) emissions that lead to secondary PM and some hazardous air pollutants such as benzene, aldehydes, and polycyclic aromatic hydrocarbons. The State of California and the U.S. EPA have identified diesel PM as a toxic compound. As a diesel substitute DME combustion emissions during use phase must be assessed in terms of their emissions of criteria, air pollutants, and hazardous air pollutants. Preliminary work reveals a significant reduction of PM emissions relative to diesel when DME is used a diesel substitute.

BioDME Life-cycle Assessment

A preliminary BioDME life-cycle assessment (LCA) was performed using CAGREET. Air emissions during each stage of the fuel life-cycle was determined, including cumulative emissions for Carbon monoxide (CO), Nitrogen oxides (NO_x), Ozone, Particulate matter, Volatile organic compounds (VOCs) such as benzene, formaldehyde, and semi-volatile organic compounds (SVOCs) such as polycyclic aromatic hydrocarbons. During the preliminary BioDME LCA, volatile organic compounds (VOCs) emissions from diesel engines using BioDME were found to be much lower compared to DME produced from natural gas. Carbon intensity of BioDME was also evaluated. The solid waste inventory for Oberon Fuels DME small scale fuel plants has been completed, and a catalyst recycling or disposal strategy has been developed. A preliminary comparison of the life-cycle of the Oberon BioDME process with large scale natural gas derived DME (NG DME) production (a default in CAGREET that assumes 70% efficiency) and California ULSD (CAGREET Default) has also been performed.

Potential Benefits of using DME as a Diesel Substitute

The use of DME as a diesel substitute in California offers several beneficial characteristics that will help California meet state renewable fuel goals. The key benefits identified in the Tier I study are summarized below.

Cleaner Burning Diesel Fuel

Preliminary assessments from the California Energy Comission (CEC) report that well-to-wheels (WTW) emissions of the criteria air pollutants NO_x, CO and PM10 from DME derived from natural gas are comparable and somewhat lower when compared on an energy basis to CA ultra-low sulfer diesel (ULSD). The CEC WTW analysis indicated that, WTW emissions of hazardous air pollutants from natural-gas-derived DME are lower than ULSD, but there are concerns about higher levels of formaldehyde from DME use compared to ULSD. Similar to LPG, the WTW modeling showed that DME fuel derived from natural gas could have VOC emmissons higher than ULSD, but these VOC emissions can be controlled. A preliminary life-cycle analysis of emissions from BioDME indicated that VOC emissions were much lower compared to DME produced from natural gas.

Reduced Carbon Intensity

BioDME can be produced from renewable biogas feedstocks. Carbon dioxide recycling during the production of BioDME is possible by using biogas feedstocks that are generated by the decomposition of agricultural waste, food waste, and other biomass sources, such as pulp and paper mill waste products.

Low DME Toxicity

DME toxicity has been examined in detail since it can safely be used as an aerosol propellant that touches the human body. The narcotic effects of DME are weak, but first responders to DME releases must use respiratory protection. Skin contact with liquid DME may cause freezing of the skin.

Minimum Post Combustion Emission Controls Compared to ULSD

DME helps eliminate diesel engine after-treatment equipment that are costly and add weight to trucks whose delivery capabilities are then decreased. When combustion is optimized, DME in its pure form burns cleanly with no soot or particulate matter. Compression ignition engines running on DME do not require diesel particulate filters to meet emissions standards for particulate matter.

Compared to diesel, DME has vastly superior cold starting, is literally smokeless, has quieter combustion, no fuel waxing in cold climates to clog fuel lines, low NO_x emissions, lower well-to-wheel greenhouse gas emissions, and potentially is a CO₂ absorber during its production. Conversion of a diesel engine to DME does not require modifications to diesel engine internal structures or components, e.g. head, block, pistons, cams, valves, manifolds, cooling pumps, turbo - the only modifications required are to the fuel system.

Key Information Gaps: Key Issues for Tier II Activities

Additional Combustion Emissions Testing

To evaluate emissions impacts of DME compared to California diesel fuel, engine testing must be conducted to characterize standard regulated emissions, including PM, NO_x, CO, THC, CO₂, and unregulated (toxics), including TACs, PAHs, VOCs, and carbonyls. The development of DME Emissions Profiles will be part of Tier II activities. Emissions data will be gathered by vehicle equipment manufacturers in conjunction with Oberon Fuels.

Additives

It is anticipated that DME used as a transportation fuel may require additives to meet several needs. These additives may include:

Odorant - Unodorized DME has a strong, unpleasant, slightly sweet smell. There remains a need to explore consideration of whether there would be benefit to have DME possess an odor that is readily detectable but unique from natural gas and propane odorants. An odorant is currently used in DME fuels in Europe, and the California Air Resources Board may also specify a need for an odorant. If an odorant is needed, then non-sulfur options for possible odorization of DME need to be explored.

Lubricity – It is generally recognized that DME use as a diesel transportation fuel requires a lubricity additive. Specific details regarding which chemicals and appropriate concentrations are being developed as part of the DME engine testing to be conducted by vehicle manufacturers in cooperation with Oberon Fuels.

Luminosity – The luminosity of DME flames can be variable. Researchers have described the DME flame as nonluminous in cool flames, moderately luminous pale blue with low brightness, or luminous dark-blue in hotter flames. However, when a lubricant is added to improve lubricity, a rather strong, luminous flame might be detected. A flame that is not readily visible poses a safety problem for DME production plant workers, fire-fighters and first responders if an ignited leak occurs. During the evaluation of the luminosity of DME flames, a key issue will be what level of luminosity is required. As part of Tier II activities, information on specific concentrations of any proposed additives needs to be specified.

Confirmation of DME Materials Compatibility

As DME is developed for the California transportation fuel market, Oberon Fuels, Inc. has been actively involved in the development of an ASTM standard for DME used as a transportation fuel. ASTM D7901, Standard Specification for Dimethyl Ether for Fuel Purposes, has been adopted and provides a list of elastomers that are compatible and perform well with DME.

Materials used in the storage, handling, and transfer of DME have to be compatible with and unaffected by DME. LPG infrastructures are widespread in the United States and basic components of LPG storage and handling technology can be used for the storage and handling of DME, but substantial swelling of a variety of seal and gasket elastomers was observed with DME. Within the DME industry, perfluoroelastomer, polytetrafluoroethylene, fluorosilicone, hydrogenated-nitrile-butadiene rubber, nitrile, and silicone elastomers as well as stainless steel have been found to performed well with DME.

The material compatibility information for seals and gaskets was obtained from a variety of sources, and these materials are commonly used within the DME industry including Oberon Fuel's operational DME production facility in Brawley, California. During the implementation of DME production using the Oberon Fuels small scale production facility, materials compatibility will comply with the ASTM DME Standard and will be verified and documented with actual devices and production and storage systems to be used in California.

Development of Specifications for California Certification Fuel for DME

In order to complete its engine testing for DME, CARB must establish specification standards for the the fuel that will be used in the engine test (“test fuel”). The test fuel must fall in the range of specifications that CARB has selected. At this point, CARB has determined that the minimum requirement for the fuel specification would be ASTM specification D7901, and the maximum requirement has not yet been set. Therefore, the DME test fuel used for engine testing as part of the Multi-Media Assessment must fall within the ASTM specification range and will be compared to life-cycle analyses of natural-gas-derived DME, BioDME, and California diesel fuel.

DME Life-cycle Impacts

Modeling life-cycle emissions attributable to transportation fuels requires characterization of emissions factors during the life-cycle of the fuel including the production and operation of the vehicle. A preliminary life-cycle analysis for BioDME, DME produced from unscrubbed (60% methane) HSAD (High Solid Anaerobic Digestion) foodscraps and yard waste, shows promise in reducing VOC emissions and carbon intensity. As part of Tier II activities, the BioDME life-cycle analysis will be confirmed and documented using any new information resulting from the DME vehicle Emission Profile testing.

EPA does not give a specific method for the sampling and analysis of DME. EPA Standard Methods to sample and detect VOCs, such as MTBE, in air and water should be applicable to DME. Verification of the applicability of these methods needs to be conducted. These methods can then be used to monitor air, surface, and subsurface water as pilot production processes are demonstrated. As DME becomes more widely used as a transportation fuel, it is possible that DME will become more widely distributed into the environment, including air and water resources. It may be prudent to include DME as one of the analytes of interest in the future.

If DME becomes more widely used and below ground storage and piping infrastructure is used, then additional research into the subsurface transport of DME and potential impacts to groundwater resources may be needed.

1. Dimethyl Ether Background Information

1.1. Introduction

Dimethyl ether (DME) is a new fuel that could help address environmental and fuel security issues. DME can be produced from a variety of feedstocks, including natural gas or bio-methane. Current production is focusing on methane-containing feedstocks, but gasification of any suitable organic source can lead to the syngas chemistry products with DME as one of the more energy efficient options. DME is a gas under ambient conditions with properties similar to those of LPG and can thus be stored as a liquid under moderate pressure, therefore not requiring the high pressure containers used for CNG or consideration of the cryogenic conditions of LNG. DME produced from bio-methane (from landfill gas or the decomposition of manure, for example) would be a non-fossil, renewable fuel.

Since DME is a new fuel, the California Air Resources Board (CARB) must provide a “multimedia risk assessment” before adopting new fuel specifications (as required by California Health and Safety Code, Section 43830.8). Further, existing law states that the “California Air Resources Board cannot adopt any regulation establishing a motor vehicle fuel specification unless a multimedia evaluation is conducted to determine whether the regulation will cause a significant adverse impact on the public health or environment” (California Senate Bill 140, 2007). The purpose of this multimedia risk assessment is to provide the State of California information that will allow an informed decision as to the relative health and environmental impacts to the State’s resources, human health and environment posed by the use DME as a transportation fuel.

As a result, the California Environmental Protection Agency (Cal-EPA) has initiated a program to assess the multimedia life-cycle impacts of DME use in California. This Tier I report is the first step in a three-tier process evaluating the cumulative health and ecological impacts from releases to air, surface water, groundwater and soil at all stages of the DME life-cycle: production, storage and distribution, and use. The risk posed by DME as a diesel alternative is assessed as a relative risk compared to ultra low California sulfur diesel currently in use.

The goal of this Tier I report is to identify what is currently known about DME along with a discussion of key uncertainties and data gaps, including:

- Physical, and chemical and environmental toxicity characteristics of the reference fuel, candidate fuel and additive components,
- Summary of all potential production, distribution, storage, and use release scenarios including a discussion of the most likely release scenarios,
- Summary of the expected environmental behavior (transport and fate conceptual models associated with release scenarios) of proposed fuel or fuel components that may be released, and

- Comparison of physical, chemical, and toxic properties of the fuel or additive components to appropriate agreed upon control fuel or fuel components.

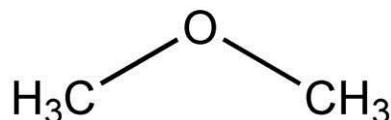
This report excludes the direct and indirect environmental, ecological, and health impacts associated with biomass production such as changes in land use and the possible net gain in carbon emissions due to feedstock production.

This Tier I report sets the stage for this multimedia assessment and follows the guidance set forth in the “Guidance Document and Recommendations on the Types of Scientific Information to be Submitted by Applicants for California Fuels Environmental Multimedia Evaluations” (2008). We consider four major life stages—feedstock production/collection, DME production, transport and storage, and fuel use (combustion).

During Tier II activities, a plan of action is developed to address these uncertainties and data gaps and conduct a life-cycle based assessment of the potential impacts DME may have to the State’s resources, human health and environment. During Tier III activities, the life-cycle based assessment is performed and the results reported to California Environmental Policy Council.

1.2. History of DME

Dimethyl ether (DME) is also referred to as dimethyl oxide, methyl ether, oxybismethane, methoxymethane, methyl oxide, wood ether, N,N-dimethyl ether. The chemical formula is CH_3OCH_3 with a molecular weight of 46.07. Its structural formula is provided below.



Literature shows that the earliest research regarding DME goes back to the medical fields. According to Donald G. Barceloux in his book “Medical Toxicology of Drug Abuse: Synthesized Chemicals and Psychoactive Plants” (2012), the anesthetic characteristics of DME were studied in some rabbits and pigeons in 1867. Although later it was successfully examined as an “anesthetic agent” in humans, DME was never considered as a trustworthy anesthesia related drug.

Traditionally, DME has been used as a propellant in a wide range of consumer products (personal care) including shaving creams, hairspray, foams, and antiperspirants (Nexant Inc., 2008). DME is used for these applications because of its higher water solubility relative to other propellants (DuPont, 2000). The first use of DME as an aerosol propellant goes back to the Akzo Nobel Corporation in 1963. Akzo Nobel produces chiefly specialty chemicals containing coatings and paints¹.

¹ <http://www.akzonobel.com/aboutus/>, accessed on 7/22/13.

In a 1997 review for the United States Department of Energy, Sinor (1997) reports that after reviewing documents from 1906 onward, there is no database showing the use of DME as an engine fuel before the modern era. In the 1970s and 1980s, oil prices were increased, and some embargos were imposed on oil. As a result, global research and development (R&D) efforts were directed at finding novel methods of monetizing oil resources by converting them into easily transportable liquid fuels (Fleisch et al., 2012). Further, there has been a significant impact on the production and use of diesel fuel as a result of new environmental regulations, specifically in the United States. Significant investments have been made to produce “cleaner diesel fuels” and other alternative fuels (Fleisch et al., 1997). From the late 1970s, Amoco (a global oil company later merged into BP) has participated in R&D work on the production of liquid fuels from natural gas (Fleisch et al., 1997). Beside those global efforts, a German patent introduces a “methanol based fuel consisting of non-distilled technical methanol, water, DME and future additives” in 1984 (Majunke & Mueller, 1984) and a U.S. patent describes a “method of operating a diesel engine with a fuel consisting of 95 to 99.9 percent DME” in 1986 (Levine, 1990). DME, used as an alternative diesel fuel, performed well in tests and revealed compliance with “the California ULEV emissions regulations for medium-duty vehicles” (Sinor, 1997; Fleisch et al., 2012).

To use DME as a diesel-engine fuel, it is necessary to make some changes into the fuel distribution substructures and consider some modifications on the engine itself; this brought some challenges into DME’s development as a fuel. Since DME had some similar properties with LPG, the main market for DME has been its blending with LPG. It was discovered that using blends of maximum 20 % DME in the whole volume of LPG performed well in regular heating and cooking applications. Also, the same blends worked well in automotive uses and Amoco patented those (Fleisch et al., 2012).

Worldwide efforts were initiated to commercialize the DME business. In the mid-to-late 1990s, Amoco in cooperation with the General Electric Co. (GE) and the Electric Power Development Corporation of Japan (EPDC) tried DME as a “gas turbine fuel”. DME performed efficiently in this test and showed low emissions. That was the start of offering guarantees for DME by GE in the majority of their advanced turbines (Fleisch et al., 2012). The result of this research was that DME, as a multipurpose fuel, can be used for “LPG blending”, “power generation”, and “the diesel market”; besides, its usage as a “chemical intermediate for novel pathways to hydrogen, olefins, acetic acid and gasoline” was understood.

In 1998, Amoco engaged in a joint project with the “India Oil Company (IOC)” and the “Gas Authority of India (GAIL)”. During the next few years The “International DME Association (IDA)”, the “Japan DME Forum (JDF)”, the “Korea DME Forum (KDF)”, and the “China DME Association (CDA)” were established around the world. Although China joined the community of DME-users relatively late, it is now known as the leader in DME production and use. Research advancements are also being made for practical use of DME for power generation.

Legislative incentives for DME and a summary of current DME market forecast is provided in Appendices A and B, respectively.

1.3. Different Uses of Dimethyl Ether

DME is listed as a High Production Volume (HPV) chemical (US Environmental Protection Agency, 2007). It is an emerging alternative to traditional fuels such as diesel and propane (Semelsberger, et al, 2006). DME production is a mature technology that is utilized in a number of countries including Canada, Japan, China, Korea, and India. It has a variety of applications:

- Use as a liquefied petroleum gas (LPG) substitute for cooking and heating. DME combustion produces very low NOx and CO emissions and no sulfur or soot emissions.
- Use as a chlorofluorocarbon (CFC) substitute for propellants in cosmetic- or paint-aerosol cans (Ohno 2001).
- Use as a diesel substitute. DME has a high cetane number (55) and can be combusted in diesel-powered vehicles that have been retrofitted to run on DME or in purpose built engines.
- Use as a precursor to dimethyl sulfate and acetic acid production
- Use as a refrigerant.
- Use as a rocket propellant.
- Use as carrier for livestock insect sprays and foggers.
- Use as a solvent for extraction of organic compounds.

Before 1990, DME was only used as an aerosol propellant commercially and known as “non-ozone-layer depleting replacement for chlorofluorohydrocarbons” (Fleisch et al, 2012). In recent times, DME is more considered as an alternative and/or additive fuel and covers a wide area of applications. It is now known for its different applications as a fuel for transportation, cooking and heating, and power generation (Erdener et al., 2011). DME has been used in limited amount to freeze meat and fish by direct immersion (Patty, 1963).

A schematic classification of DME usage is displayed in Figure 1.1 and it shows that currently DME is mainly used either as a fuel or chemical feedstocks. DME as a fuel is used for “a combustion fuel itself” and also “a feedstock for reforming”. The power generations, diesel engines, and some home devices are using DME as their combustion fuel.

Volvo and Nissan have developed heavy duty diesel engines modified to run on DME. Further, DME can be used to make Synthesis natural gas (SNG) as well as produce hydrogen for fuel cell electric vehicles (Japan DME forum, 2007; Marchionna, 2008).

The mixture of different pre-defined proportions of DME and LPG, which is called “synthetic LPG”, is applicable as a domestic cooking and heating fuel. Also, some power generation

manufacturers like General Electric, Mitsubishi and Hitachi have approved DME as a fuel for their gas turbines².

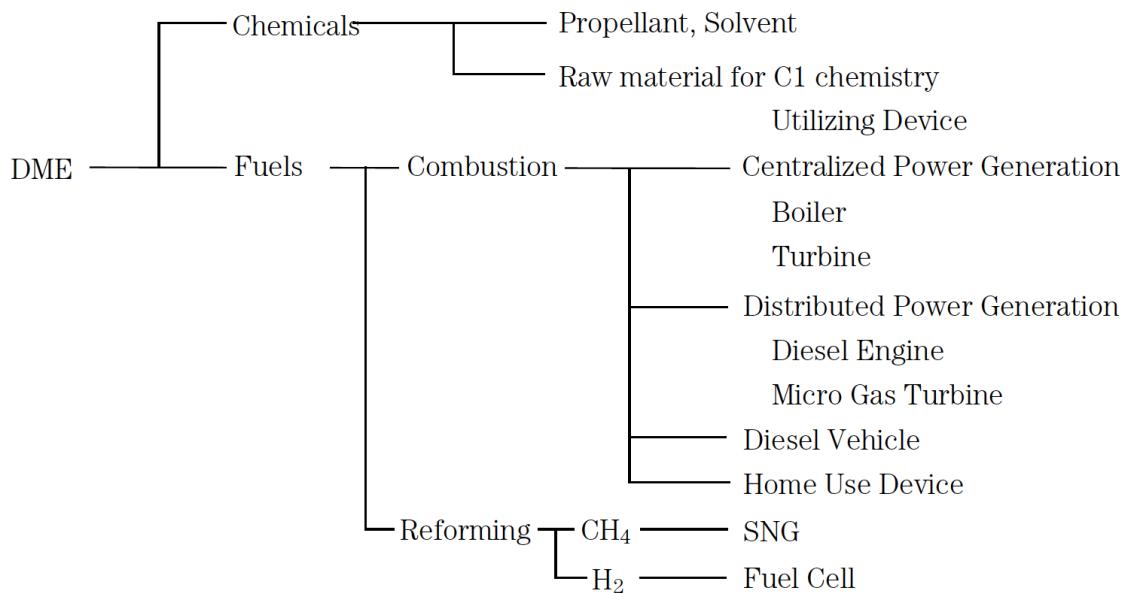


Figure 1.1. Different applications of DME (Japan DME Forum, 2007).

1.4. DME Environmental Standards and Regulations

Residues of dimethyl ether are exempted from the requirement of a tolerance when used as a propellant in accordance with good agricultural practice. This exemption is applied to inert (or occasionally active) ingredients in pesticide formulations applied to growing crops or to raw agricultural commodities after harvest (40 CFR 180.910 and 40 CFR 180.930: Code of Federal Regulations, 2007a).

The Code of Federal Regulations, 2007b, (40 CFR 60.489) promulgates standards of performance for equipment leaks of Volatile Organic Compounds (VOC) in the Synthetic Organic Chemical Manufacturing Industry (SOCMI). The intended effect of these standards is to require all newly constructed, modified, and reconstructed SOCMI process units to use the best demonstrated system of continuous emission reduction for equipment leaks of VOC, considering costs, non-air quality health and environmental impact and energy requirements. DME produced by process units, either as an intermediate or a final product, is covered under this regulation. The 8-hr time-weighted average Workplace Environmental Exposure Level (WEEL) for DME is 1000 parts per million (ppm) (American Industrial Hygiene Association, 2007).

² <http://www.aboutdme.org/index.asp?bid=219>, accessed on 09/23/2013.

1.5. Comparison fuels

1.5.1. Comparison of DME to Diesel Fuel

The liquid density of DME is about 80% of diesel fuel, and specific energy content (lower heating value) is about 70%. Thus it is necessary to inject about twice the fuel volume of DME compared to diesel fuel to yield the same power output (Sato et al., 2005). The compressibility of DME is significantly higher with lower viscosity and lower lubricity. DME cannot be used in conventional diesel engines without modifications to the fuel systems and selection of appropriate lubricity additives.

Since 2006, a new standard to reduce the sulfur content of diesel fuels was introduced by the U.S. Environmental Protection Agency (US EPA, 2006) for highway diesel fuels which is known as “Ultra Low Sulfur Diesel (ULSD)”. Based on the EPA standard, ULSD is required to have 15 parts per million (ppm) of sulfur in diesel fuels. This is 97 percent lower than the previous standard of Low Sulfur Diesel (LSD, 500 ppm) in the United States. Using ULSD in the heavy-duty highway vehicles regulates the “advanced emission control systems” and decreases the harmful pollutions from these buses, trucks, construction equipment, and all diesel engine cars. According to the US EPA, it is mandatory that all diesel fuels sold in the U.S. meet ULSD standards, and all the new highway diesel fuel engines are equipped to use ULSD clean fuels. DME is an alternative diesel fuel that meets ULSD rules.

1.5.2. Comparison of DME and LPG

Liquefied petroleum gas (LPG) is a mixture of hydrocarbons (primarily methane, propane and butane) used for heating, cooking, domestic appliances and in vehicles. The similarities between LPG and DME chemical properties (Table 1.2), makes DME an attractive alternative fuel source for existing LPG appliances and vehicles, although modifications to burners, fuel delivery systems and storage tanks would be needed.

Because of these similarities, the existing LPG infrastructure and distribution system could be converted for use with DME. With regards to fueling infrastructure, DME handles like propane. It is a gas at ambient conditions but under 5 atmospheres of pressure at 20°C, is a liquid. (Japan DME Forum 2007). Similar to propane, the fueling and storage infrastructure is relatively simple and inexpensive. Propane-style tanks can be used for storage, but the seals must be changed when storing 100% DME (rather than 80/20 propane/DME as is used internationally for cooking fuel). DME is an excellent solvent and degrades rubber materials; issues of materials compatibility are addressed in section 3.2.

1.5.3. Comparison to LPG for Infrastructure Storage, Distribution, and Use

Many similarities exist between DME and Liquified Petroleum Gas (LPG) fuel properties and make it easier to consider using the available LPG infrastructures for DME (Japan DME Forum, 2007; Semelsberger et al., 2006; Erdener et al., 2011). At normal atmospheric pressures, both are in the gas phase, but under any mild pressure or low temperature circumstances, they are

changed into liquid. Comparison between DME and LPG shows that they have similar physical properties, but there are some differences in their thermal characteristics (Table 1.1; Table 1.2). Actually, DME has lower energy content (Figure 1.1), which for equivalent use, requires a 20-35% increase in stored mass (Marchionna et al., 2008).

Unlike natural gas, which is either pure or a mixture of naturally occurring products, DME is synthesized from natural resources such as natural gas, coal, biomass or other organic wastes through gasification or chemical conversion to produce synthetic fuel. DME is produced through dehydration of methanol or in a direct or indirect step process from a variety of methane containing feedstocks. DME can also be blended with LPG mixtures or pure methane, propane, or butane. Some LPG contains sulfur while DME is sulfur free. LPG feedstocks contain varying

Properties	DME	LPG
Bottle Fill (%)	85	80
Mass per Bottle Unit Vol. (Kg/m ³)	567	432
Energy per Bottle Unit Vol. (GJ/m ³)	16.3	19.9

Table 1.1. Technical characteristics of DME compare to LPG which is often a mixture of propane and butane (International DME association, 2010).

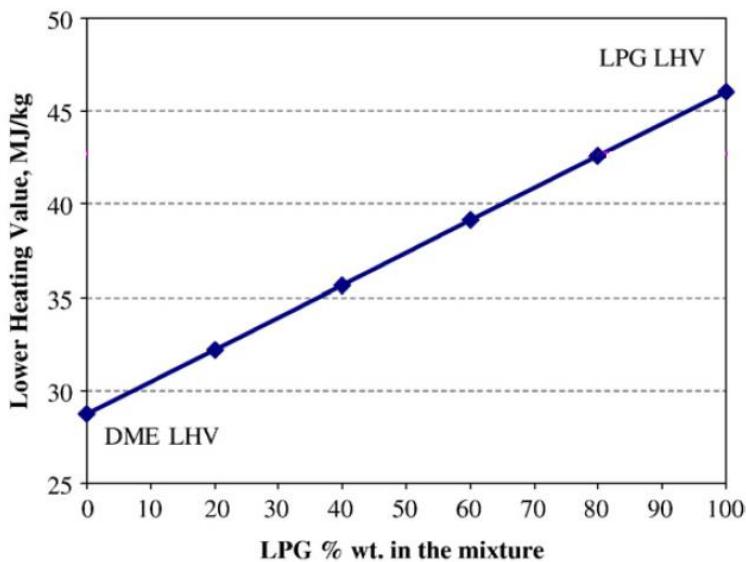


Figure 1.2. Comparison between DME's and LPG's Lower Heating Value (LHV) with DME/LPG mixture values (Marchionna et al., 2008).

amount of nitrogen which lead to NO_x gas production during combustion. However, DME is relatively smokeless and the exhaust gas contains very low amounts of NO_x. Because DME

emissions are lower in NO_x, SO_x, and CO, DME is an attractive alternative fuel for diesel engines. Both LPG and DME can be easily compressed to liquid at standard temperatures and pressures. Compared to LPG, DME has 50~65% of the calorific value based on weight or 62~63% based on volume. Although the energy content is lower, given the higher liquid density of DME, it can be stored with 75~85% of the energy that LPG would contain in a tank of the same size. Conversely, DME in the gas state contains 165% of the energy contained in methane gas based on volume. In short, it is useful to consider LPG infrastructures as comparison fuel infrastructures for DME.

1.6. Physical/chemical properties of DME

Characteristic	DME	Methane	Propane	n-Butane	Diesel Fuel
Chemical formula	CH ₃ OCH ₃	CH ₄	C ₃ H ₈	C ₄ H ₁₀	-
Boiling point [°C]	-25.1	-161.5	-42	-0.5	180-370
Liquid Density [g/cm ³ , 20°C]	0.67	-	0.49	0.57	0.83
Relative gas density (air = 1)	1.6	0.55	1.52	2.07	-
Vapor Pressure [MPa, 25°C]	0.61	-	0.93	0.24	0.53
Max burning velocity [cm/s]	50	37	43	41	-
Explosion limit [%]	3.4~17	5~15	2.1~9.4	1.9~8.4	-
Ignition temp [°C]	235	650	470	365	250
Cetane number	55~60	0	5	10	40-55
Lower heating value [MJ/Nm ³]	59.3	35.9	91.0	118	-
Lower heating value [MJ/kg]	28.8	49.0	46.3	45.7	42.7

Table 1.2. Comparison of DME to gases used in LPG fuels. Adapted from *DME Handbook* (Japan DME Forum, 2007) and Sato et al., 2005.

Physical/Chemical Properties	DME
Melting point, °C	-145.1
Molecular weight, g/mol	46.07
Critical temperature, °C	126.9
Critical pressure, MPa	5.37
Critical volume, cm ³ /mol	178
Solubility in water, g/100ml	3.5* - 7.6**
Liquid viscosity, cP	0.15
Gas viscosity, 10 ⁻⁶ P	9.160
Gas diffusion coefficient, cm ² /s	0.11
Theoretical oxygen ratio, kg/kg	9
Flash Point, °C	-41.1
Cetane number	55
Ignition point, °C	350

Table 1.3. Physical/chemical properties of DME. *(US EPA, 2000). **(Appendix C: Matheson DME Safety Data Sheet).

DME is an invisible gas at standard atmospheric conditions and when pressurized above 0.5 MPa it condenses to a liquid. Physical properties for DME are reported from US EPA (2000), Japan DME Forum (2007), and Appendix C (Matheson DME Safety Data Sheet) and are collected here in Tables 1.2 and 1.3, above. Some inconsistencies among sources are noted (*e.g.*, the ignition temperature), but the properties that serve as primary controls for processes involved in multimedia risk are fairly well-established.

2. Production of Dimethyl Ether

2.1. DME Production Pathways

DME can be produced through three different production pathways: a two-step, a one-step, and a liquid-one-step process called bireforming. DME is typically produced through a two-step process using syngas as a feedstock. The syngas is converted to methanol, which is then converted to DME (Equations 1 through 4). CO₂ is produced at 0.96 grams of CO₂ per gram of DME or 33 grams per MJ DME used.

$CO + 2H_2 \rightarrow CH_3OH$	methanol formation	1
$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$	methanol dehydration with solid-acid catalyst	2
$H_2O + CO \rightarrow CO_2 + H_2$	water gas shift reaction	3
$3H_2 + 3CO \rightarrow CH_3OCH_3 + CO_2$	net	4

The most common process used in Japan, Korea, and China is a single-step process (Equations 5-6). This DME synthesis step merges the methanol formation, methanol dehydration, and water-gas shift reaction. If methane is the feedstock, methane must be converted to syngas through a methane-dry-reforming step prior to the single-step process. One company, Japan Steel Engineering, has achieved a production volume of 100t DME/day using this process (Olah, et al. 2009). A mass of 1.43 grams of CO₂ per gram DME is consumed in this process. However, the net production process sequesters only 0.48 grams of CO₂ per gram of DME.

$3CH_4 + 3CO_2 \rightarrow 6CO + 6H_2$	methane-dry-reforming	5
$6CO + 6H_2 \rightarrow 2CH_3OCH_3 + 2CO_2$	DME synthesis	6
$3CH_4 + CO_2 \rightarrow 2CH_3OCH_3$	net	7

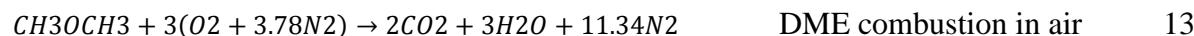
An emerging third process for DME production is called bireforming (Equations 8-12). Metgas is a syn-gas with a 2:1 H₂:CO mix, designed to optimize methanol production. Metgas is produced through a methane-steam-reforming and methane-dry-reforming step. These steps are followed by methanol formation and methanol dehydration. The water from methanol dehydration is used to supply the methane-steam-reforming step.

Per gram of DME produced, 0.48 grams of CO₂ are consumed. There are no CO₂ emissions from the bireforming process itself, but there will be CO₂ emissions associated with the process's energy requirements.

$2CH_4 + 2H_2O \rightarrow 2CO + 6H_2$	methane-steam-reforming	8
$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	methane-dry-reforming step	9
$4CO + 8H_2 \rightarrow 4CH_3OH$	methanol formation	10
$4CH_3OH \rightarrow 2CH_3OCH_3 + 2H_2$	methanol dehydration	11



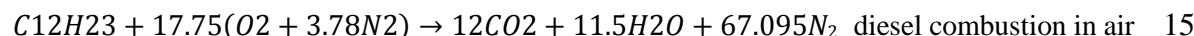
In air, the stoichiometric combustion of one gram of DME also yields 1.91 grams of CO₂ (Equation 13). This is equivalent to 66 g of CO₂ per MJ (LHV) of combusted DME.



The stoichiometric combustion of one gram of propane yields 3 grams of CO₂.



The stoichiometric combustion of one gram of diesel C₁₂H₂₃ yields 3.16 grams of CO₂.



In theory, the combustion of one gram of DME in air would emit 1.1 g CO₂ less than one gram of propane and 1.25 less than one gram of diesel.

2.2. Overview of DME Feedstocks

DME can be produced from any methane-containing feedstock. Examples include pipeline natural gas, biogas, landfill and waste water treatment gas, and stranded natural gas. Depending on the technology used, DME can be produced from natural gas in accordance with the following primary chemical reactions:

- (1) Partial oxidation reforming: CH₄ + 0.5O₂ = CO + 2H₂;
- (2) Steam reforming: CH₄ + H₂O = CO + 3H₂,
- (3) CO₂ reforming: CH₄ + CO₂ = 2CO + 2H₂,
- (4) Methanol synthesis: 2CO + 4H₂ = 2CH₃OH and CO₂ + 3H₂ = CH₃OH + H₂O,
- (5) Methanol dehydration: 2CH₃OH = CH₃OCH₃ + H₂O,
- (6) DME direct synthesis: 3CO + 3H₂ = CH₃OCH₃ + CO₂ and 4H₂ + 2CO = CH₃OCH₃ + H₂O.

2.3. Indirect Synthesis Technology

Synthesis of DME has initially been based upon dehydration of methanol, according to reaction (5) above. Production of methanol from natural gas is a mature industry. Addition of a DME production plant, consisting of the dehydration step, to an existing methanol production facility, has been accomplished at several facilities in China.

2.4. Direct Synthesis Technology

DME can be produced directly from syngas, according to reaction (6) above. The water formed from this reaction helps to drive the water-gas shift reaction to produce more hydrogen, which helps drive reaction (4) above to produce more methanol. It is for this reason that the direct synthesis reactions increase the per pass conversion of syngas to DME over the indirect synthesis method.

2.5. Particular Production Process Proposed by Oberon

The Oberon Fuels methane-gas-to-DME process consists of three major steps: syngas production, methanol synthesis, and simultaneous DME synthesis and separation via catalytic distillation. An illustration of the Oberon small site plant sample layout is provided in Figure 2.1. While the first two process steps are common in large scale industrial applications, further development of these processes for small scale applications is open for improvement and implementation. Catalytic synthesis of DME coupled with purification is a well-researched topic that is both promising and feasible, and was not proven industrially until the operation of the Oberon Fuels plant located in Brawley, CA. All production and storage, including piping, tanks, and valves, will only be above ground.

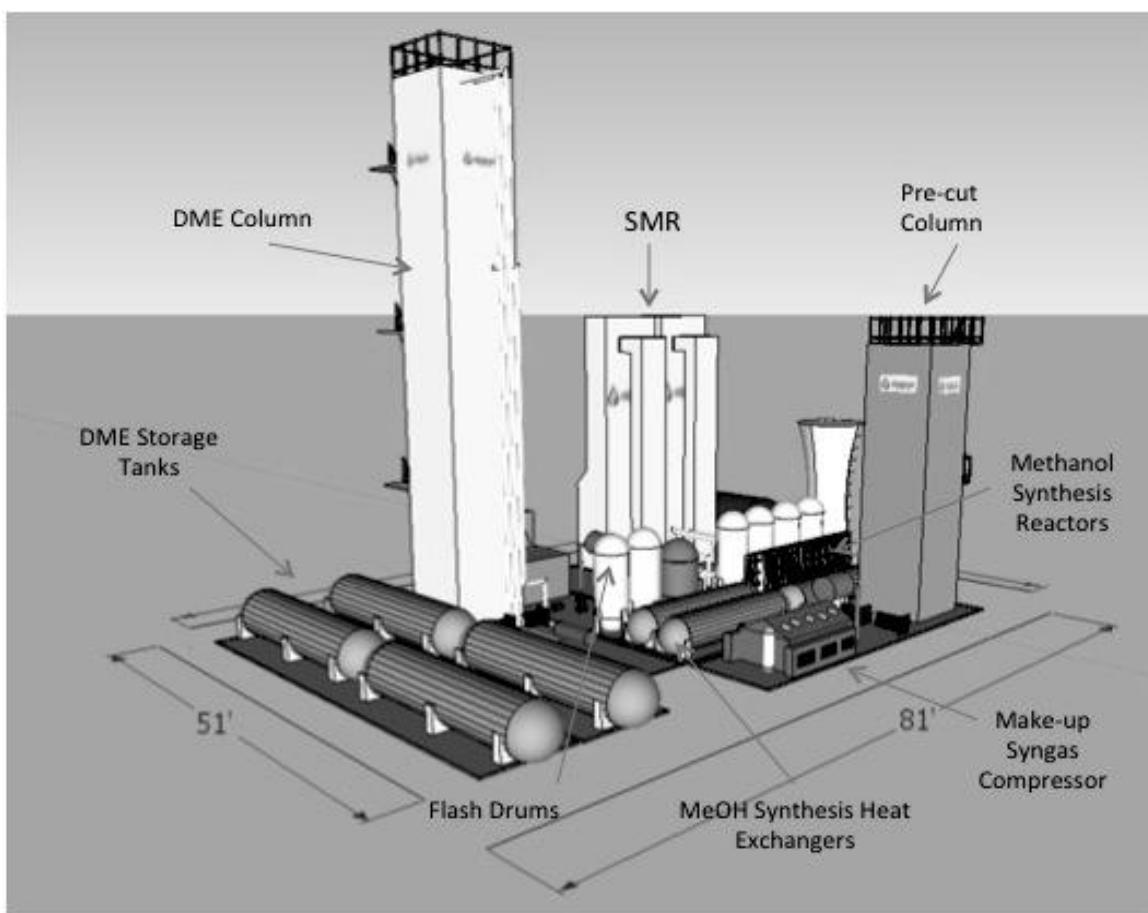


Figure 2.1. Oberon small scale plant sample layout.

The proposed Oberon process can utilize various feedstocks as inputs to convert methane and carbon dioxide to DME (MMWG, 2013; Oberon, 2013). For the purpose of this report, DME produced from unscrubbed (60% methane) HSAD (High Solid Anaerobic Digestion) of foodscraps and yard waste will be referred to as BioDME. BioDME and DME are the exact same

product chemically, the only difference is the methane-based feedstock used. BioDME is produced from biogas (gas typically produced from an anaerobic digester), while DME is produced from pipeline natural gas.

This first step in this process is steam methane reformation (SMR) wherein biogas, shale gas, or methane is converted to syngas containing carbon monoxide and hydrogen gas (Simpson et al., 2007). The next step, catalytic conversion, utilizes three adiabatic methanol reactors and a Cu/Zn/Al₂O₃ catalyst to produce methanol. This step is carried out at 250°C and 77 bar (MMWG, 2013). During the final step, catalytic dehydration and distillation of DME is carried out in a reactive distillation column with an ion exchange catalyst.

The SMR step of the Oberon process is highly endothermic and requires an external heat input. This can be supplied through combustion of biogas, methane or with excess hydrogen gas produced during this step.

The properties of DME that are relevant to the Oberon process are (from Tables 1.2 and 1.3):

- Boiling point at standard pressure (-25.1°C)
- Critical temperature (126.9°C)
- Critical pressure (5.37 MPa)
- Critical volume (178 cm³/mol)
- Gas diffusion coefficient (0.11 cm²/s)
- Flash point (-41.1 °C)

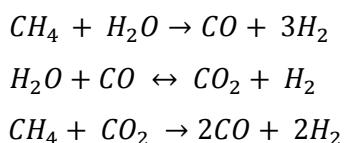
2.5.1. Syngas Production

Syngas production is accomplished by converting natural gas to a CO, H₂, and CO₂ mixture via steam methane reforming. Excess CO₂ may be added to the natural gas feed in this step to adjust the modulus ratio, M. The optimum M ratio for methanol synthesis is two, however; higher ratios are common and can be accommodated.

$$M = \frac{H_2 - CO_2}{CO + CO_2}$$

The overall syngas production process is endothermic and requires a high temperature heat source. Excess hydrogen in the methanol recycle purge stream along with additional natural gas will provide the energy necessary to produce syngas.

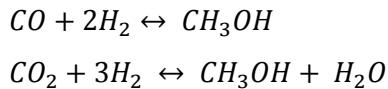
Reformer Reactions:



2.5.2. Methanol Synthesis

Methanol synthesis occurs between 230 - 300°C and 50-100 bar and utilizes a commercial Cu/Zn/Al₂O₃ catalyst available from multiple providers. The methanol synthesis reaction is exothermic, so a boiling water reactor (BWR) or multiple adiabatic reactors are traditionally utilized for temperature control. Multiple adiabatic reactors are more cost efficient at small scale and are less complicated to start up and maintain, so Oberon will utilize this configuration in its DME units. The methanol synthesis reaction is equilibrium limited, making recycle of unreacted syngas necessary to achieve high overall syngas conversion. The size of syngas recycle and purge streams depend on syngas M ratio and reactor type.

Methanol Synthesis Reactions:

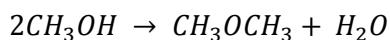


Methanol and water that is flash separated from the syngas recycle stream undergo depressurization and are then passed to a light gas removal column where any remaining dissolved gasses are removed from the stream.

2.5.3. DME Synthesis

The final process step includes simultaneous synthesis and separation of DME in a catalytic distillation column. Heat generated in the exothermic DME synthesis reaction is used to reduce the separation column's reboiler heat requirement, making catalytic distillation a cost-effective DME production method.

DME Synthesis Reaction:



Commercially available ion exchange catalysts are ideal for use in this process, relieving the need for any immediate catalyst development.

2.5.4. Introduction of Additives to DME During Production

Fuel additives are introduced after the final DME product is produced, ideally prior to transport of the product. Transporting the product will encourage complete mixing of the fuel additives in the product DME.

2.5.5. Trace Impurities

A process model (Aspen) has been used to estimate the potential impurities in the final DME that is produced during production using the Oberon process. The data in Table 2.1 are preliminary results from the Aspen simulation. These data will be verified during Tier II testing. The results indicate that DME produced through the Oberon process will meet or exceed ASTM D7901 standards.

Depending on the source, Oberon Fuels may need to scrub the biogas used in the BioDME production system to yield methane, carbon dioxide, inert gases and 5ppm or less of sulfur. Sulfur is currently scrubbed away within the steam methane reformation (SMR) step using iron beds. If needed, siloxanes and H₂S (the more common contamination threat to the Oberon BioDME production system) will likely be scrubbed via a combination of pressure swing adsorption (PSA) systems and chemical beds depending on the contamination level. Any waste generated during the scrubbing process will be dealt with following standard procedures.

Table 2.1. Aspen simulation of estimated DME impurities during the Oberon BioDME production process.

Impurity	Mass Fraction	Mole Fraction
Methane, CH ₄	0.00E+00	0.00E+00
Carbon Dioxide, CO ₂	0.00E+00	0.00E+00
Nitrogen, N ₂	0.00E+00	0.00E+00
Oxygen, O ₂	0.00E+00	0.00E+00
Water, H ₂ O	1.08E-05	2.75E-05
Carbon Monoxide, CO	0.00E+00	0.00E+00
Hydrogen, H ₂	0.00E+00	0.00E+00
Ammonia, NH ₃	0.00E+00	0.00E+00
Methanol, CH ₄ O	7.44E-05	1.07E-04
DME, C ₂ H ₆ O-1	0.9998861	0.9998427
Acetic Acid, C ₂ H ₄ O ₂	1.23E-15	9.45E-16
Acetone, C ₃ H ₆ O-01	2.87E-05	2.28E-05
Ethanol, C ₂ H ₆ O-02	1.11E-08	1.11E-08
Ethane, C ₂ H ₆	0.00E+00	0.00E+00
Propane, C ₃ H ₈	0.00E+00	0.00E+00

2.5.6. Production Plant Fugitive Emissions

Carbon monoxide and methanol fugitives are monitored and analyzed as part of the Oberon Fuels, Inc. production plant air permit and it is anticipated that these emissions will be within

regulatory limits. The methanol is continuously contained in a pressurized vessel throughout the DME production process. The CO, part of the syngas mixture, is completely consumed during the DME production process. The estimated total methanol fugitive emissions for one plant equals approximately 168 pounds per day. The emissions estimate is arrived at by using a standard calculation, used for all standard air permits, based on the number of valves and is often an overestimate of what actually leaks.

2.5.7. Water Resources Used During DME Production

During DME production, using a water cooled plant, 3.1 gallons of water is used per gallon of DME produced with a plant consumption rate of 21.5 gpm. During DME production, using an air cooled plant, 1.9 gallons of water is used per gallon of DME produced with a plant consumption rate of 13.2 gmp. Wastewater produced is 5 gpm or 0.72 gallons of wastewater per gallon of DME produced in a 10,000 gallon DME production plant per day. The startup boilers will use approximately 40 gpm until the SMR step is operating at full capacity.

The Oberon process will utilize city water or an available alternative, such as untreated canal water in areas where city water is not available. Water is pre-treated if necessary to bring it up to city water standards. Water is used in the process heat exchangers for process cooling via a cooling tower loop. Water is also used on startup of the plant for a temporary duration in the process startup boilers. Process wastewater is generated as column bottoms from the DME catalytic distillation column, and along with cooling tower and boiler blowdown water, is disposed of as allowed by the authority having jurisdiction. Potable water is used in the plant's eyewash stations and safety showers, and in the plant's operations building for bathrooms (sinks and toilets).

2.6. DME Production Summary

DME can be produced through three different production pathways: a two-step, a one-step, and a liquid-one-step process called bireforming. DME is typically produced through a two-step process using syngas as a feedstock. The syngas is converted to methanol, which is then converted to DME. DME can be produced from any methane-containing feedstock, including pipeline natural gas, biogas, landfill gas, and stranded natural gas.

The Oberon Fuels methane-gas-to-DME small scale production plant process consists of three major steps: syngas production, methanol synthesis, and simultaneous DME synthesis and separation via catalytic distillation. While the first two process steps are common in large scale industrial applications, further development of these processes for small scale applications is open for improvement and implementation. Catalytic synthesis of DME coupled with purification is a well-researched topic that is both promising and feasible but has not been industrially implemented to date.

3. Storage and Distribution of Dimethyl Ether.

3.1. Facilities and Equipment

3.1.1. Applicability of Existing LPG infrastructure to DME

The boiling point of DME is between those of propane and butane. Because its characteristics are similar to those of propane and butane, the principal components of LPG, and basic components of LPG storage and handling technology can be used for the storage and handling of DME.

LPG infrastructures are widespread in the United States and can be used to support DME as a transportation fuel (Japan DME forum, 2007; Semelsberger et al., 2006). Although it is necessary to invest in the construction and installation of new equipment for distributing and storing DME, there is potential for converting existing LPG infrastructures to DME specifications with less cost (Japan DME forum, 2007). It is expected that some modifications would be required for the equipment (*e.g.*, seals, valves, pressure regulators, gaskets, pumps) in the LPG storage and distribution infrastructures (Semelsberger et al., 2006).

To address the lack of existing fueling infrastructure, DME producers, like other alternative fuels producers, will initially adopt a hub and spoke model for fuel distribution (Figure 3.1). DME is centrally produced and delivered to customers as needed on a daily, weekly, or monthly basis. Therefore, early adopters would be fleets involved in local and regional haul that drive in and out of the same terminal daily and refuel at their base site. As the market develops, more DME production units will be deployed in each region, and new regions will be added across the country in sync with market growth. Eventually, a national infrastructure will service long haul applications.

3.2. Storage Containers and Materials Compatibility

DME is stored, handled, and transferred as a liquefied gas under pressure. While handling of DME is similar to propane, pumps, valves, and seals on propane tanks and propane infrastructure must be made of specific materials. ASTM specification D7901 provides limited guidance on safety and handling of DME, including elastomer selection for gaskets and seals (see Table 3.1), since there is a risk of seal and gasket failures. DME storage and distribution systems will only utilize aboveground components.

3.2.1. Cylinder tanks

The DME fuel cylinder is a welded cylinder that consists of a cylinder shell and panel and has accessories consisting of a filling valve, an outlet valve, a return valve, a safety valve, an overfill prevention device, a quick coupling, and a fluid level display device. The structure complies with LP gas vehicle structural handling standard, and the pressure tightness and air tightness comply with the cylinder standard.

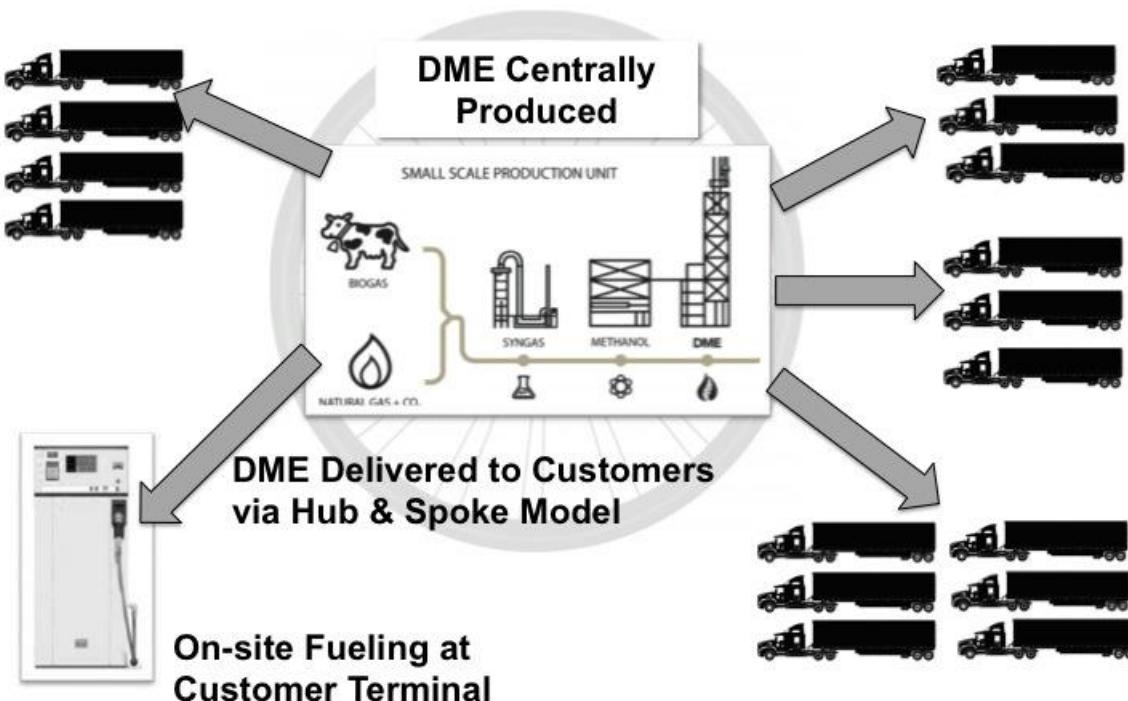


Figure 3.1. Oberon DME distribution process.

A typical small-scale Oberon production plant may include four 30,000 gallon storage cylinder tanks. This provides enough DME running stock to secure both typical operation and consumption at the supply destination and to be able to deal with the seasonal variation in the demand-and-supply balance. Storage cylinder tanks must meet high pressure gas safety law and inspection and re-inspection requirements. Since DME is denser than propane, the supports and foundation must be stronger than those for propane storage generally.

One litre of liquid DME will vaporize to produce 374 L of gas when expanded to 15°C and 100 kPa. The liquid expands and contracts with temperature. The expansion of liquid with temperature increases is critical to determine maximum filling densities for both storage and vehicle tanks. Temperature correction for volumetric measuring of liquid DME is important to dispensing and metering (Paas, 1997). Carbon dioxide is highly soluble in DME and should not be used as a purge gas or pressure medium (Paas, 1997).

3.2.2. Penetration of seals and gaskets

Materials used in the storage, handling, and transfer of DME have to be compatible with, and unaffected by, DME. DME reacts differently to seal and gasket materials than LPG, therefore in

cases where DME or DME/LPG mixtures will be used as alternative fuels, appropriate seal and gasket materials must be incorporated. When repurposing LPG storage, transportation, production and combustion equipment for use with DME, the composition of seals and gasket materials must be considered as incompatible materials can lead to leakage.

3.2.2.1 Swelling of seal materials and resins

Rubber and plastics swell and degrade easily in the presence of DME when compared to LPG. Nitrile rubber seals (NBR) and fluoro rubber seals (FKM) have been used with LPG, but swell and increase the risk of leakage when used with DME.

3.2.2.2 Classification of gasket materials

Gasket and seal materials were classified by the JDF in order to assess the different reactions of these materials with DME and LPG (Figure 3.2). Seals were divided into two groups: those which are static (“seal”) and those that work in conjunction with moving parts (“packing”). The static seals (used with flanges and piping parts) were grouped into metallic, non-metallic, and semi-metallic materials. The seals that work with moving parts (with reciprocating, spiral, or rotating motion) were grouped by contact, non-contact, isolation types. All types of seals were classified by base materials.

3.2.2.1 Seal/gasket locations in LPG import base and industrial facilities

Surveys were conducted with over 400 import base and industrial LPG facilities to determine the typical locations and materials of seals and gaskets within the facilities (Japan DME forum, 2007). The materials most widely used for static seals were nitrile rubber (NBR) and polytetrafluoroethylene plastic (PTFE). Various other processes utilized fluoro rubber (FKM), silicone rubber (VMQ), chloroprene rubber (CR), ethylene-propylene rubber (EPDM), butyl rubber (IIR), and hydrogenated acrylonitrile-butadiene rubber (HNBR).

3.2.2.2 Seal/gasket materials and tests

Screening experiments were conducted on forty rubber seals with differing heat and oil resistances and five plastics. The plastics were polytetrafluoroethylene (PTFE), perfluoroalkoxy (PFA), high density polyethylene (HDPE), polyvinyl chloride (PVC) and polyamide 11 (PA11). Additionally, three types of compressed sheet gaskets, three gland packing seals, and two types of spiral wound gaskets found in LPG facilities were tested (Japan DME forum, 2007). Materials were immersed in DME (from 1 and 2 step synthesis processes) and LPG and tested for changes in thickness, tensile strength, elongation and hardness. Moreover, swelling ratios, leak measurements, and compression set measurements were conducted on four types of rubber O-rings (NBR, HNBR, IIR and FFKM) with DME from one and two step synthesis processes and LPG.

3.2.2.3 Summary of materials test results

Spiral wound gaskets, sheet gaskets, and gland packing used for LPG were determined to be suitable for use with DME. As for plastic materials, polyvinyl chloride (PVC) works with LPG,

but is readily dissolved in DME and is therefore unsafe. However, polyamide 11 (PA11), perfluoroalkoxy (PFA), polytetrafluoroethylene (PTFE), and high density polyethylene (HDPE) are compatible with both DME and LPG.

Substantial swelling of fluoro-rubber (FKM) samples was observed with DME, although perflouro elastomer (FFKM) performed well with all fuels. For chloroprene rubber (CR), ethylene-propylene rubber (EPDM), and butyl rubber (IIR), tests with intended devices must be used to determine compatibility with DME and/or LPG.

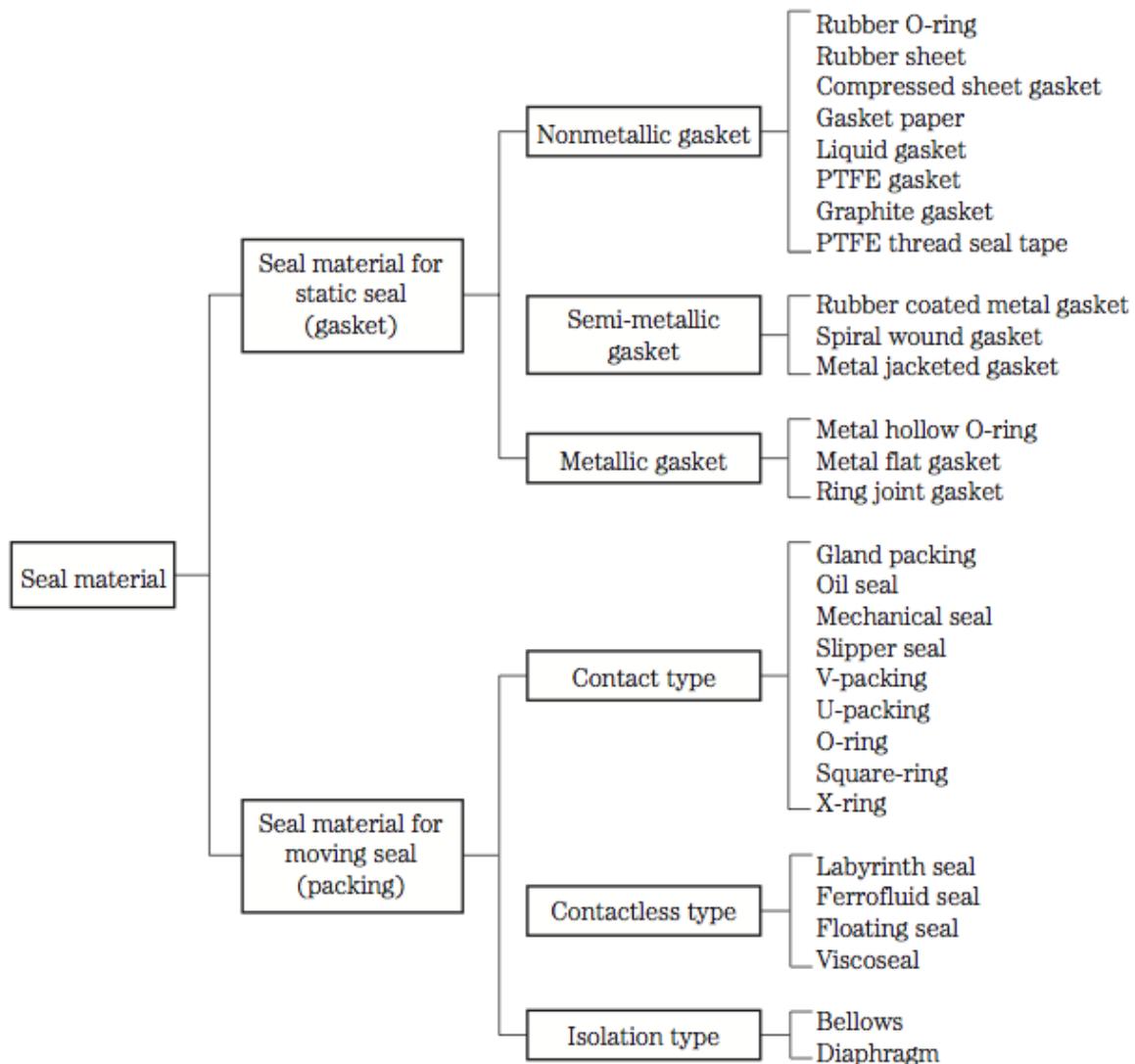


Figure 3.2. Seal/gasket classification adapted from *DME Handbook* (Japan DME forum, 2007).

In summary, the following materials have been found to be compatible with DME: Nitrile (NBR, BUNA-N), Hydrogenated NBR (HNBR), Silicone (VMQ), Fluorosilicone (FVMQ), Perfluoroelastomer (FFKM), polytetrafluoroethylene (PTFE), and stainless steel. See Table 3.1

for various elastomer compatibilities. This material compatibility information has been generated by commercial DME handlers, as a general reference, and listed in ASTM D7901.

Elastomer	Compatibility rating for DME Use ¹
Natural Rubber (NR), Isoprene	4
Butadiene Styrene (SBR, Buna S), Butadiene (BR)	4
Butyl (HR)	4
Ethylene Propylene (EPR, EPDM, EP)	4
Nitrile (NBR, BUNA-N)	1
Hydrogenated Nitrile Butadiene Rubber (HNBR)	1
Polychloroprene (Neoprene, CR)	3
Chlorosulfonated Polyethylene (CSM)	3
Polyacrylate (ACM)	4
Polysulfide (T)	2
Silicone (VMQ)	1
Fluorosilicone (FVMQ)	1
Fluoroelastomer – Dipolymer	4
Fluoroelastomer – Terpolymer	4
Perfluoroelastomer (FFKM)	1
Polytetrafluoroethylene (PTFE)	1

¹ Rating legend (all ratings are for room temperature)

1 = Little or minor effect, 0 to 5% volumne swell

2 = Minor to moderate effect, 5 to 10% volumne swell

3 = Moderate to severe effect, 10 to 20% volumne swell

4 = Not recommended for DME use

Table 3.1. Elastomer compatibility with DME (ASTM D7901).

3.2.3. Filling Valve

The filling valve is equipped with a quick coupling at the inlet and an overfill prevention device in the cylinder. The outlet valve and the return valve have excess flow valves to prevent fuel from flowing out by closing their openings when fuel in the cylinder flows abnormally. Each valve is provided as a discharge opening for the fuel in the cylinder and return opening for fuel from the engine. Each valve is controlled manually by handle, and these handles are color-coded according to usages. The safety valve opens to the vapor phase in the cylinder and has been constructed to operate with a pressure (1.44 MPa) of 80% or less of the pressure test.

3.2.4. Overfill prevention device

The overfill prevention device has a structure that uses a float to determine the level when the liquid reaches the maximum mass as set forth in Article 22 of the cylinder safety rules, and operates automatically. Fuel tanks will be equipped with automatic shutoff functions. Fuel dispensing pumps will be programmed to shut off when required by the automatic shutoff function of the fuel tank.

3.2.5. Quick coupling

The quick coupling has a structure that opens only when it is connected with the filling gun in order to make fueling easier. It is necessary to make the shape of joint of the filling gun differ from that of LPG to prevent improper filling at the filling location.

3.2.6. Fluid level display device

The standard float material included in a general propane level sensing application is a propane compatible thermoplastic. For DME service, the float should be exchanged for one made of a DME compatible material such as stainless steel or brass.

3.2.7. Electroconductivity

DME has low electroconductivity and the flow of DME during fuel transfer or vaporization of the DME can build up a static electrical charge. It is necessary to provide adequate electrical grounding for all tank and piping to route any charge away from fill connections and other areas where there might be the presence of DME vapors. (Paas, 1997).

3.3. DME Storage and Distribution Summary and Data Gaps

LPG infrastructures are widespread in the United States and basic components of LPG storage and handling technology can be used for the storage and handling of DME. Substantial swelling of a variety of seal and gasket elastomers was observed with DME. Materials used in the storage, handling, and transfer of DME have to be compatible with and unaffected by DME.

Perfluoroelastomer, polytetrafluoroethylene, fluorosilicone, hydrogenated-nitrile-butadiene rubber, nitrile, and silicone elastomers as well as stainless steel performed well with DME. These

materials have been found to be compatible by the DME industry and listed within ASTM D7901, Standard Specification for Dimethyl Ether for Fuel Purposes. During the implementation of DME production using the Oberon Fuels small scale production facility, materials compatibility will comply with the ASTM DME Standard guidelines and will be verified and documented with actual devices and production and storage systems to be used in California.

4. Use of Dimethyl Ether as a Transportation Fuel

4.1. Vehicle Operability Issues

As a diesel blend stock, DME has a high cetane number (>55) but a low energy density. DME blending in conventional diesel can reduce sulfur, particulate, and NOx emissions. DME is more corrosive, flammable, and volatile than petroleum diesel (Farrell and Sperling, 2007). About 1.8 L of pure DME is equivalent to 1.0 L of diesel fuel, on a lower heating value (LHV) basis, and about 1.6 kg of pure DME is equivalent to 1.0 kg of LPG, on an LHV basis (Fleisch, et al., 2012).

DME is an isomer of ethanol and both have the same stoichiometric air/fuel ratio and similar energy content on a mass basis (Szybist, et al., 2014). The absence of any C-C bonds and high oxygen content promotes smokeless combustion and high oxidation rates of particulates in compression-ignition engines (Arcoumanis, et al., 2008). DME has lower viscosity than diesel fuel which can cause leakage from a fuel system that relies on small clearances for sealing. A good review of DME operability issues is provided in the *DME Handbook Supplement* (Japan DME Forum, 2011) and Arcoumanis, et al., 2008.

Viscosity of DME is 1/20 of diesel fuel. To protect engine fuel injection equipment, the JDF suggests that it is necessary to add a lubricity additive at about 100 ppm to maintain the lubricity of the fuel equal to that of diesel fuel.

4.1.1. Additives

4.1.1.1 Lubricity Additive

The viscosity of a fluid is a measure of its resistance to a shear stress, such as friction on a pipe wall. Lubricity is a qualitative assessment of a fluid's ability to reduce friction, which cannot be measured directly, but is determined through wear tests. Low viscosity fuels have decreased lubricity around moving parts in fuel delivery system (the plunger and the injectors) and lead to seizing, sticking, and wearing. Preventative measures include additives to increase viscosity, changing the materials of the fuel delivery system, and surface treatment of materials. Another concern with low viscosity fuels is that they can leak from injection equipment more easily than higher viscosity fuels.

Lubricity is a known issue for DME as a transportation fuel. Liquid DME has a viscosity that is about 1/20th that of diesel fuel. Because DME does not possess any natural lubricity and because of its low viscosity, DME can contribute to fuel injection pump, common rail pump and fuel injector wear (Arcoumanis, et al., 2008). A variety of lubricity additives have been considered for DME, and test results have shown that adequate lubricity can be achieved at treat rates of as little as 100 ppm. However, if a fatty acid-based lubricity additive is used, then oxidative stability of the additive itself may become a concern. Historically, a commercial additive, Lubrizol 539, has been used widely at treat rates of 500 – 1000 ppm. In addition, Teng, McCandless and Schneyer (2002) provide a detailed overview of the viscosity and lubricity of

DME. Considering the physicochemical properties of DME, they suggest that “any good boundary lubricant, as long as it is soluble in DME and it does not affect the combustion characteristics of DME significantly, can be a lubricity additive for DME.” However, as pointed out by many investigators, the lubricity additive should burn sufficiently cleanly that it does not generate nanoparticle emissions from the combustion process, which would undermine the clean burning characteristics of DME.

However, at this time, we do not have any data available from OEMs regarding a specific lubricity requirement. The Japan DME Forum (2011) recommends that an optimization is needed to formulate and select lubricity agents that provide sufficient wear resistance, as tested by the modified HFRR test (“High Frequency Reciprocating Rig”), an ASTM test method for lubricity.

4.1.1.2 Need for an Odorant

Since DME is handled much like propane and LPG, similar odorization strategies used for propane, LPG and natural gas can be applied to DME. Oberon staff who work with DME report that the ether smell in DME is both strong and unpleasant. Whether this odor is sufficient or must be augmented remains unaddressed. The need for odorant in liquefied petroleum gas is currently addressed the US Code of Federal Regulations 49CFR (173.315). Odorants for commercial, residential and transportation applications of these hydrocarbon gases have typically been based on a class of compounds referred to as “mercaptans.” The mercaptans fulfill the essential requirements for odorant compounds in that they have a strong olfactory response at low concentration and do not saturate the olfactory lobes (*i.e.*, you continue to be able to smell the odorant). However, the mercaptans contain sulfur, and since DME is a sulfur free fuel, it is counterproductive to put sulfur compounds into DME. So, mercaptans can be used as odorants for DME, but non-sulfur based odorants would be preferred. The *DME Handbook Supplement* provides a review of an odorant design and selection study (Japan DME Forum, 2011). There remains a need to explore non-sulfur odorant options for odorization of DME including consideration of whether there would be benefit to have DME possess an odor that is readily detectable but unique from natural gas and propane odorants.

4.1.1.3 Additive to Show An Open Flame

There is not a standard for flame luminosity for DME, but there have been consideration of additives or blending agents for creating luminosity for fuels that have a non-luminous flames such as methanol and hydrogen (for DME, see section 6.1.1.1). For methanol, organic compounds that have a high sooting tendency could be added, as could organometallic compounds (Fanick and Smith, 1994). These kinds of additives could be a source of organic and inorganic nanoparticles, which may be undesirable and counterproductive given the clean burning characteristics of DME. It may suffice to include a small amount of propane or LPG in the DME to potentially give a flame some luminous character without generating particulate emissions.. A unresolved issue is the level of luminosity that may be needed.

4.1.2. Aspects special to a DME diesel engine

4.1.2.1 Minimum Post Combustion Emission Controls

Compression ignition engines running on DME do not require a diesel particulate filters (DPF) in order to meet emissions standards for particulate matter. This aftertreatment filter is costly and adds weight to trucks whose delivery capabilities are then decreased.

4.1.2.2 Fuel Injector Design

Due to low viscosity, special fuel injection pumps are required to prevent DME leaking into engine crankcase which can cause an engine fire. Precise control both of temperature and pressure is necessary to avoid vaporization in fuel supply line.

A DME fuel feed system pressurizes DME beyond its saturated vapor pressure in order to not allow DME to vaporize as it flows to the fuel injection pump. Since the fuel temperature in the fuel injection pump goes up to about 80°C, the feed pumps pressurize the fuel to higher than 2.0 MPa. The feed system consists of three feed pumps. These are connected in series and the feed system can increase tank pressure to a supply pressure of 2.0 MPa using these three pumps. The feed pump is a trochoid type pump and is an in-tank type.

Fuel injection timing tends to be delayed due to its high compressibility. The injection instability due to the large compressibility of DME is solved by changing the nozzle design and control of fuel temperature.

About two times the diesel fuel volumetric fuel injection rate is required due to DME's low heating value per unit volume. About twice the injection volume is necessary compared with diesel, because the volumetric calorific value for DME is lower. It is therefore necessary to increase the capacity of the fuel tank. Multiple fuel tanks may be needed to use space efficiently.

It is necessary that the DME is pressurized up to about 2 MPa by a fuel feed pump in diesel engine to enable injection of the liquid with high pressure fuel injection equipment. It is also necessary to change the strength of fuel lines, for example with steel tubing because the rubber tubing is used for a part in this fuel system in a usual diesel engine. Further, improving seals for fuel pumps and injectors is necessary for conversion of LPG or diesel injection engines to DME injection engines.

4.1.2.3 Bulk Modulus

A substance's bulk modulus is a measure of its resistance to uniform compression. The bulk moduli of DME and diesel are 6.37×10^8 N/m² and 1.49×10^9 N/m², respectively. Thus liquid DME has approximately $\frac{1}{2}$ the bulk modulus of diesel, meaning that DME is a relatively compressible fuel. Therefore, it has a large change in volume with respect to changes in pressure and/or temperature. The lower bulk modulus of DME makes it difficult to create high pressure in fuel injection units. During fuel injection, fuel is injected by the plunger and pressure increases, and because DME has a low bulk modulus, the volume decreases and less DME is supplied to the combustion chamber. The increased temperature leading to the combustion chamber further decreases the bulk modulus. Consequently, standard diesel fuel injection systems running DME

experience a 20-30% decrease in torque, especially at higher engine speeds, warranting the development of a specific DME injection system which results in comparable torque to a diesel engine.

4.2. Development of DME Specification

California law requires that all fuel sold or distributed within the State have a fuel specification established by a consensus organization, such as ASTM or SAE. Therefore, development of an ASTM Standard Specification for DME is an important step towards the legal use of DME as a fuel in California. The California Department of Food and Agriculture, Division of Measurement Standards (CDFA) is a strong proponent of the development of an ASTM DME fuel standard.

In order to complete its engine testing for DME, CARB must also establish specification standards for the fuel used in the engine test (“test fuel”). The test fuel must fall in the range of specifications that CARB has selected. At this point, CARB has determined that the minimum requirement for the fuel specification would be ASTM specification D7901 and the maximum requirement has not yet been set. Therefore, the test fuel used for engine testing as part of the Multi-Media Assessment must fall within the ASTM specification range.

4.2.1. ASTM Standards for DME

Work Item WK38123 was established for the development of an ASTM Standard Specification for Dimethyl Ether for Fuel Purposes. Following Committee D02 voting which closed on November 4, 2013, the Standard Specification for Dimethyl Ether for Fuel Purposes passed and the official DME ASTM standard was published in January 2014 as ASTM D7901: Standard Specifications for Dimethyl Ether for Fuel Purposes (ASTM, 2014). Since its first publication in January 2014, the specification has already been updated to include a lubricity warning and was re-released in July 2014 as D7901-14a. The DME ASTM standard provides detailed requirements for dimethyl ether fuels including allowable methanol, water, methyl formate, sulfur, vapor pressure, copper strip corrosion, and evaporative residues. The test methods to be used to verify these requirements is also provided by the ASTM DME Standard. ASTM specification D7901 provides limited guidance on safety and handling of DME, including elastomer selection for gaskets and seals (see Table 3.1).

4.3. DME Use Summary and Data Gaps

4.3.1. Conventional Diesel Engine Modifications

Compression ignition engines running on DME do not require diesel particulate filters (DPF) in order to meet emissions standards for particulate matter. This aftertreatment filter is costly and adds weight to trucks whose delivery capabilities are then decreased. Conventional diesel engines require modifications to fuel storage and delivery system to use DME as a fuel. The conversion of seals for fuel pumps and injectors is necessary for conventional diesel injection engines to DME injection engines.

4.3.2. DME Additives

It is anticipated that DME will require a lubricity additive due to its low inherent lubricity. Further it is anticipated that original equipment manufacturers (OEMs) may specify an engine-cleaning additive or that local jurisdictions will require an odorant such as ethyl mercaptan. There is also a possibly an additive to increase flame luminescence may be needed. However, information on specific concentrations of each of these additives has not been made available by OEMs at this point in the development of DME as a fuel.

4.3.3. Development of Specifications for California Certification Fuel for DME

California law requires that all fuel sold or distributed within the State have a fuel specification established by a consensus organization, such as ASTM or SAE. ASTM D7901, Standard Specification for Dimethyl Ether for Fuel Purposes, has been adopted and is an important step towards the legal use of DME as a fuel in California.

In addition, in order to complete its engine testing for DME, CARB must also establish specification standards for the fuel used in the engine test (“test fuel”). The test fuel must fall in the range of specifications that CARB has selected. At this point, CARB has determined that the minimum requirement for the fuel specification would be ASTM specification D7901 and the maximum requirement has not yet been set. Therefore, the test fuel used for engine testing as part of the Multi-Media Assessment must fall within the ASTM specification range.

5. Environmental Transport and Fate of Dimethyl Ether.

5.1. A Multimedia Framework for Fate, Transport, and Exposure

A multimedia transport, fate and exposure assessment synthesizes information about partitioning, reaction, and multimedia-transport properties of a chemical in a representative or generic environment with information about exposed humans or wildlife to assess impacts, such as health risk. The multimedia impact characterization approach is illustrated in Figure 5.1. This assessment is typically carried out using models supplemented with limited sampling analyses. In the modeling approach for characterizing potential impacts, the environment is treated as a set of compartments that are homogeneous subsystems exchanging water, nutrients, and chemical contaminants with other adjacent compartments. A cumulative multi-pathway exposure assessment for humans relates contaminant concentrations in multiple environmental media to concentrations in the media with which a human population has contact (for example; personal air, tap water, foods, household dusts, and soils). The potential for harm is assessed either as the average daily intake or uptake rate or as time-averaged contact concentration.

Multimedia contaminant fate and exposure models have been useful to decision makers because these models provide an appropriate quantitative framework to evaluate our understanding of the complex interactions between chemicals and the environment. The greatest challenge for multimedia models is to provide useful information without creating overwhelming demands for input data and producing outputs that cannot be evaluated. The multimedia modeler must struggle to avoid making a model that has more detail than can be accommodated by existing theory and data while also including sufficient fidelity to the real system to make reliable classifications about the source-to-dose relationships of environmental chemicals. In the early 1990s, the California Environmental Protection Agency adopted a multimedia approach for setting clean-soil goals through its CalTOX program (McKone, 1993), and the European Union adopted a multimedia multipathway framework for chemical risk assessment (RIVM, 1994.)

Deploying a multimedia assessment framework requires basic chemical properties information about the substances under consideration. These properties include multiphase partitioning properties that describe how a substance will distribute itself among the major components of the environment—air, water, and organic phases such as lipids and organic materials in soil.

In the sections below, we identify the important multiphase transport properties needed for the multimedia impact assessment and summarize available information and information gaps. Where there are information gaps, we consider how these gaps contribute to overall uncertainty and suggest approaches for increasing available information.

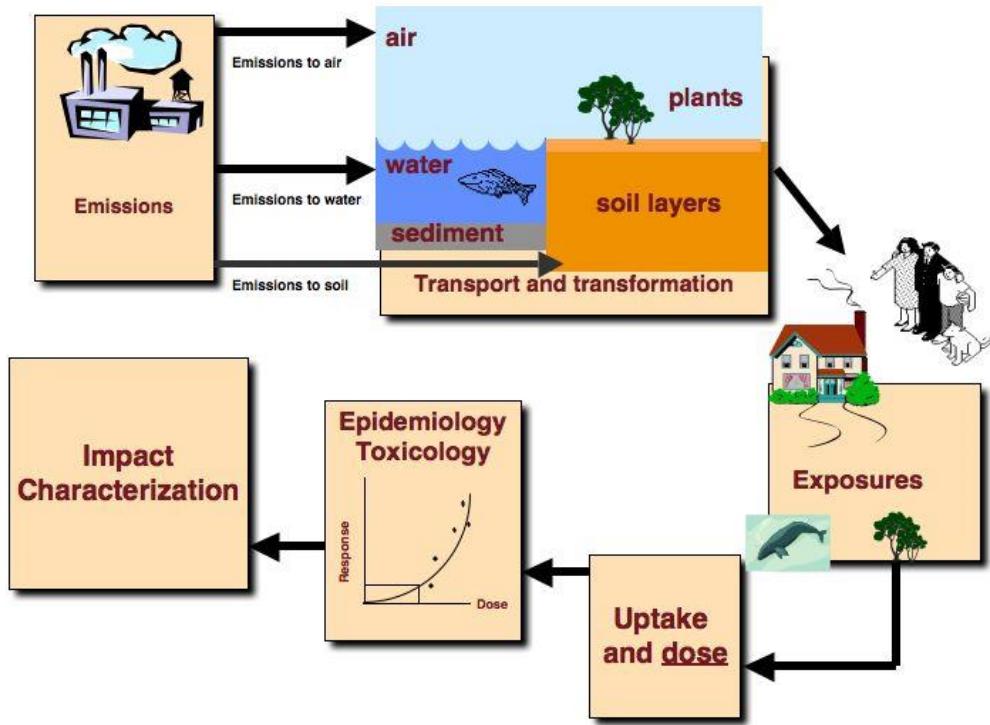


Figure 5.1. A conceptual illustration of how pollutant emissions from each life-stage of DME production and use enter air, water, and or soil, undergo multimedia transport into exposure media, followed by contact with humans and ecosystems.

5.2. Data Needs for Multimedia Transport Assessment

Multimedia transport and transformation models require three different types of input data. First, they require chemical properties data. Next, they require data describing the climate, soil, and hydrologic properties of the environment or landscape receiving the contaminants, and finally, information on emissions patterns and mode of entry (air, soil, water, groundwater). In this section, we focus on data needs for the first of these, chemical properties.

5.2.1. List of Physical-chemical Properties Impacting DME Fate & Transport

DME may enter the environment in the event of a spill, through leakage, or during fueling. The fate and transport of DME in the environment is dependent on the chemical properties of DME and of the environmental media (Tables 1.2 and 1.3).

DME is chemically inert and stable in weakly acidic, neutral, and weakly basic solution. DME is the smallest ether and has the chemical formula CH_3OCH_3 with a molecular weight of 46.07 g/mol. DME is a colorless gas with a slightly sweet smell at ambient temperature and pressure, although it can be liquefied at 20°C under 5 atm of pressure.

The basic chemical properties needed to describe the environmental fate of a chemical, are those that define equilibrium distribution among the key environmental phases and those describing

removal rates by biological or chemical degradation in air, water, and soil. Partitioning involves following media pairs:

- Air-Water
- Air-Atmospheric particulates (aerosols)
- Air-Soil
- Water-Solids (suspended solids, sediments and soil).
- Non-aqueous phase liquid (NAPL) and
- Pure phase

Degradation in air, water, and soil involve one or more of the following processes:

- Biodegradation
- Hydrolysis
- Photolysis
- Oxidation

The basic physical and chemical properties available for DME are listed in Tables 1.2 and 1.3. For non-polar, non-ionizing organic substances, a number of assumptions have been found to be reasonable for establishing partitioning among the primary environmental media. These are the air-water, KAW; octanol-water, KOW and octanol-air, KOA partition coefficients. Other phase distributions can be derived from this basic set. For example, sorption to solids in air, water, soil, and sediments is dominated by partitioning or absorption into the organic fractions of these solids. KOW and KOA have been useful proxies for these solid-phase partition factors.

These three partition coefficients, as well as those partition coefficients involving the pure substance phase (vapor pressure, solubility in water and solubility in octanol) are interrelated as shown in Figure 5.2 (Wania, 2001).

5.2.2. Phase Distribution Assessment and Degradation

Figure 5.2 shows that the minimum data requirements for describing phase partitioning of non-polar organic substances are:

- Any two of the three partition coefficients KAW, KOW, and KOA. The third can be estimated from the other two or:
- Any three of the six properties listed in the above figure as long as they do not form a triangle. (For example, if vapor pressure, water solubility and log KOW are known, the remaining partition coefficients can be deduced from these. However, if only vapor pressure, water solubility and log KAW are known, partitioning into organic solids cannot be established).

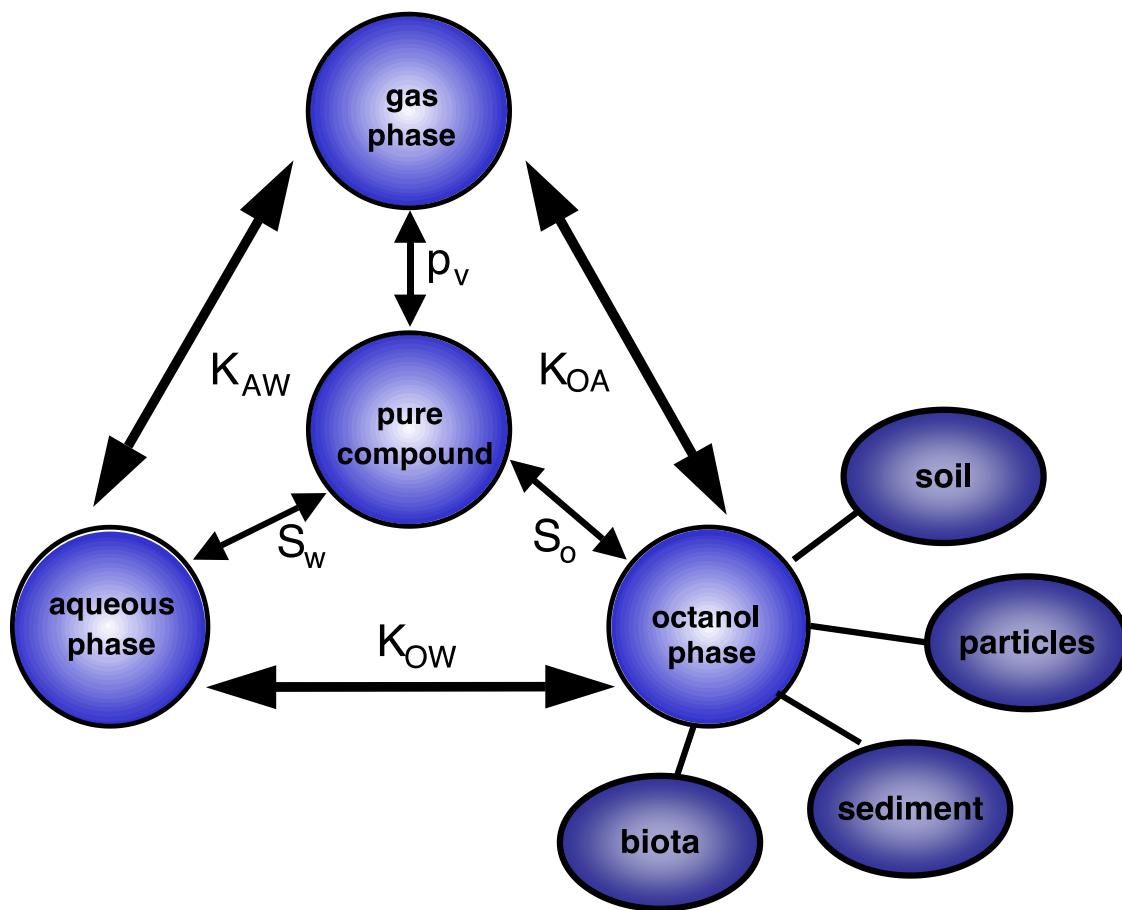


Figure 5.2. Phase distribution equilibria involving pure phase partition coefficients (water solubility S_w , solubility in octanol S_o and vapor pressure p_v) showing the links for describing environmental phase partitioning (K_{AW} air/water partition coefficient, K_{OW} octanol/water partition coefficient, K_{OA} octanol/air partition coefficient). The octanol phase is used for soil, sediment, particles and biota).

The approach outlined above for the non-polar substances may also be applicable to polar substances. Compounds that ionize in the aqueous phase can be treated as non-electrolytes by multiplying the partition coefficients K_{AW} and K_{OW} for the neutral species by the fraction that is undissociated, which in turn can be calculated from the dissociation constant of the compound pK_A and the pH of ambient water. This approach assumes that the dissociated form does not volatilize and does not sorb to solids. This approach neglects, however, that the dissociated form might associate with the non-organic part of soil materials such as minerals. For many other compound classes, such as metals, surface active substances, extremely water insoluble or involatile substances, polymers, or biological macromolecules, the environmental phase distribution can not be estimated using the octanol-based approach outlined for non-ionizing chemicals. For example, their sorption to solids is not necessarily dominated by simple phase partitioning into the organic fraction, but other mechanisms, such as specific surface sorption may become important. It may still be possible to describe them with the help of multimedia

models, if the relevant environmental phase distributions can be quantified directly or if different estimation methods exist that allow the estimation of these phase distributions. However, it should be noted that multimedia models are meant to describe the environmental fate of chemicals that distribute into more than one environmental phase. For chemicals that occur predominantly in one medium of the environment, multimedia models help guide us to which components of the environment require the most detail in making an impact assessment. For example, a multimedia model will show that there we do not gain insight when estimating a characteristic atmospheric travel distance for a polymer or a biological macromolecule.

Reactivity information (*i.e.*, degradation rates) for the various environmental compartments is required to carry out a multimedia assessment. The reaction rates in the various media can either be measured or estimated. Experimentally obtained rate data are preferred over estimated data. Accurate degradation rates are only needed for those compartments in which a significant part of the total chemical mass in the system resides. Because the question of how much of a chemical can be found in which environmental compartment strongly depends on the partitioning properties of the chemical, one way to estimate the presence of a chemical in the different compartments is based on its partition coefficients. It has been suggested that for compartments with less than 5% of the chemical mass present, as estimated from partitioning coefficients, a rough estimate of the degradation rate is sufficient (Woodfine et al. 2001).

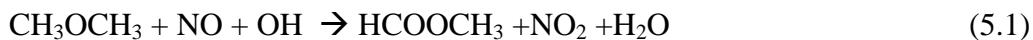
5.3. Partitioning and Phase Interface Relationships

DME may enter the environment through leakage or spillage during production, transport, storage, and usage. The chemical properties of DME determine how it partitions in the atmosphere, soil, and water. DME is a polar gas that liquefies and becomes partially miscible with water under pressure. The solubility of DME in water is 7.6 g/100ml at 291K (up to 6% by mass, Arcoumanis, et al., 2008). and at ambient temperatures and pressures liquid DME volatilizes due to its relatively low boiling point of -25.1°C and heat of vaporization (21.51 kJ/mol). Phase equilibria experiments of DME/water mixtures were conducted (Pozo et al., 1984; Japan DME Forum, 2007). At ambient temperatures and pressures (corresponding to a spill or leakage scenario), the aqueous phase of the mixtures had a DME mole fraction of 0.08, and as pressure increased, liquid phases reached DME mole fractions of 0.8 as shown in Figure 5.3 (Japan DME Forum, 2007). Thus, DME evaporation is expected under ambient conditions. When DME is mixed with CO₂ it becomes more miscible with water and more able to transport polar molecules from the aqueous phase into the solvent phase (Tallon et al., 2010).

5.3.1. Fate of DME in the Atmosphere

DME is a volatile organic compound and will exist primarily in the gas phase when it is released to the atmosphere. The main transport and removal mechanism of DME in the atmosphere will be dispersion. In urban atmospheres, DME is transformed by hydroxyl (OH) radicals and to a lesser extend by nitrate radicals (Howard, 1989) to form methyl formate as well as water, NO₂ and some CO₂. An atmospheric half-life of 5.1 - 5.4 days (Good et al, 1998) was estimated for

DME reacting with hydroxyl radicals and 123 days for DME reacting with nitrate radicals³ (US EPA, 2000). The mechanism for the potential atmospheric oxidation of DME by OH radicals is shown in equation 5.1 as proposed by Japar et al. (1990).



Atmospheric OH, or the Cl used during laboratory experiments by Japar et al, (1990), will abstract an alkyl hydrogen, and the alkyl radical formed will add O₂ to form an alkyl peroxy radical. The alkyl peroxy radical will react with NO to form an alkoxy radical. In the case of DME, each molecule consumes one OH radical and leads to the conversion of 2 molecules of NO to NO₂, but all of the carbon ends up in methyl formate, which is unreactive within urban atmospheres.

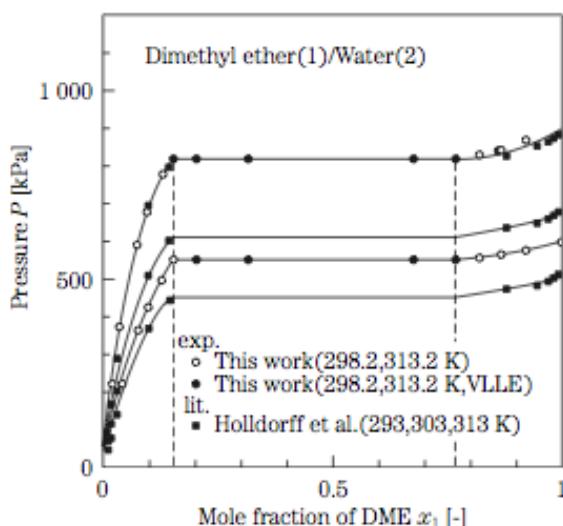


Figure 5.3. Vapor-liquid equilibrium for DME/water from 293-313K (Japan DME Forum, 2007).

The lifetime of the alkoxy radical is estimated to be about 2 msec (Japar et al, 1990). DME is not expected to be highly efficient in the formation of atmospheric ozone (Chang and Rudy, 1990). Direct photolysis is not expected to be an important process (Howard, 1989; DuPont, 2000). DME is not regarded as a greenhouse gas. DME partitioning into rainwater can be expected to be low as atmospheric concentrations of DME are expected to be low.

Since DME is heavier than air, during a bulk DME release, it is possible that a cold DME vapor cloud, denser than air, could form and settle into low lying surface features such as basements, storm drains, creek beds, or drainage ditches. If these vapors reach an ignition source, a significant explosion could occur.

³ <http://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+354>

Atmospheric partitioning of DME into rainwater is expected to be low as atmospheric concentrations of DME are expected to be low. On the other hand, if rainfall occurs through a DME vapor cloud that has settled into low-lying area, this rain could adsorb DME and percolate to groundwaters.

5.3.1.1 Exhaust Emissions

The California Energy Commission (CEC) has made preliminary assessments that report well-to-wheels (WTW) emissions of the criteria air pollutants NO_x, CO and PM10 from DME derived from natural gas. The CEC report indicates that the DME emissions are comparable and somewhat lower when evaluated on an energy basis to CA ultra-low sulfur diesel (ULSD) (CEC, 2007). The CEC WTW analysis also indicated that, WTW emissions of hazardous air pollutants from natural-gas-derived DME are lower than ULSD, but there are concerns about higher levels of formaldehyde from DME use compared to ULSD. Similar to LPG, the WTW modeling showed that DME fuel derived from natural gas could have VOC emissions higher than ULSD, but these VOC emissions can be controlled (CEC, 2007). These preliminary WTW estimates need confirmation using engines designed and optimized for DME combustion.

Recent DME emissions testing by Oak Ridge National Laboratory using a prototype combustion-ignition engine indicated that unburned hydrocarbons, NOx, and CO emissions were higher than diesel due to transient spikes during variable driving conditions using the prototype test engines. During steady cruise conditions, these emissions were comparable or lower than diesel (Szybist, et al., 2014). The same study found that the PM emissions for DME were sufficiently low enough that they do not approach the detection limit, and were a minimum of an order of magnitude below the 2010 U.S. emission standard without the use of a diesel particulate filter.

In spite of the emissions spikes in the prototype DME truck engine tested, cumulative NOx, HC, emissions were significantly below both European and U.S. emission limits for hydrocarbons. Methane emissions were an order of magnitude below Euro V standard for heavy-duty natural gas engines. Particulate matter emissions were near zero, and the study confirmed that particulate matter after treatment is not required for a DME engine (Szybist, et al., 2014).

Improved engine controller technology for DME may help eliminate the observed emission spikes seen during variable driving conditions. Salsing, 2011, found that DME engine design modification resulted in significantly reduced exhaust emissions, including CO, and increased combustion efficiency. DME engine combustion can be improved using a piston design that promotes flame spread; a nozzle configuration that improves mixing late during diffusion combustion. By raising the injection pressure, CO emissions could be reduced without raising NO_x emissions.

The issue of formaldehyde emissions is complicated by the lack of detailed engine emissions studies for DME combustion in diesel engines. However, there is published information that can help to formulate an expectation for the impact of DME utilization on ambient levels of formaldehyde.

Formation of formaldehyde and acetaldehyde is an essential component of the low temperature auto-ignition of most fuels of interest (Japan DME Forum, 2007; Chapter 3), and formaldehyde is a combustion intermediate for all hydrocarbons, alcohols, ethers and other oxygenates. Formaldehyde emissions could be 1-10% of the non-methane hydrocarbon emissions. Aldehydes may also be high due to higher CO emissions. Formaldehydes can easily be reduced by oxidation catalysts to negligible concentrations (Arcoumanis, et al., 2008). The detailed combustion reaction mechanism (Curran et al., 1998) includes a direct route for formation of formaldehyde from DME and a methyl radical during high temperature reactions, which would be followed by subsequent oxidation of the formaldehyde to form CO and finally CO₂ or by hydrogen abstraction to form the formyl radical and then CO and finally CO₂. Aldehydes formed during combustion are generally consumed (or decompose) rapidly. However, during the quenching of combustion intermediates in internal combustion engines, aldehydes can be emitted by the engine.

In gas turbine combustion studies under low NO_x conditions using a multi-cluster burner, formaldehyde emissions from pure DME were below detection limits but were 1.4 ppm using a “fuel grade DME” that contained 10% methanol. In this case, the methanol serves as the source of the measurable aldehyde emissions (Japan DME Forum, 2007; Chapter 5). It is worth noting that DME used presently in vehicle demonstrations complies with ASTM D7901, which limits methanol content to 0.05 mass percent.

In homogenous charge compression ignition (HCCI) engine applications, the very low temperature for onset of aldehyde formation and low temperature heat release for DME, helps to enable ignition and prevent excessively rapid ignition (knock). Also, due to its abundant low temperature reactivity, DME supports high levels of exhaust gas recirculation and/or fuel stratification, which allows high temperature heat release to be spread out spatially and temporally, preventing “knocking ignition (Japan DME Forum, 2007; Chapter 5).

Exhaust after-treatment to control CO and aldehyde emissions relies on oxidation catalysts. Precious metal catalysts display oxidation of DME at temperatures starting between 150 to 200°C, and such catalysts should be highly effective at or above their light-off temperature for controlling aldehyde and CO emissions. (Japan DME Forum, 2007; Chapter 5).

Impurities in the “Fuel Grade” DME previously described which contained 10% methanol (not ASTM grade) can contribute to incomplete combustion of DME, and lead to formaldehyde emissions. With sufficient exhaust temperature, near zero (< 1 ppm) formaldehyde emissions are observed downstream of an oxidation catalyst using an Isuzu 6 cylinder in-line common rail diesel engine, regardless of impurities such as methanol and water at 5% addition to the DME (Japan DME Forum, 2007; Chapter 4).

Salsing et al. (2012) showed that engine-out emissions of formaldehyde can be high (as much as 200 ppm engine-out) under certain conditions where fuel-air mixtures in the cylinder are somewhat fuel rich and low temperature. This can be combatted with exhaust after-treatment

devices but was shown along with high CO emissions as an area for further development of the combustion chamber design and fuel-mixing in DME engines.

Yu-sheng et al. (2007) compared formaldehyde emissions from a direct injection diesel engine fueled on DME and on diesel fuel and found the engine-out emissions of formaldehyde to be comparable. These same authors later showed that with optimization of the combustion chamber design (by increasing piston crevice volumes to promote retention of unburned fuel to post-oxidize species during the exhaust stroke), engine-out formaldehyde emissions from DME combustion could be substantially reduced (Yu-sheng et al., 2008).

Overall, since formaldehyde is an essential combustion intermediate during the oxidation of most fuels of interest, it is expected to be formed in the combustion chamber during the ignition and combustion processes. Its engine-out emissions can be controlled with a precious metal-based oxidation catalyst and needs to be incorporated in a DME-fueled diesel engine to limit both formaldehyde and CO emissions. With such exhaust after-treatment strategies, the tailpipe emissions of formaldehyde from DME utilization should not be measurably higher than for diesel vehicles operated on conventional fuels.

5.3.2. Fate of DME in Surface Waters

Based on its Henry's Law constant (3.17683×10^{-3} atm m³/mol [Safety Data Sheet Appendix C]; 7.63×10^{-3} atm m³/mole⁴; 5.9×10^{-3} atm m³/mole)⁵ DME is expected to volatilize rapidly following releases to water surfaces. As with a DME release to soils, a release to a body of surface water would result in rapid, possibly explosive, volatilization of DME. A cold vapor cloud could form on the surface of the water. Wind direction and speed will play an important role in the transport of the cold vapor cloud. The reported literature solubility of DME in water is variable (35 to 76 g/L). The solubility changes with pressure and temperature. At 100 kPa and 18°C water can hold 7 percent by weight and at 500 kPa and 23.5°C water can hold 35 percent by weight (Paas, 1997).

The estimated volatilization half-life from a model river (1 m deep, flowing 1 m/sec, wind velocity of 3 m/sec) is approximately 2.6 hours. The estimated volatilization half-life from a model lake (1 m deep, flowing 0.05 m/sec, wind velocity of 0.5 m/sec, at 25°C) is approximately 2.8 days (Howard, 1989; Lyman, et al., 1990). Lacking a hydrolyzable functional group, DME is not expected to undergo hydrolysis in the environment (DuPont, 2000).

DME has an estimated bioconcentration factor of 3 which suggests that the potential for bioconcentration in aquatic organisms is low (Meylan et al., 1999; Franke et al., 1994). Biodegradation of DME is slow. Aerobic degradation of 100 mg/L DME only reached 0 – 1% of its theoretical biological oxygen demand in four weeks using an activated sludge inoculum (Japan Chemical Industry Ecology – Toxicology Center, 1992).

⁴ http://www.arb.ca.gov/db/solvents/solvent_pages/Propellants-HTML/dimethyl_ether.htm

⁵ <http://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+354>

A DME release into surface waters during the use of watercraft is anticipated to be minimal since the near-term use of DME in marine diesel engines is not planned in California. DME has a strong unpleasant slightly sweet smell and residual taste and odor issues for DME in surface drinking water resources have not been tested.

5.3.3. Fate of DME in Subsurface Soil Environment and Ground waters

EPA does not give a specific method for the sampling and analysis of DME. EPA Standard Methods to sample and detect VOC such as MTBE in air and water should be applicable to DME. As part of Tier II activities, confirmation of the applicability of these methods needs to be conducted. These methods can then be used to monitor air, surface, and subsurface water as pilot production processes are demonstrated. As DME becomes more widely used as a transportation fuel, it is possible that DME will become more widely distributed into the environment, including air and water resources. It may be prudent to include DME as one of the analytes of interest in the future.

Both wholesale and retail DME storage and distribution systems will only utilize aboveground components and any associated pipes and valves will also be above ground.

Because of its high volatility, a bulk DME release onto the soil surface would rapidly transition into the vapor phase. Bulk releases of DME can result in explosive volatilization that can create a destructive shock wave. Near by equipment or soil particulates may be displaced by these forces (JDF 2007).

DME is chemically inert and chemical interaction with soil particulates or organic materials coating the particulates is unlikely. DME is not expected to sorb to sediments or suspended particles in water, or to hydrolyze in groundwater. As a result, DME has a high potential for mobility in vadose zone soils and groundwater, but DME impact to the subsurface could be confined to the shallow subsurface environment unless DME is dissolved into groundwater that reaches the water table.

Due to rapid DME evaporation, it may be expected that a bulk release to the soil surface would result in localized, shallow, soil freezing rendering the soil impermeable to deeper transport until thawing occurs. DME permeation was tested on soils of varying size and water content. Diffusion was faster and more extensive in soils with lower water content (10%). In soils with higher water content (30%), water froze due to DME's heat of vaporization and allowed the DME to evaporate to the atmosphere. In non-uniform dry sand with large particle size distribution (0.2-0.8 mm diameter), the velocity and extent of diffusion was greater than it was for smaller particles (0.2-0.3 mm diameter). Diffusion was reduced with both particle size distributions when waster was present (JDF 2007). Thus, groundwater contamination resulting from a small spill is considered minimal, and any DME vapors trapped in the subsurface soils would eventually disperse to the atmosphere due to vadose zone barometric pumping.

As with surface waters, DME that enters subsurface environment can be expected to have a slow rate of biotic or abiotic degradation. Since DME is a good solvent, it is possible that organic material associated with the soil matrix may be mobilized and displaced.

To explore the potential for a larger DME spill DME to reach groundwater, a hypothetical release scenario is proposed. In this scenario a dense cold vapor cloud forms in a ditch following a bulk DME release from tanker truck. First -responders use a water spray to knock-down the DME vapor cloud. This scenario was used to estimate the upper bound for the concentration of DME in spray water that accumulates in the ditch and could possibly enter the subsurface. The details of this scenario and a highly simplified calculation are summarized in Appendix D.

The results of this rough yet conservative estimate is that the concentration of DME in spray water accumulating in the ditch would not exceed 8-10 parts per million (g/m^3). Further, because the maximum concentration of DME in the knock-down water occurs at the beginning of the knock-down spray, the longer the vapor/air cloud is sprayed, the more DME mass is contributed to the groundwater, but at an increasing overall dilution, with the result that longer sprays lead to lower overall concentrations in the potential source to groundwater.

The toxicity of DME summarized in Section 7 of this document indicates DME has low toxicity and that exposure to water containing 8-10 ppm DME would not be expected to be hazardous. The impact of these estimated concentrations in water on the taste and odor of drinking water is unknown.

This scenario is relatively unlikely, and the potential threat to groundwater resources is minor. Any limited amount of spray water contaminated with DME that reaches groundwater can be remediated with air stripping technologies.

5.3.3.1 Comparative DME Chemical Properties and Soil Transport

Past experiences in California with the di-alkyl ether, MTBE, has created subsurface environmental problems because it is more dispersive in soil and ground water environments than gasoline components such as benzene. Due to these experiences with MTBE in California, we have prepared a more detailed analysis of subsurface transport potential of the di-alkyl ether DME in comparison to MTBE. To address this concern we reviewed and evaluated the chemical properties of MTBE and DME with a focus on comparing transport and groundwater transport potential. The results of this analysis are provided in Table 5.1, which provides, for both DME and MTBE, a summary of basic chemical properties, the partition factors K_{ow} and K_{aw} , a soil half-life as a persistence measure, and the chemical mobility in soil as expressed by the so-called “soil penetration” depth (McKone and Bennett, 2003). K_{ow} is the dimensionless octanol-water partition coefficient and K_{aw} is the dimensionless form of the Henry’s law ratio, obtained by dividing the Henry’s law ratio by the universal gas constant and by absolute temperature. The soil half lives obtained from the cited EPA reports tend to be less reliable than other properties.

The DME half-life is obtained from the ChemSpider⁶ website providing results from the EPI Suite model version 4.11 and described in EPA *Robust Summary for Dimethyl Ether*⁷ and posted on an EPA website⁸. The EPA EPI Suite Level III fugacity model reports the persistence (half-life of DME) of DME in the range of 40 to 50 days. The soil half-life of MTBE has been reported as being at least ten times greater than the 50-day soil half life of benzene (EPA, 2008) but EPA (2008) reports that it can range from less than a year to several years. McKone and Bennett (2003) report an MTBE soil half life of 400 days and a benzene half life of 50 days.

Table 5.1. Selected Chemical and Contaminant Transport Properties of DME and MTBE.

Chemical Property	DME ¹	MTBE ¹
Boiling Point	24.8 °C	55.2 °C
Vapor Pressure	4450 mm Hg at 25°C	245 mm Hg at 25 °C
Water Solubility	35.3 g/L at 25 °C	51 g/L at 25 °C
Henry's law ratio	7.6 x 10-3 atm-m3/mol at 25 °C	5.87 x 10-4 atm-m3/mol at 25°C
K _{ow}	1.26	16.6
K _{aw}	0.316	0.0245
Soil half life	~ 50 d	~ 500 d
Soil penetration depth ²	~ 1 m	~ 2 m

¹ All properties other than soil penetration depth come from EPA Robust Summary for Dimethyl Ether.⁹

² Soil penetration depth reflects the likely distance that a chemical can be transported in soil before significant degradation.

Table 5.1. indicates that DME has some chemical properties similar to MTBE, but significant differences with regard to partition factors and soil persistence—properties that strongly impact subsurface transport. For example, at room temperature DME is a gas and MTBE is a liquid. But

⁶ Chemspider (2014) <http://www.chemspider.com/Chemical-Structure.7956.html?rid=6a03d8c6-dc90-4056-b759-0f50870c1ce5>.

⁷ US EPA (2000) Robust Summary for Dimethyl Ether
<http://www.epa.gov/hpv/pubs/summaries/dimeth/c12794rs.pdf>.

⁸ USEPA (2014) EPI Suite <http://www.epa.gov/opptintr/exposure/pubs/episuite.htm>.

⁹ US EPA (2000) Robust Summary for Dimethyl Ether
<http://www.epa.gov/hpv/pubs/summaries/dimeth/c12794rs.pdf>.

because of its greater partitioning into the gas phase of soils, DME is likely to be more mobile than MTBE, but DME will be a gas at ambient pressures and there are no plans for DME to be stored underground at this point. However the key metric of soil transport is mobility as reflected in the soil penetration depth and this is strongly dependent on soil half life.

McKone and Bennett (2003) developed and evaluated a novel approach for constructing soil transport algorithms for multimedia fate models. Their approach to soil transport accounts for diffusion in gas and liquid components; advection in gas, liquid, or solid phases; and multiple transformation processes. They also provided an explicit quantification of the characteristic soil penetration depth, which is a metric of mobility and transport potential--for example transport to groundwater. The penetration depth is the distance from a source required to see a drop in concentration by a factor of 3. In their first paper on this approach they demonstrate and evaluate the performance of the algorithms in a model with applications to benzene, benzo(a)pyrene, MTBE, TCDD, and tritium. Here we used the McKone and Bennett (2003) approach and the properties in Table 5.1. to compare the subsurface dispersion potential of DME and MTBE. In Table 5.1. the reported estimate of the DME characteristic penetration depth is 1 m, which is half of the estimated 2 m dispersion depth of MTBE. However these are both larger than the 0.3 m dispersion depth reported for benzene by McKone and Bennett (2003). In addition there are significant uncertainties contributing to these estimates. The soil penetration calculation is very sensitive to the value of soil half life, which is often difficult to measure and quantify. In contrast to MTBE, because of its high volatility, low water solubility, and relatively high K_{aw} , we do not expect significant amounts of DME to enter the soil from atmospheric concentrations (EPA, 2000; McKone and Bennett, 2003).

Additionally, DME will not be stored or distributed underground. Dispersion into soil is only an issue if there is a mechanism to deliver appreciable quantities of DME into the soil. If at some point in the future DME is planned to be stored or transported underground, then at that time, there will be a need to confirm the observation that DME is less dispersive than MTBE and thus less likely to penetrate to groundwater. If there is any potential for DME emissions to soil, the contaminant transport properties of DME should be further evaluated at that point. This testing may include experiments to assess the soil dispersion properties of DME and/or more detailed modeling assessments using multimedia transport models such as the Cal-EPA CalTOX model.

5.4. Summary of DME Transport and Fate Data

DME may enter the environment through leakage or spillage during production, transport, storage, and usage. The chemical properties of DME determine how it partitions in the atmosphere, soil, and water.

DME will exist primarily in the gas phase when it is released to the atmosphere. As a result, the main transport and removal mechanism of DME in the atmosphere will be dispersion. Direct photolysis of DME is not expected to be an important process. DME is not regarded as a greenhouse gas. Atmospheric dispersed DME decomposes to carbon dioxide and water via a

reaction with photochemically produced hydroxyl radicals during the day and during the night-time by nitrate radicals in the atmosphere. DME degradation in the atmosphere occurs by reaction with hydroxyl and nitrate radicals with estimated half-lives of 5.4 and 123 days, respectively.

DME is expected to quickly volatilize from water. Estimated half-lives in a model flowing river and model lake are 2.4 hours and 2.8 days, respectively. DME has a strong, unpleasant, slightly sweet smell, and residual taste and odor issues for DME in drinking water resources have not been tested. DME has a slow process of biodegradation in water. DME is not expected to hydrolyze, bioconcentrate in aquatic organisms, or directly photolyze when it is released to surface waters.

A DME release into surface waters during the use of watercraft is anticipated to be minimal since the near-term use of DME in marine diesel engines is not planned in California.

Because of its high volatility, a bulk DME release on to the soil surface would rapidly transition into the vapor phase. This rapid volatilization can occur so rapidly that explosive forces may be generated. Near by equipment or soil particulates may be displaced by these forces.

Due to rapid DME evaporation, it may be expected that a bulk release to the soil surface would result in localized, shallow, soil freezing rendering the soil impermeable to deeper transport until thawing occurs. DME is chemically inert and chemical interaction with soil particulates or organic materials coating the particulates is unlikely. DME is not expected to sorb to sediments or suspended particles in water, or to hydrolyze in groundwater. As a result, DME has a high potential for mobility in vadose zone soils and groundwater, but DME impact to the subsurface could be confined to the shallow subsurface environment unless DME is dissolved into groundwater that reaches the water table. If water spray is used to knock-down DME vapors, the transport of DME to subsurface waters is a remote possibility with minimal impact. Residual taste and odor issues for DME in drinking water resources have not been tested.

DME will be stored in above ground storage tanks and any associated pipes and valves will also be above ground. If this should change and there is any potential for DME emissions to soil, the contaminant transport properties of DME should be further evaluated at that point. This testing may include experiments to assess the soil dispersion properties of DME and/or more detailed modeling assessments using multimedia transport models.

EPA does not give a specific method for the sampling and analysis of DME. EPA Standard Methods to sample and detect VOC such as MTBE in air and water should be applicable to DME. As part of Tier II activities, confirmation of the applicability of these methods needs to be conducted. These methods can then be used to monitor air, surface, and subsurface water as pilot production processes are demonstrated.

6. Safety and Potential Release Scenarios for DME Fuels

6.1. Safety

Companies manufacturing, distributing and marketing DME as a fuel in California have to comply with all existing regional and federal environmental, health and safety laws, and regulations. These laws and regulations govern the production, handling, storage, transportation and end-use of DME.

All of Oberon Fuels facilities will be subject to OSHA's Process Safety Management (PSM) and EPA's Risk Management Plan (RMP). For plants located in California, California's Accidental Release Prevention (CalARP) regulations apply as well. These regulations will apply to facilities with over 10,000 lbs (approximately 1,800 gallons) of DME stored onsite. One of the main purposes of these regulations is to prevent release of regulated substances through the establishment of prevention programs such as mechanical integrity, emergency response, hot work permits, standard operating procedures, and employee training. Another requirement of the regulations is the completion of studies showing the impact of a large release of regulated substance on the immediate vicinity, and HAZOP (hazards and operability), which aims to assess and prevent potential release scenarios in the design phase of a plant.

Oberon Fuels' DME production facilities comply with OSHA's Process Safety Management, EPA's Risk Management Plan, and CalOSHA's California Accidental Release Prevention programs. All of these programs serve to reduce the risk of accidental release scenarios and protect workers. Appendix E summarizes the requirements of Process Safety Management Program.

In 2007, the *DME Handbook* was published by the Japan DME Forum (JDF). The *DME Handbook* included information regarding production, distribution, and use of DME. The *DME Handbook* also included the results of various tests in connection with safety. During 2001 to 2002, the High Pressure Gas Safety Institute of Japan, supported by the Japan Oil, Gas and Metals National Corporation, conducted DME basic research regarding the safety of DME, and the results are included in the *DME Handbook*. The results of additional research (March 2002 to March 2005) into the safety of DME fuel was also included in the Handbook and was supported by the Petroleum Distribution and Retail Division of the National Resources and Fuel Department of the Agency for natural Resources and Energy. These results of these investigations into the stability, fire and explosion potential of DME are summarized below along with other safety considerations.

6.1.1. Storage and Stability

6.1.1.1 Storage Procedures

DME is required to be stored in accordance with all current regulations and standards including U.S. OSHA 29 CFR 1910.101 regulations. DME should be stored outside or in a detached building avoiding flames, sparks and other sources of ignition. DME is incompatible with

combustible materials, halogens, oxidizing materials, and strong acids. See Appendix C, Safety Data Sheet for DME, and Appendix F, DME Materials Safety Data Sheet (MSDS) for additional regulatory and storage information.

DME is a volatile organic compound that is stable but is extremely flammable and may form potentially explosive mixtures with air (3.4~17%). Above ground storage tanks (ASTs) holding large quantities of DME are subject to local siting approval and generally should not be located near heavily populated areas. DME ASTs are subject to California Emergency Management Agency oversight and California Accidental Release Prevention Program (CalARP) guidelines (California Emergency Management Agency, 2005). A hazard assessment is required for DME ASTs over 10,000 gallons (See Appendix F for Oberon DME Hazard Assessment). Inspections are conducted every two years.

6.1.1.2 Formation of DME Hydrate

DME of 34 wt% or less and DME of 94 wt% or more can be dissolved in water under pressure. DME that dissolves in water easily generates a stabilized solid crystal hydrate (DME hydrate) under low temperature and high pressure. For example, if DME is released into snow during winter, DME hydrate may form. Further, there is a potential for the gaseous DME generated by melting the DME hydrate to be ignited by static electricity. The generation of the DME hydrate has the possibility of causing blockage problems in piping during the handling of DME.

6.1.1.3 Explosive Peroxides

It is important to prevent contact with oxygen and to interrupt the generation of peroxides in order to use DME safely. In general, ethers in contact with atmospheric oxygen for a long time can auto-oxidized and thereby generate peroxides. Peroxides are dangerous because they are essentially unstable and very sensitive to friction, heating and impact, resulting in explosion or fire.

In the case of DME, during research into alternatives to chlorofluorocarbon propellants, peroxide generation by the auto-oxidation of DME is reported to be extremely low compared with other ethers. The DuPont DME Product Safety Summary Sheet (Appendix C) indicates that DME will not form potentially explosive peroxides. The DME Material Safety Data Sheet indicates that hazardous decomposition products should not be produced under normal storage and use conditions (Appendix F).

It is likely that a variety of different materials will come in contact with and will be added to DME for various purposes when DME is consumed, produced, transported, and stored. The influence of those materials must be examined because of the possibility of peroxide formation during storage for lengthy periods of time.

6.1.1.1 Safety Issue for Open DME flames

There is a safety concern for any gas combustion about flame visibility. DME flames have three times the radiant emittance of methanol or ethanol flames, but only about half that of typical hydrocarbon flames. Combustion efficiency can be observed by noting the luminosity of the

flame produced. Less efficient fuel combustion produces soot (material that could have been further burned and produced more energy), resulting in a yellow flame, called a luminous flame. More efficient fuel combustion burns fuel to a greater extent and results in a blue flame and sometimes difficult to see flame, called a non-luminous flame.

The luminosity of the DME flame depends on the definition and application of the flame luminosity. Based on pressure and temperature of DME there may be different flame height, strength, color, luminous zone, or duration of luminous flame. Frye et al., 1999, using a burner, notes, “The appearance of the DME flame is noteworthy in that even at fuel-rich conditions, only a small, fuel-rich yellow inner cone was observed. Fuel-lean DME flames were pale blue and only moderately luminous.” Wattanavichien, 2009, observes that “... DME displays a visible blue flame, similar to natural gas, over a wide range of air/fuel ratios”. Brackmann et al., 2007, also have seen “a luminous blue disc located around 3 mm” from the burner nozzle in their experiments. McEnally et al., 2007, mentioned that the DME flame includes a blue outer part and a yellow cone inside the flame and that the flame luminosity depends on the temperature of the flame. Suzuki et al. (2012) mentioned that DME has strong luminosity zone in hot flames and weak luminosity for cool flames.

Kaiser et al., 2000, stated that very little luminosity is observed from the DME diffusion flame” and “when the volume flow of DME is increased to $335 \text{ cm}^3 \text{ min}^{-1}$, the DME flame produces visible luminosity.” Wakai et al., 1998, mentioned that “a non-luminous flame was observed in the ignition process of the DME spray”. Lee et al., 2011, working on DME/LPG blends, indicated that “When the DME fraction increased to 100 mole%, the color and the shape of the flame changed from thin, luminous, dark-blue to thick, non-luminous, pale-blue”.

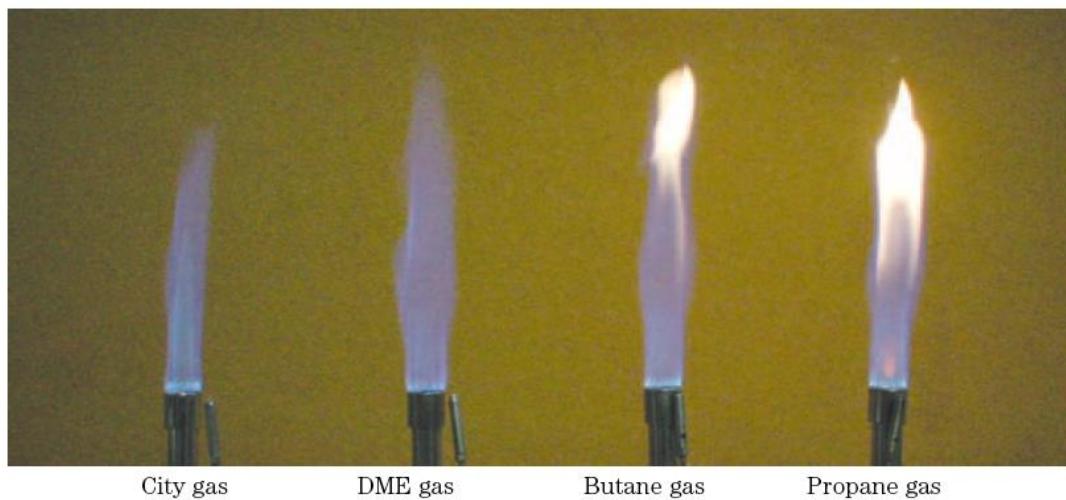


Figure 6.1. Flame tests of DME for comparison to LPG constituents (Japan DME Forum, 2007).

Bunsen burner flame tests (which supply close to theoretical oxygen demand) were conducted on city gas, DME, pure butane and pure propane by the Japan DME Forum (Japan DME Forum,

2007). They showed that DME and city gas burned with non-luminous flames while propane and butane burned with luminous flames (Figure 1.3.). Yellow tipped flames from pure butane and pure propane are a result of sulfur compounds leading to soot formation. The blue flame from pure DME indicates no soot formation. SO_x emissions form particulate matter in the air, degrade air quality, and contribute to acid rain. Pure DME contains no sulfur compounds. Thus it is a cleaner burning fuel that generates no SO_x emissions in the exhaust gas. Because DME burns efficiently and generates no SO_x, exhaust gases are free of particulate matter and sooty smoke.

The concern about DME flame visibility may be alleviated by additives needed for increasing lubricity. When a lubricant is added to increase DME's low lubricity, "a rather strong luminous flame might be detected." (*DME Handbook* pg. 255). The question here is, what level of luminosity is needed to meet safety guidelines and what kind and level of additive is needed to achieve this goal?

Since DME can burn with a non- or low- luminosity in open flames, open flames should be approached with caution. The use of an additive to make the DME flame more visible may be needed.

6.1.2. DME Potential Fire and Explosion Hazards

Because the relative gas density of DME is heavier than air (1.59), vapors may collect in low lying areas such as ditches, sewers, basements, and can ignite at distances far from the source and flash back (Department of Transportation [DOT], 2000). The safety measures currently in place for propane are also applicable to DME.

Handling conditions present risks across the various possibilities for heat exposure, shock, static electricity generation, contamination, decomposition due to contamination, oxide generation, the deterioration of material such as containers due to environmental influences. It is therefore essential to be aware of potential hazards and to take the appropriate safety measures. (Japan DME Forum, 2007).

Dimethyl ether is handled as a liquefied gas, it can leak as either a gas or a liquid. DME vapors are heavier than air. Vapors or gases may ignite at distant ignition sources and flash back. Vapor/air mixtures are explosive. Containers may rupture or explode if exposed to heat. Electrostatic discharges may be generated by flow or agitation resulting in ignition or explosion (Appendix C: Safety Data Sheet for DME). DME has a broad explosion limit of 3.4~27 vol%, compared to propane (2.2~9.5 vol%) and butane (1.9~8.5 vol%) (Japan DME Forum, 2007). Further, Bulk DME spilled onto the ground or water surface can result in explosive volatilization (Japan DME Forum, 2007). All means of ignition should be eliminated where DME is produced or used. Enclosed areas into which it may disseminate by accident should be provided with exhaust ventilation (International Labour Office, 1971). A fine water spray can be used to knockdown DME vapors (Association of American Railroads, 2005; Appendix C – DME Safety Data Sheet).

6.1.3. Fire Suppression Technology

Since DME is soluble in water, a DME fire can effectively be extinguished with water. In large scale DME production facilities, water cannons are used as a primary fire fighting device. Both CO₂ and nitrogen are effective fire suppression technologies for DME, but the concentrations required for flame suppression are higher than for propane or natural gas fire suppression (Japan DME Forum, 2007).

6.1.4. Confined Spaces and Respiratory Protection

DME is heavier than air and may be retained in confined spaces. Additionally, DME is a mild anesthetic which depresses the central nervous system. Fire fighters should use self contained breathing apparatus to protect against possible exposure. In confined spaces where DME vapors are mixed with air, the explosion intensity for DME was found to be greater than LPG. Further, experiments indicated that DME has a greater tendency for transition to detonation than propane (Japan DME Forum, 2007).

Experimental results in the *DME Handbook* included a test where a container containing liquid DME that was heated to the point where the container failed, and the DME was released and ignited. Compared to LPG, the DME fireball was much smaller. The combustion velocity of DME is thought to be about 1/3 of that of LP gas based on the above result. It was proposed that the reason the combustion velocity of DME was slower, was because the contribution of the radiant energy from the DME flame is low, as DME has a non-luminous flame.

6.1.5. Leak Detection Technology

In general, hydrocarbon leak detectors that are sensitive to LPG (propane) will detect DME as well, but may need to be adjusted to a lower alarm point due to the differences between the LEL for DME and propane.

6.1.6. Fire Protection Management of DME

At this point DME is not specifically listed in the National Fire Protection Association's (NFPA) Codes and Standards. However, after discussion with the NFPA in July and November of 2014, it is clear that DME is already regulated in the Compressed Gas Code Section, NFPA 55 by its properties as a compressed liquified gas. Oberon Fuels has engaged the NFPA 55 Technical Committee and a task force was created to determine if a Temporary Interim Amendment that would amend NFPA 55 to specifically incorporate DME into the code and borrow provisions from NFPA 58 *Liquified Petroleum Gas Code's* Chapter 5: *LP-Gas Equipment and Appliances* and Chapter 6: *Installation of LP Gas Systems*.

Oberon Fuels asked the NFPA 55 committee to consider a Temporary Interim Amendment to specifically include DME in NFPA 55, for the following reasons:

- Public Safety: A more detailed code will leave little to interpretation. Resulting in fewer accidents, provide easily enforceable requirements for fire inspectors, and offer clear requirements for fire safety consultants.
- Uniform Standard: Adoption of a well-developed, code that includes design elements, will allow fuel consumers, fuel dispensers, maintenance shops, and regulatory bodies to provide a safer, more uniform rollout of a new fuel.
- DME Will Soon Be Used in Demonstrations: Oberon Fuels has partnered with Volvo and Safeway Grocers to accept a grant from the San Joaquin Valley Air Pollution Control District to test two DME trucks powered by Oberon DME. It is important that both consumers and Fire Marshalls are familiar with the protocols of handling DME prior to commercial adoption of DME. Our demonstration partners have already inquired about the standards they should be using when installing a fueling system at their sites.

6.1.7. Dispenser and Fueling System Certification

In order for a DME dispenser to be commercially sold in the United States, it must be certified by the National Conference of Weights and Measures (NCWM) and listed by an independent laboratory such as UL or ETL. NCWM is the only recognized entity in the United States that can both certify and validate a dispenser, through the National Type Evaluation Program (NTEP) certification process. It certifies that a dispenser is providing acceptable accuracy to the purchaser of the fuel. After certification, a dispenser must be tested periodically throughout the life of the equipment in service.

Additionally, in recent years the LPG Autogas industry has been increasingly requiring that the entire fuel dispenser assembly be listed by UL/ETL or other recognized laboratory, to validate that it is safe for installation and use. Listing a DME dispenser on the UL or ETL is proof that the item has been independently tested and meets applicable standards.

Parafour Innovations, a company providing innovative technologies to the growing alternative fuels market, worked with (i) the NCWM to obtain certification of its dispenser and (ii) ETL to list the DME dispensing product by an independent laboratory. On July 2, 2014, NTEP issued a Certificate of Conformance for Weighing and Measuring Devices (Certificate No. 13-041A2) for a Retail Motor Fuel Dispenser for dispensing DME as a vehicle fuel or for transportable cylinder refueling. In September of 2014, a DME dispenser was ETL listed to UL495 / 1238 / and 1203.

6.1.8. Environmental Sampling and Analysis

DME can be detected in air, soils, and water using routine US EPA sampling and analysis methods. Because of its wide spread and high volume use, it is not unexpected that DME has been detected in drinking water, food, air, municipal waste water, and breast milk¹⁰. Routine

¹⁰ US National library of Medicine: TOXNET, Hazardous Substances Data Bank, accessed November 2013.
<http://toxnet.nlm.nih.gov/cgi-bin/sis/search/r?dbs+hsdb:@term+@rn+@rel+115-10-6>.

analysis of air resources and ground and surface drinking water resources do not generally include DME as an analyte of interest. As DME becomes more widely used as a transportation fuel, it is possible that DME will become more widely distributed into the environment, including air and water resources. It may be prudent to include DME as one of the analytes of interest in the future.

6.2. DME Potential Release Scenarios

DME is chemically inert and stable in weakly acidic, neutral, and weakly basic solution. When DME gas is released into the atmosphere it decomposes to carbon dioxide and water through a photochemical reaction with hydroxy and nitrate radicals. During production, DME fuel can leak from containers and be released into the atmosphere or permeate into water or soil. DME has a low boiling point (-25.1°C), meaning that if a spill occurs over soil DME will off-gas, causing the water in the soil to freeze and reducing the rate of DME permeation through the soil. In the event of an extremely large DME spill (1,500 m³), the low gas diffusion coefficient (0.11cm²/s) would keep atmospheric DME concentrations below concentrations that cause anesthetizing effects (8-12%).

Where DME is used as fuel on a large scale, a hazard assessment is required. General fire safety considerations for DME will mirror those for propane, and thus fire safety protocols that apply to propane-fueled vehicles will apply to DME-fueled vehicles. An excellent source of guidance is the US DOT document on the application of LPG in transit vehicles (Raj, et al., 1996). This document adapts the safety guidance from NFPA 58, which applies to the storage and handling of liquefied petroleum gases, and outlines the minimum requirements that LPG facilities and vehicles must meet to ensure safety. The same standards should apply to DME facilities and vehicles, accounting for the uniqueness of DME and the differences that exist between DME and propane with regard to flammability and explosion limits.

Appendix G provides a DME hazard assessment for a DME production and distribution facility located in a rural area of California. The hazard assessment includes a compliance matrix that identifies all applicable California and Federal regulations that must be met for a variety of release scenarios. The hazards assessment includes consideration of potential public receptors that may be affected by a worst-case release scenario as well as alternative release scenarios that may be more likely than the worst case scenario.

6.2.1. Ruptured High Capacity Tank: DME Vapors Ignited in Unconfined Space

The hazard release assessment detailed in Appendix G assumes a massive release of two 30,000 gallon storage tanks into an unconfined space in a rural setting which is then ignited. The radius of the explosive over pressure sufficient to break windows (1 psi overpressure) was estimated to about 0.5 miles from the release. In the rural setting for the release, no human population was affected.

6.2.2. Alternative Release Scenario: Leaking Pipe With Vapor Explosion.

The criteria for the alternative release scenario is that:

- The alternative scenario should be more likely to occur than the worst case scenario; and
- The alternative scenario should reach an endpoint offsite.

The radius of the Lower Flammable Limit (64 mg/L) was estimated to about 0.1 miles from the release. In the rural setting for the release, no human population was affected.

6.3. DME Safety Summary and Data Gaps

DME is required to be stored in accordance with all current regulations and standards. Above ground storage tanks (ASTs) holding large quantities of DME are subject to local siting approval and generally should not be located near heavily populated areas. DME is a volatile organic compound that is stable but is extremely flammable and may form potentially explosive mixtures with air. Because the relative gas density of DME is heavier than air, vapors may collect in low lying areas such as ditches, sewers, basements, and can ignite at distances far from the source and flash back.

Unodorized DME has a strong, unpleasant, slightly sweet smell. There remains a need to explore consideration of whether there would be benefit to have DME possess an odor that is readily detectable but unique from natural gas and propane odorants.

Researchers have described the DME flame as nonluminous in cool flames, moderately luminous pale blue with low brightness, or luminous dark-blue in hotter flames. However, when a lubricant is added to improve lubricity, a rather strong, luminous flame might be detected. A flame that is not readily visible poses a safety problem for DME production plant workers, fire-fighters and first responders if an ignited leak occurs. During the evaluation of the luminosity of DME flames, a key issue will be what level of luminosity is required.

DME can be detected in air, soils, and water using routine US EPA sampling and analysis methods. As DME becomes more widely used as a transportation fuel, it is possible that DME will be come more widely distributed into the environment, including air and water resources. It may be prudent to include DME as one of the analytes of interest in the future.

7. Dimethyl Ether Toxicity

7.1. Introduction

Here, we consider the toxic hazards associated with potential exposures of both humans and ecosystems to dimethyl ether. The focus is on both acute and chronic effects. The toxicity assessment addresses “hazard” as the possibility of harm rather than “risk” as the probability of harm. So the review below does not forecast the expected harm associated with DME use, but reports the potential for harm derived primarily from laboratory studies with animals exposed at relatively high levels. The review begins with a summary of the dialkyl ethers as a chemical group and what has been observed with regard to the potential harm for this family of chemicals. We then look specifically at Dimethyl ether (DME) and systematically review what has been reported regarding acute and chronic harm. DME is a colorless, highly volatile and flammable liquid with narcotic properties but with a rather low order of toxicity on both an acute and chronic basis (Dupont-EPA, 2000; EFSA, 2009; DuPont, 2011).

7.2. Dialkyl Ethers

DME is one of a group of dialkyl ethers that are and have been used widely as solvents and at times as fuels and anesthetics (Sigma-Aldrich, 2012a; 2012b; 2013). The lower carbon-number members of this group have been used more extensively and thus have more available toxicity data—including DME, diethyl ether (DEE), dipropyl ether (DPE) and dibutyl ether (DBE). They are primarily associated with narcotic effects at high doses but with little reported data on chronic health effects at lower long-term exposures and no evidence yet reported on carcinogenicity, teratogenicity, or reproductive harm.

7.2.1. Diethyl Ether (DEE)

DEE is quite volatile and can cause acute harm at high doses but has few reported health effects from chronic, low level exposures (Sigma-Aldrich, 2012a). If inhaled, DEE can cause respiratory tract irritation, drowsiness and dizziness and, if ingested or absorbed through skin, can cause potentially harmful narcotic effects. DEE also causes skin and eye irritation on contact. The DEE oral LD₅₀ in rats is 1,215 mg/kg, and the 30-min. inhalation LC₅₀ is 31,000 ppm (Sigma-Aldrich, 2012a). With regard to chronic effects, there is no reported evidence of carcinogenicity, reproductive toxicity, or teratogenicity for DEE (Sigma-Aldrich, 2012a).

7.2.2. Dipropyl Ether (DPE)

DPE is a volatile liquid and can cause acute harm at high doses but has few reported health effects from chronic, low level exposures (Sigma-Aldrich, 2012b). If inhaled, DPE can cause respiratory tract irritation, drowsiness and dizziness and, if ingested or absorbed through skin, can cause potentially harmful narcotic effects. It works as an anesthetic. DPE also causes skin and eye irritation on contact. There is no reported oral LD₅₀ for DPE and the 15-hr. inhalation LC₅₀ is 163,000 mg/m³ (Sigma-Aldrich, 2012b). With regard to chronic effects, there is no

reported evidence of carcinogenicity, reproductive toxicity, or teratogenicity for DPE (Sigma-Adrich, 2012b).

7.2.3. Dibutyl Ether (DBE)

DBE is a liquid at room temperature and, similar to other dialkyl ethers, can cause acute harm at high doses but has few reported health effects from chronic, low level exposures (Sigma-Adrich, 2013). If inhaled, DBE can cause respiratory tract irritation and it is reported to be harmful if ingested but there is no report of narcotic or anesthetic effects (Sigma-Aldrich, 2013). DBE also causes skin and eye irritation on contact. The DBE oral LD₅₀ in rats is 7,400 mg/kg, and the 15-hr. inhalation LC₅₀ is 169,000 mg/m³ (Sigma-Adrich, 2013). With regard to chronic effects, there is no reported evidence of carcinogenicity, reproductive toxicity, or teratogenicity for DBE (Sigma-Adrich, 2013).

7.3. Human and Ecological Health Impacts of DME

The current literature provides sufficient information to assess the potential impacts of DME to human and ecological receptors. Since the 1970's when DME began to be used practically as a fluorocarbon substitute, there have been many studies and investigations into the safety of DME, such as its influence on the human body by leakage or use and its influence on the atmosphere by exposure etc. from manufacturing, transportation, storage, filling of small containers such as cans, circulation, and consumption. Key references for the discussion provided in this section include (a) the "Robust Summary for Dimethyl Ether" as a high-production-volume (HPV) chemical prepared by the Dupont company for the US EPA as part of the HPV challenge program and available on the EPA website (Dupont-EPA, 2000); (b) a scientific opinion on the "safe in use of dimethyl ether as an extraction solvent" prepared by the European Food Safety Authority (EFSA, 2009); and (c) the Dupont Toxicity Summary for Dimethyl Ether (DME); Dymel A Propellant (DuPont, 2011). Table 7.1, which is reproduced from the "Robust Summary" report (Dupont-EPA, 2000), provides an overview of the key DME toxicity questions that have been addressed. See Appendix C for the DME Safety Data Sheet and Appendix E for the Materials Safety Data Sheet.

DME is a volatile organic compound, but to date has not been identified as carcinogenic, teratogenic, or mutagenic, and exhibits extremely low toxicity potential for a broad range of health endpoints (Semelsberger et al, 2006). The main physiological action of DME is that of "weak anesthesia" when inhaled at high levels. Its 4-hour LC₅₀ for rats is 164,000 ppm (DuPont, 2011). Barceloux (2012) notes that during the early years of 1920s, adequate anesthesia was obtained in cats using 65% DME, and deep anesthesia with respiratory arrest was the result of using 85% DME. This discovery indicated that DME has some undesirable features including "a feeling of suffocation during induction", "excessive salivation", and "persistent muscle activity during anesthesia". In 1925, the effect of 20% DME administration as an anesthesia in humans was reported (Barceloux, 2012). DME can also, in gross misuse situations, sensitize the heart to the body's own adrenaline. Cardiac sensitization has been observed only at inhaled

concentrations of 200,000 ppm and higher. In pharmacokinetic investigations for animals and humans, DME has shown no evidence of accumulation in tissues and appears to have a very short biological half-life (DuPont, 2011).

Because DME was developed as an aerosol propellant that can contact the human body directly, the safety of DME has been evaluated in detail. Unlike diethyl ether, which is a very similar ether, the narcotic properties of DME are weak and similar to those of LP gas used as an aerosol propellant. External changes do not occur to the human body with a high-density exposure such as 7.5 vol%, although mild throat irritation occurs. However, skin contact with the liquid may cause freezing of the skin. Eye contact with the vapor may produce mild irritation of the eyes.

In the subsections below, we provide key findings regarding acute and chronic toxicity in mammals, genotoxicity, reproductive and developmental toxicity, air quality issues, and aquatic toxicity.

Dimethyl Ether CAS No. 115-10-6	Data Available	Data Acceptable	Testing Required
Study	Y/N	Y/N	Y/N
Physical/Chemical Characteristics			
Melting Point	Y	Y	N
Boiling Point	Y	Y	N
Vapor Pressure	Y	Y	N
Partition Coefficient	Y	Y	N
Water Solubility	Y	Y	N
ENVIRONMENTAL FATE			
Photodegradation	Y	Y	N
Stability in Water	Y	Y	N
Transport (Fugacity)	Y	Y	N
Biodegradation	Y	Y	N
ECOTOXICITY			
Acute Toxicity to Fish	Y	Y	N
Acute Toxicity to Invertebrates	Y	Y	N
Acute Toxicity to Aquatic Plants	Y	Y	N
MAMMALIAN TOXICITY			
Acute Toxicity	Y	Y	N
Repeated Dose Toxicity	Y	Y	N
Developmental Toxicity	Y	Y	N
Reproductive Toxicity	Y	Y	N
Genetic Toxicity Gene Mutations	Y	Y	N
Genetic Toxicity Chromosomal Aberrations	Y	Y	N

Table 7.1. Summary of DME data availability, acceptability, and required testing.

Acute Toxicity

7.4. Acute Toxicity

DME has been studied for acute toxicity primarily for inhalation exposures and found to be of low toxicity (Dupont-EPA, 2000; EFSA, 2009; DuPont, 2011). The EFSA (2009) has concluded there is also sufficient evidence to conclude low toxicity by ingestion. The Dupont-EPA (2000) report observes that there is limited data so far but no suggestion of dermal toxicity beyond skin sensitization. Following inhalation in mammals, DME is rapidly taken up and distributed in various tissues and organs. It is reported that upon exposure in rats to an atmosphere with 1000 ppm (equivalent to 1884 mg/m³) dimethyl ether levels of 14 to 22 mg/kg have been found in different organs and tissues. Organ distribution appears to be proportional with atmosphere concentrations in the range of 750 to 2000 ppm (equivalent to a concentration in atmosphere of 1413 and 3768 mg/m³) (EFSA, 2009).

In a key study summarized in the Dupont-EPA (2000) report, male rats were exposed to dimethyl ether gas via inhalation (whole-body) at concentrations of 84,000, 121,000, 152,000, 169,000 and 205,000 ppm (~158, 228, 286, 318 and 385 mg/L) for 4 hours. Mortality was 0/10, 3/10, 2/10, 7/10 and 7/10 in the 84,000, 121,000, 152,000, 169,000 and 205,000 ppm groups, respectively. All but one death (205,000 ppm) occurred during the exposure. Clinical signs included ataxia (\geq 84,000 ppm), unresponsiveness to noise (\geq 121,000 ppm), anesthesia (\geq 84,000 ppm), paw waving (84,000 ppm), roving eyeballs (84,000 ppm) and coma (\geq 121,000 ppm). The survivors rapidly awoke following cessation of exposure and showed transient weight loss for 1 – 2 days and sporadic lung noise. As a result of this study the LC50 was determined to be 308 mg/L or the equivalent of 308 g/m³ (air).

7.5. Chronic Toxicity and Carcinogenicity

In a lifetime inhalation toxicity and carcinogenicity bioassay carried out at DuPont's Haskell Laboratory, DME produced slight hemolytic (blood) effects at 25,000 ppm (2.5% DME) and was negative for carcinogenicity (Dupont-EPA, 2000; DuPont, 2011). In this study, the no-observable-adverse-effect-level (NOAEL) for this life-time inhalation study was 2000 ppm (0.2% DME) and was based on an increase in body weight and decrease in survival in male rats exposed at 10,000 and 25,000 ppm, and on the blood effects seen at the 25,000 ppm exposure level. Details of this study with regard to carcinogenicity is detailed below (Dupont-EPA, 2000).

In a 2-year combined chronic toxicity/carcinogenicity study, Sprague-Dawley rats (100/sex/concentration) were exposed whole-body to dimethyl ether vapor at 0, 2000, 10,000 or 25,000 ppm (~ 3.8, 18.8 or 47.0 mg/L) for 6 hours/day, 5 days/week. In female rats, the overall incidence of clinically observable masses, primarily ventral (axillary, inguinal and perineal), was higher in all exposure groups than in the control group. A statistically significant increase (37%, p < 0.05) in the incidence of mammary tumors (benign or malignant) was observed in female rats at 25,000 ppm. However, the incidence of this type of tumor in the control rats of this study (27%) was lower than the historically observed in controls in this laboratory (53%). Therefore, the study authors did not consider the increase in tumor incidence treatment-related. No other

neoplastic lesions were observed that could be attributable to dimethyl ether exposure. Dimethyl ether did not increase the incidence of tumors in a 2-year inhalation toxicity/carcinogenicity study.

7.6. Genotoxicity

Based on a number of *in-vitro* studies, DME has not shown genotoxicity potential (Dupont-EPA, 2000; DuPont, 2011). Two *in-vitro* studies are significant with regard to this finding.

In a mutation study reported by Dupont-EPA (2000), there were two independent bacterial reverse mutation assays, *Salmonella typhimurium* strains TA97a, TA98, TA100 and TA1535 and *Escherichia coli* WP2uvrA (pKM101) exposed to dimethyl ether in gas chambers at 0, 20, 30, 40, 50 and 75% in the presence and absence of metabolic activation. No evidence of mutagenicity was observed in trial 1, although treatment-related toxicity was observed in all tester strains except TA100 and TA1535 in the absence of metabolic activation. In trial 2, treatment-related toxicity was seen in all tester strains with or without metabolic activation. No mutagenicity was observed except an equivocal response in the *S. typhimurium* strain TA98 in the presence of metabolic activation. A third trial was conducted to confirm the results of the second trial using *S. typhimurium* strain TA98 with metabolic activation system at concentrations of 0, 45, 55 and 65%. Dimethyl ether was negative for mutagenicity with evidence of toxicity at the high concentration, confirming that dimethyl ether is not mutagenic. All positive controls gave appropriate responses in all three trials. Dimethyl ether was not mutagenic in these assays.

In a chromosome aberration study also reported by Dupont-EPA (2000), two assay protocols, with human lymphocytes were exposed to dimethyl ether as follows: Assay 1 – 0, 35, 50 and 70% dimethyl ether for 3 hours with and without metabolic activation and 16 hours of recovery; Assay 2 – 0, 35, 50 and 70% dimethyl ether for 3 hours with metabolic activation and 16 hours of recovery and 0, 20, 35 and 50% dimethyl ether for 19 hours without metabolic activation. The negative and positive controls gave the appropriate responses. DME did not cause an increase in the proportion of aberrant cells either in the presence or absence of metabolic activation. However, an increase in the proportion of polyploid cells was noted at the highest dose in the presence and absence of metabolic activation. Dimethyl ether did not induce chromosomal aberrations in these assays.

7.7. Reproductive and Developmental Toxicity

Two reproductive and developmental inhalation toxicity studies reported with dimethyl ether have shown no compound-related effects at relatively high doses with one study establishing a no-effect level of 1,250 ppm (equivalent to 2,355 mg/m³). Assuming that the rat body weight is 0.25 kg, that rats have a breathing rate of 240 ml/min and an inhalation absorption efficiency of 75 % for an exposure duration is six h/day, the daily internal exposure to dimethyl ether arising

from the lowest no-effect level identified in the embryo-fetal inhalation toxicity study in rats (2355 mg/m³) can be estimated to be approximately 630 mg/kg bw/day (ESFA, 2009).

7.7.1. Reproductive Toxicity

In a reproductive-toxicity study summarized in Dupont-EPA (2000), evaluations of reproductive organs reported in a 2-year combined chronic toxicity/carcinogenicity study were used to address the reproductive endpoints for the purposes of the HPV Challenge Program. In the 2-year combined chronic toxicity/carcinogenicity study, Sprague-Dawley rats (100/sex/concentration) were exposed whole-body to dimethyl ether vapor at 0, 2000, 10,000, or 25,000 ppm (~ 3.8, 18.8 or 47.0 mg/L) for 6 hours/day, 5 days/week. No treatment-related effects on the reproductive organs of either male or female rats were observed. Although a statistically significant increase (37%, p < 0.05) in the incidence of mammary tumors (benign or malignant) was observed in female rats in the 25,000 ppm dimethyl ether group, the incidence was not considered to be treatment-related because the incidence of this tumor in the control group was uncharacteristically low (27%) when compared to the historical control data (53%) at the same laboratory.

7.7.2. Developmental Toxicity

In a developmental-toxicity study summarized in Dupont-EPA (2000), Pregnant Sprague-Dawley rats (27/concentration) were exposed via inhalation to 0, 1250, 5000 or 20,000 ppm dimethyl ether (~ 0, 2.35, 9.40 or 37.6 mg/L/day) for 6 hours/day on days 6 to 15 of gestation. At 20,000 ppm, decreased fetal body weight and increased incidences of several skeletal variations were observed. One malformed fetus with an umbilical hernia was also seen at 20,000 ppm. At 5000 ppm, a treatment-related increase of extra ossification centers in the lumbar area was seen. No maternal toxicity was seen. Although body, liver and uterine weights of dams were measured and dams examined for gross pathological changes, the observed effects were not provided in the robust summary. The NOAEL (developmental toxicity) is ~ 2.35 mg/L/day and LOAEL (developmental toxicity) ~ 9.40 mg/L/day.

7.8. Toxic Air Pollutants and Human Health

Fossil fuel combustion for transportation has been associated with a number of criteria pollutants such as NO_x, SO_x, ozone, CO, particulate matter (PM) and hydrocarbon (HC) emissions that lead to secondary PM and some hazardous air pollutants such as benzene, aldehydes, and polycyclic aromatic hydrocarbons. The PM and HC emissions from diesel fuel combustion are suspected of causing cancer and other life threatening illnesses in exposed populations. The State of California and the U.S. EPA have identified diesel PM as a toxic compound.

In addition to leaks and spills of DME from production and transportation, the combustion of DME in vehicles gives rise to emissions of combustion products. As a diesel substitute, DME combustion emissions during use phase must be assessed in terms of their emissions of criteria, air pollutants, and hazardous air pollutants.

When released to the atmosphere, DME is a photochemical oxidant and has a low ozone-forming potential (Paas, 1997). DME is not on the South Coast Air District toxic screening list (Rule 1401). However, under Rule 102 DME is not listed as an exempt VOC. In Rule 102, there is a list of Ozone Depleting Compounds (referencing the EPA's 40 CFR, Part 82, Appendix A, Subpart A), and DME is not listed as an Ozone Depleting Compound. A recent Oak Ridge National Laboratory (Szybist et al., 2014) found that the PM emissions for DME were sufficiently low enough that they do not approach the detection limit, and were a minimum of an order of magnitude below the 2010 U.S. emission standard without the use of a diesel particulate filter.

7.9. Aquatic Toxicity

There are three studies reported in the Dupont-EPA HPV study (2000) that provide useful insight on the aquatic toxicity of DME. Here again, there is evidence that impacts occur only at high concentrations—those above 100 mg/L, which are concentrations that are unlikely to occur in water bodies impacted by either normal or off-normal releases of DME.

7.9.1. Acute Toxicity to Fish

Guppies (*Poecilia reticulata*; 7/concentration) were exposed to dimethyl ether at nominal concentrations of 1900 and 3200 mg/L in sealed flasks for 96 hours under semi-static conditions. Renewal of test solutions occurred after 48 hours. No mortality was seen. The measured concentration varied with time and renewal. Due to uncertainties about this study (unreliable measured concentration with high volatility of dimethyl ether), a 96-hour LC₅₀ for fish, estimated by ECOSAR (version 1.00), was used to support evaluation of the acute toxicity of this chemical. 96-h LC₅₀ > 4000 mg/L 96-h LC₅₀ = 1800 mg/L (estimated).

7.9.2. Acute Toxicity to Aquatic Invertebrates

Daphnia magna (6-7/concentration) were exposed to dimethyl ether at nominal concentrations of either 1000 or 3200 mg/L for 48 hours in sealed flasks in two replicates. The measured concentrations varied with time. All animals survived. Due to uncertainties about this study (unreliable measured concentration with high volatility of dimethyl ether), a 48-hour EC₅₀ for daphnid, estimated by ECOSAR (version 1.00), was used to support evaluation of the acute toxicity of this chemical. 48-h LC₅₀ > 4000 mg/L 48-h EC₅₀ = 760 mg/L (estimated).

7.9.3. Toxicity to Aquatic Plants

Because a standard acute toxicity test for algae is not available for dimethyl ether, a 96-hour EC₅₀ for green algae, estimated by ECOSAR (version 1.00), has been used to evaluate the acute toxicity of DME. The submitter supported the estimated data with a measured EC₅₀ value of 1000 mg/L for a structurally similar chemical, diethyleneglycol monobutyl ether (CASRN 112-34-5), using the green algae, *Scenedesmus quadricauda*. 96-hr EC₅₀ = 150 mg/L (estimated). These results suggest that the acute toxicity of dimethyl ether to fish, aquatic invertebrates and aquatic plants is low.

7.10. DME Toxicity Summary and Data Gaps

DME has low toxicity on both an acute and chronic basis. DuPont has established a 1,000 ppm Acceptable Exposure Limit (AEL) for its workplace environment (DuPont, 2011). The main physiological action of DME is that of “weak anesthesia” at high inhalation levels. Its 4-hour LC50 for rats is 164,000 ppm (DuPont, 2011). DME can also, in gross misuse situations, sensitize the heart to the body’s own adrenaline, similar to the action mental screening studies using dogs and simulating stress with a large injected dose of adrenaline, cardiac sensitization was observed only at inhaled concentrations of 200,000 ppm and higher (DuPont, 2011).

DME did not induce chromosomal aberrations in genotoxic assays. At high inhalation exposures (20,000 ppm), decreased fetal body weight and increased incidences of several skeletal variations were observed. At similar inhalation exposure concentrations, no treatment-related effects on the reproductive organs of either male or female rats were observed. As an ether, DME has relatively low general toxicity. The aquatic toxicity of DME to fish, aquatic invertebrates, and aquatic plants is low.

In addition to DME leaks and spills from production and transportation, the combustion of DME in vehicles gives rise to emissions of combustion products. Fossil fuel combustion for transportation has been associated with a number of criteria pollutants such as greenhouse gases (GHGs), NOx, SOx, ozone, CO, volatile organic compounds (VOCs), particulate matter (PM); hydrocarbon (HC) emissions that lead to secondary PM and some toxic air contaminants (TACs) such as benzene, formaldehydes, and polycyclic aromatic hydrocarbons.

The CEC WTW analysis indicated that, WTW emissions of hazardous air pollutants from natural-gas-derived DME are significantly lower than ULSD, but there are concerns about higher levels of formaldehyde from non-ASTM standard DME use compared to ULSD. Similar to LPG, the CEC WTW modeling showed that DME fuel derived from natural gas could have VOC emissions higher than ULSD, but these VOC emissions can be controlled (CEC, 2007). These preliminary WTW estimates need confirmation using engines designed and optimized for DME combustion.

8. Dimethyl Ether Life-cycle Impacts

8.1. Life-cycle Assessment

The purpose of a life-cycle assessment (LCA), applied to a new fuel such as DME, is to compare over the entire DME life-cycle, the environmental flow of resources and pollutants (to and from the environment) associated with DME relative to a baseline fuel such as California diesel and/or other renewable diesel fuels. The flows of resources and pollutants provide framework for assessing human-health, environmental-systems, and resource impacts. LCA addresses a broad range of requirements and impacts for technologies, industrial processes and products in order to determine their propensity to consume natural resources or generate pollution. The term “life-cycle” refers to the need to include all stages of a process—raw material extraction, manufacturing, distribution, use, and disposal including all intervening transportation steps—so as to provide a balanced and objective assessment of alternatives. A comprehensive LCA for a transportation fuel must address cumulative impacts to human health and the environment from all stages, impacts from alternative materials, and impacts from obtaining feedstocks and raw materials. Figure 8.1 illustrates the DME life-cycle.

An important advantage of DME is that it can be produced from both fossil and renewable feedstocks. A European Commision (Edwards, et al., 2013) report found that DME produced from natural gas or biomass resulted in lower energy use and greenhouse gases when compared to other gas-to-liquid or biomass-to-liquid fuels. The report also concluded that DME as an automotive fuel would require modified vehicles and infrastructure similar to LPG.

For the purpose of this report, the results of a preliminary life-cycle analysis of emissions for BioDME, DME produced from unscrubbed (60% methane) HSAD (High Solid Anaerobic Digestion) of foodscraps and yard waste are presented. BioDME and DME are the exact same product chemically, the only difference is the methane-based feedstock used. BioDME is produced from biogas (gas from an anaerobic digester), while DME is produced from pipeline natural gas.

We have compared the life-cycle of the Oberon BioDME process with large scale natural gas derived DME (NG DME) production (a default in CAGREET that assumes 70% efficiency) and California ULSD (CAGREET Default).

The life-cycle of DME and/or diesel includes the following stages:

- Feedstock production,
- Transportation of feedstock to refineries,
- Fuel production--refining the final product blend,
- Transportation, storage and distribution of fuel, and
- End-use of the fuel product--combustion.

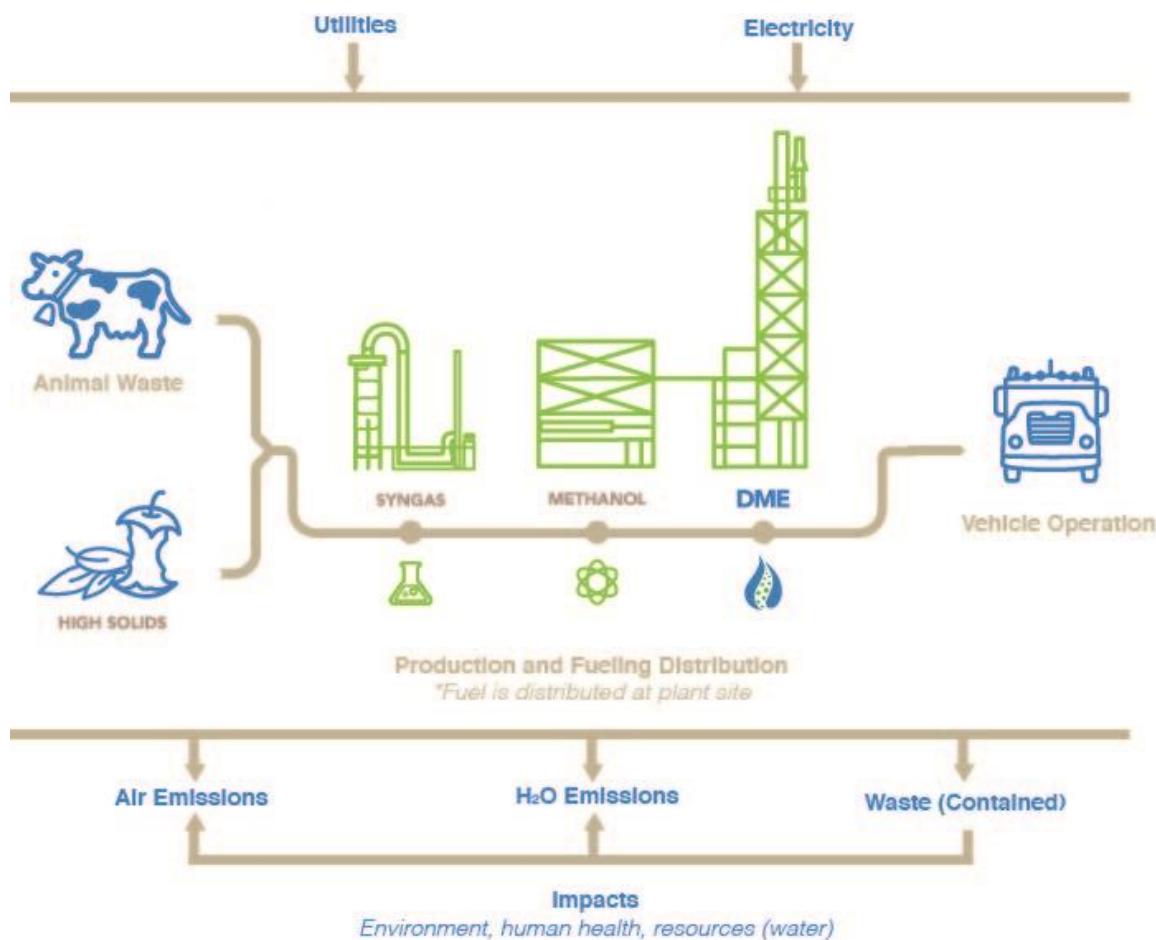


Figure 8.1. An illustration of life stages and some potential life-cycle pollutant emissions for DME.

8.1.1. Pollutant Categories:

For each of these stages we must address emissions to the environment for the following pollutant categories:

- Greenhouse gases including carbon dioxide (CO₂),
- carbon monoxide (CO),
- Nitrogen oxides (NOx),
- Ozone,
- Particulate matter,
- Hydrocarbons (HCs),
- Toxic air contaminants (TACs) including volatile organic compounds (VOCs) such as benzene, formaldehyde, etc., and semi-volatile organic compounds (SVOCs) such as polycyclic aromatic hydrocarbons,
- Metals,
- Fuel product leaks and spills,

- Hazardous wastes
- Pesticides

8.2. DME Life-cycle Definition and Assessment

Modeling the life-cycle emissions attributable to transportation fuels requires characterization of emissions factors for both the life-cycle of the fuel and the production and operation of the vehicle. ADME life-cycle assessment was performed by Oberon Fuels, Inc. using CAGREET (California Air Resources Board, 2009). Emissions from feedstock production, transport, fuel production, distribution, and vehicle fueling and combustion were evaluated. Air emissions in each stage of the fuel life-cycle enables one to determine cumulative emissions per fuel liter produced (and per joule delivered to a vehicle) for carbon monoxide (CO), nitrogen oxides (NOx), ozone, particulate matter, volatile organic compounds (VOCs) such as benzene, formaldehyde, and semi-volatile organic compounds (SVOCs) such as polycyclic aromatic hydrocarbons. Available software makes it possible to assess human health burden and the monetized damages from this burden for these pollutants.

8.2.1. Feedstock Production

In CAGREET (California Air Resources Board, 2009), Feedstock Production is represented by the following phases: Gas Recovery, Gas Recovery Leakage, Gas Processing, Gas Processing Leakage, Gas Processing: Non-Combustion Emissions, Flared/biogas Credit (Table 8.1). For ULSD, the feedstock production is labeled as crude oil phase in CAGREET.

Table 8.1. Emissions from feedstock production (g/mmBtu).

Feedstock Production Emissions	CA ULSD	NG DME	Oberon BioDME
VOC	5.4	5.8	0
CO	19.7	10.4	10.4
NOx	62.7	19.1	19.1
PM10	2.4	0.4	0.4
PM2.5	1.6	0.3	0.4
SOx	5.4	10.8	10.8
CH ₄	89.9	109.6	-3,000
N ₂ O	0.10	0	0.06
CO ₂	6579	4689	-30406
CI (tons CO₂e/MJ)	8.4	7.1	-114.7

8.2.2. Feedstock Transport

In CAGREET, Feedstock Transport is represented by Gas Transmission and Distribution to FT and Gas Transmission and Distribution Leaks. In the case of HSAD Biogas, Oberon assumes that

the anaerobic digester will be located adjacent to the plant and feedstock transport will be negligible and therefore, feedstock transport contributes 0g/mmBtu of all pollutants.

8.2.3. Fuel Production

In CAGREET, fuel production is represented by: production, FT Production non-combustion, Natural Gas reform fuel, Power input (Table 8.2). Fuel production is represented by fuel production and refining in the California ULSD CAGREET model.

Table 8.2. Emissions during fuel production (g/mmBtu).

Fuel Production Emissions	CA ULSD	NG DME	Oberon BioDME
VOC	4.4	6.7	7
CO	7.2	14.5	23.7
NOx	14.3	24.2	34.6
PM10	7.0	11.9	14.2
PM2.5	2.8	11.9	14.2
SOx	10.3	4.8	7.4
CH ₄	10.9	57.3	86.7
N ₂ O	0.1	0	0.4
CO ₂	12175	16556	42853
CI (tons CO2e/MJ)	11.9	17.1	42.8

8.2.4. Fuel Distribution and Reforming

The Oberon model assumes that Oberon BioDME will be distributed from the production site (adjacent the fuel plant), therefore emissions associated with fuel distributions are negligible. The reforming step in the Oberon process is included through the production.

8.2.5. Vehicle Fueling and Combustion

In CAGREET, vehicle fueling and combustion is represented by: DME fugitives, DME Storage and the vehicle inputs (Tables 8.3). For California ULSD, it is labeled as the fuel combustion phase.

With regards to tailpipe emissions, based on publically available data referenced throughout this report, Oberon Fuels expects that future commercial DME vehicles will meet the emissions standards for heavy duty trucks and that particulate matter will be reduced to a negligible amount without the use of a diesel particulate filter (DPF). As a result of this assumption, many tailpipe emissions results are identical between ULSD and DME. Table 8.4 summarized results where differences were found. Additional emissions data will be part of ongoing Tier II and Tier III activities.

Table 8.3. Preliminary comparison of tailpipe emissions for DME produced from natural gas (NG DME), California ultra low sulfur diesel (ULSD) and Oberon BioDME.

Fuel:	CA ULSD	NG DME	Oberon BioDME
Technology:	CI ICEV	CI ICEV	CI ICEV
mpg	6.11	3.31	3.31
Vehicle Emissions (g/mi)			
Exhaust PM10	0.531	0	0
Exhaust PM2.5	0.064	0	0
Emissions (g/MJ)			
PM10	0.024	0	0
PM2.5	0.0029	0	0
SO _x	0.00051	0	0
CO ₂ (Incl. VOC and CO)	74.1	66.2	66.2
Total GHG Emissions (g CO₂e/MJ)	74.7	66.9	66.9
Source: GREET_1_2011 Defaults, Year 2015 Time Series * Compression Ignition Internal Combustion Vehicle			

8.2.6. Carbon Intensity of BioDME

The carbon intensity of Oberon BioDME, NG DME and California ULSD is shown in Table 8.4 and Figure 8.2.

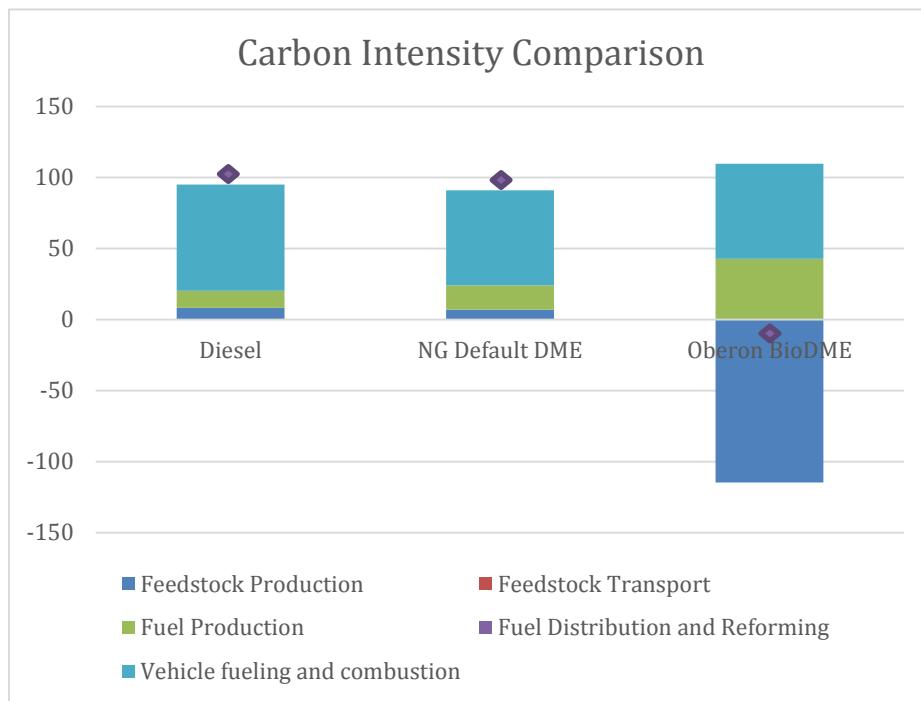
Table 8.4. Carbon Intensity of BioDME (gCO₂e/MJ).

Fuel	CA ULSD	NG DME	Oberon BioDME
Feedstock Production	8.4	7.1	-114.7
Feedstock Transport	0	0	0
Fuel Production	11.9	17.1	42.8
Fuel Distribution and Reforming	0	0	0
Vehicle fueling and combustion	74.7	66.9	66.9
Total gCO₂e/MJ (losses not included)	95.0	91.1	-5.0

Since Oberon BioDME uses biogas, carbon is recycled resulting in a reduced carbon intensity during feedstock production. This reduction in carbon intensity negates the carbon emissions that

occur during the other DME life-cycle phases. Natural Gas based DME (assuming GREET Model defaults which assume large scale, 70% efficiency system) produces slightly less overall emissions compared to diesel.

Figure 8.2. Carbon intensities by life-cycle phase.



8.2.7. Hazardous Wastes

Catalytic synthesis of DME coupled with purification is a well-researched topic that is both promising and feasible but has not been industrially implemented to date until Oberon's current plant in Brawley, CA. The solid waste inventory for Oberon Fuels DME small scale fuel plants has been completed. The DME small scale fuel plants use four different types of catalysts to assist in necessary reactions (Table 8.6). The catalysts do not accumulate hazardous materials during the DME production process.

Unlike the other three catalysts, the methanol (MeOH) synthesis catalyst is the only hazardous substance due to the zinc oxide ingredient (UN3077). Catalysts are held in place within welded trays, so release is highly unlikely. In the event of a weld failure, catalyst material would be trapped by the downstream filters, and the system would be shut down until cleanup was complete. Every 3-7 years the 150 cf of methanol catalyst will be disposed of through the metal recovery industry or through a corporate recycling program as recommended by the catalyst supplier. Disposal will be in accordance with local, state or national legislation.

The companies that provide the catalyst also collect and reuse the valuable components in the catalysts. Additionally, local catalyst recovery companies (companies that recover nickel and other valuable metals) can be contacted to dispose of the catalysts.

Given an estimated annual DME production volume of 3,650,000 gal/year, and if the MeOH catalyst is replaced every three years, then the hazardous waste production volume can be estimated to be 1.36E-5 cf/gal or 1.085E-5 cf/L.

Catalyst	Usage
SMR Catalyst 1	800 kg/3-7 yr.
SMR Catalyst 2	1,120 kg/3-7 yr.
MeOH Catalyst	150 ft ³ /3 yr.
DME Catalyst	865 kg/3 yr.

Table 8.6. Oberon catalyst usage.

8.3. DME Life-cycle Summary and Data Gaps

A DME life-cycle assessment was performed using CAGREET. Air emissions during each stage of the fuel life-cycle was determined, including cumulative emissions for Carbon monoxide (CO), Nitrogen oxides (NO_x), Ozone, Particulate matter, Volatile organic compounds (VOCs) such as benzene, formaldehyde, and semi-volatile organic compounds (SVOCs) such as polycyclic aromatic hydrocarbons. Carbon intensity of BioDME was also evaluated. The solid waste inventory for Oberon Fuels DME small scale fuel plants has been completed, and a catalysis recycling or disposal strategy has been developed.

Early engine testing using engines designed for conventional diesel indicated that tailpipe combustion emissions including volatile organic compounds (VOCs), and formaldehyde, from diesel engines using DME could be higher than with ULSD. Newer DME engine design modifications were found to result in reduced exhaust emissions, including CO, and increased combustion efficiency (Szybist, et al., 2014; Salsing, 2011; Salsing et al. 2012). To evaluate emissions impacts of DME compared to ULSD, testing must be conducted on standard regulated emissions, including PM, NO_x, CO, THC, CO₂, and unregulated (toxics), including PAHs, VOCs, and carbonyls. The development of DME Emissions Profiles will be part of Tier II activities. Emissions data will be gathered in conjunction with vehicle equipment manufacturers.

If DME becomes more widely used and below ground storage and piping infrastructure is used, then additional research into the subsurface transport of DME and potential impacts to groundwater resources may be needed.

9. Tier I Conclusions

Through a review of the current literature and technical documentation on the use of dimethyl ether (DME) in both fuel and non-fuel applications, we have compiled a review and evaluation of potential health and environmental impacts for DME use as a fuel in California. This report provides input to aid the CalEPA Multimedia Working Group in formulating recommendations to the California Environmental Policy Council regarding the consequences of using DME as a diesel substitute in California. The key goals of this report are to (a) identify the life-cycle benefits of using DME in California relative to the current fuel mix in use in California, (b) identify the important knowledge gaps for a Multimedia Assessment, and (c) identify possible approaches to address these gaps. Addressing the knowledge gaps identified here does not necessarily involve additional experiments but could include additional requests for information from the fuel proponents of any new fuel to be used in California.

9.1. Summary Findings on the Potential Impacts of DME

9.1.1. Production of DME

DME can be produced through three different production pathways: a two-step, a one-step, and a liquid-one-step process called bireforming. DME is typically produced through a two-step process using syngas as a feedstock. The syngas is converted to methanol, which is then converted to DME. DME can be produced from any methane-containing feedstock including pipeline natural gas, biogas, landfill gas, and stranded natural gas.

The Oberon Fuels methane-gas-to-DME small scale production plant process consists of three major steps: syngas production, methanol synthesis, and simultaneous DME synthesis and separation via catalytic distillation. While the first two process steps are common in large scale industrial applications, further development of these processes for small scale applications is open for improvement and implementation. Catalytic synthesis of DME coupled with purification is a well-researched topic that is both promising and feasible but has not been industrially implemented to date. Any needed fuel additives are introduced after the final DME product is produced, ideally prior to transport of the product.

9.1.2. Storage and Distribution of DME

DME is stored, handled, and transferred as a liquefied gas under pressure. DME storage and distribution systems will only utilize aboveground components and any associated pipes and valves will also be above ground. If DME becomes more widely used and below ground storage and piping infrastructure is used, then additional research into the subsurface transport of DME and potential impacts to groundwater resources may be needed.

LPG infrastructures are widespread in the United States and basic components of LPG storage and handling technology can be used for the storage and handling of DME. While handling of DME is similar to LPG, tanks and infrastructure such as pumps, valves, and seals etc, on DME

tanks and infrastructure must be made of specific compatible materials. ASTM specification D7901 provides limited guidance on safety and handling of DME including elastomer selection for gaskets and seals.

Substantial swelling of a variety of seal and gasket elastomers was observed with DME. Materials used in the storage, handling, and transfer of DME have to be compatible with, and unaffected by, DME, and materials compatibility is a key issue for the tanks, pipes, and valves used for DME storage and distribution. The following materials have been found to be compatible with DME: Nitrile (NBR, BUNA-N), Hydrogenated NBR (HNBR), Silicone (VMQ), Fluorosilicone (FVMQ), Perfluoroelastomer (FFKM), polytetrafluoroethylene (PTFE), and stainless steel. This material compatibility information has been generated by commercial DME handlers, as a general reference, and listed in ASTM D7901.

To address the lack of existing DME fueling infrastructure, DME producers are likely to initially adopt a hub and spoke model for fuel distribution. DME is centrally produced and delivered to customers as needed on a daily, weekly, or monthly basis. Early adopters are likely to be fleets involved in local and regional haul that drive in and out of the same terminal daily and refuel at this base site.

9.1.3. Use of DME as a Transportation Fuel

There are a number of DME characteristics that require consideration before its wide-spread use as a diesel equivalent fuel in California. Roughly 1.8 L of pure DME is equivalent to 1.0 L of diesel fuel, on a lower heating value (LHV) basis. Viscosity of DME is 1/20 of diesel fuel.

Compression ignition engines running on DME do not require diesel particulate filters (DPF) in order to meet emissions standards for particulate matter. This after-treatment equipment is costly and adds weight to trucks whose delivery capabilities are then decreased. Conventional diesel engines require modifications to fuel storage and delivery system to use DME as a fuel. The conversion of seals for fuel pumps and injectors is necessary for conventional diesel injection engines to DME injection engines.

California law requires that all fuel sold or distributed within the State have a fuel specification established by a consensus organization, such as ASTM or SAE. Therefore, development of an ASTM Standard Specification for DME is an important step towards the legal use of DME as a fuel in California. ASTM recently adopted an ASTM specification for DME as a transportation fuel (ASTM D7901).

In order to complete engine testing for DME, CARB must establish specification standards for the fuel used in the engine test (“test fuel”). The test fuel must fall in the range of specifications that CARB has selected. At this point, CARB has determined that the minimum requirement for the fuel specification would be ASTM specification D7901, and the maximum requirement has not yet been set. Therefore, the test fuel used for engine testing as part of the Multi-Media Assessment must fall within the ASTM specification range

It is anticipated that DME will require a lubricity additive due to its low inherent lubricity. To protect engine fuel injection equipment, there are industry recommendations to add a lubricity additive at about 100 ppm to maintain the lubricity of the fuel equal to that of diesel fuel. Further, it is anticipated that original equipment manufacturers (OEMs) may specify an engine-cleaning additive or that local jurisdictions will require an odorant such as ethyl mercaptan.

It is also possible that an additive to increase flame luminescence may be needed. There is not a standard for flame luminosity for DME, but there have been consideration of additives or blending agents for creating luminosity for fuels that have a non-luminous flames such as methanol and hydrogen. However, information on specific concentrations of each of these additives has not been made available by OEMs at this point in the development of DME as a fuel.

9.1.4. DME Environmental Transport and Fate

A multimedia transport, fate and exposure assessment synthesizes information about partitioning, reaction, and multimedia-transport properties of a chemical in a representative or generic environment with information about exposed humans or wildlife to assess impacts, such as health risk. DME may enter the environment through leakage or spillage during production, transport, storage, and usage. DME will exist primarily in the gas phase when it is released to the atmosphere. Summarized below are the key finding regarding DME releases and the associated with environmental fate and transport leading to human and environmental exposures.

Verification of DME Environmental Sampling and Analysis Methods

EPA does not give a specific method for the sampling and analysis of DME. EPA Standard Methods to sample and detect VOC such as MTBE in air and water should be applicable to DME. As part of Tier II activities, confirmation of the applicability of these methods needs to be conducted. These methods can then be used to monitor air, surface, and subsurface water as pilot production processes are demonstrated.

Bulk DME release to surface and subsurface soils

It is anticipated that bulk DME will be stored in above ground storage tanks, and any associated pipes and valves will also be above ground. Because of its high volatility, a bulk DME release on to the soil surface would rapidly transition into the vapor phase. This volatilization can occur so rapidly that explosive forces may be generated. Nearby equipment or soil particulates may be displaced by these forces.

Due to rapid DME evaporation, it may be expected that a bulk release to the soil surface would result in localized, shallow, soil freezing rendering the soil impermeable to deeper transport until thawing occurs. DME is chemically inert and chemical interaction with soil particulates or organic materials coating the particulates is unlikely. DME is not expected to sorb to sediments or suspended particles in water or to hydrolyze in groundwater. As a result, DME has a high potential for mobility in vadose zone soils and groundwater similar to methyl tert-butyl ether

(MTBE). Because of localized, shallow, soil freezing during a bulk DME release, the potential impact to the subsurface could be confined to the shallow subsurface environment unless DME is dissolved into surface water that eventually reaches the water table. For example, if water spray is used to knock-down DME vapors, the transport of DME to subsurface waters is a remote possibility with minimal impact. Residual taste and odor issues for DME in drinking water resources have not been tested.

The DME that enters subsurface environment can be expected to have a slow rate of biotic or abiotic degradation. Since DME is a good solvent, it is possible that organic material associated with the soil matrix may be mobilized and displaced. Any DME vapors trapped in the subsurface soils could eventually disperse to the atmosphere due to vadose zone barometric pumping.

Bulk DME release to surface waters

As with a DME release to soils, a release to a body of surface water would result in rapid, possibly explosive, volatilization of DME. A cold vapor cloud could form on the surface of the water. Wind direction and speed will play an important role in the transport of the cold vapor cloud.

The solubility of DME vapor in water changes with pressure and temperature. At 100 kPa and 18°C water can hold 7 percent by weight and at 500 kPa and 23.5°C water can hold 35 percent by weight. DME is expected to quickly volatilize from the water. DME is not expected to hydrolyze, bioconcentrate in aquatic organisms, or directly photolyze, when it is released to surface waters. Estimated half-lives in a model flowing river and model lake are 2.4 hours and 2.8 days, respectively. Moreover, it is not expected that DME reacts with hydroxyl radicals produced from photochemical processes in the water, and DME has a slow process of biodegradation in water. DME has a strong unpleasant slightly sweet smell and residual taste and odor issues for DME in drinking water resources have not been tested.

A DME release into surface waters during the use of watercraft is anticipated to be minimal since the near-term use of DME in marine diesel engines is not planned in California.

Fate of DME in the atmosphere

DME will only exist as a gas if it is released to the atmosphere. The main transport mechanism in the atmosphere will be dispersion. Since DME is heavier than air, during a bulk DME release, it is possible that a cold DME vapor cloud, denser than air, could form and settle into low lying surface features such as basements, storm drains, creek beds, or drainage ditches. If these vapors reach an ignition source, a significant explosion could occur.

Direct photolysis of DME is not expected to be an important process. DME is not regarded as a greenhouse gas. Atmospheric dispersed DME decomposes to carbon dioxide and water via a reaction with photochemically produced hydroxyl radicals during the day and during the night-time by nitrate radicals in the atmosphere. DME degradation in the atmosphere occurs by reaction with hydroxyl and nitrate radicals with estimated half-lives of 5.4 and 123 days, respectively.

Atmospheric partitioning of DME into rainwater can be expected to be low as atmospheric concentrations of DME are expected to be low. On the other hand, if rainfall occurs through a DME vapor cloud that has settled into low-lying area, this rain could adsorb DME and percolate to groundwaters.

DME Combustion emissions

In addition to leaks and spills of DME from production and transportation, the combustion of DME in vehicles gives rise to emissions of combustion products. Fossil fuel combustion for transportation has been associated with a number of criteria pollutants such as NO_x, SO_x, ozone, CO, particulate matter (PM); hydrocarbon (HC) emissions that lead to secondary PM and some hazardous air pollutants such as benzene, aldehydes, and polycyclic aromatic hydrocarbons. Preliminary assessments from the California Energy Commission (CEC)(2007) report that well-to-wheels (WTW) emissions of the criteria air pollutants NO_x, CO and PM10 from DME derived from natural gas are comparable and somewhat lower when compared on an energy basis to CA ultra-low sulfur diesel (ULSD). The CEC WTW analysis indicated that WTW emissions of hazardous air pollutants from natural-gas-derived DME are significantly lower than ULSD, but there are concerns about higher levels of formaldehyde from non-ASTM standard DME use compared to ULSD. Similar to LPG, the WTW modeling showed that DME fuel derived from natural gas could have VOC emissions higher than ULSD, but these VOC emissions can be controlled (CEC, 2007). A preliminary life-cycle analysis of emissions from BioDME indicated that VOC emissions were lower compared to DME produced from natural gas.

9.1.5. DME Safety

DME is required to be stored in accordance with all current regulations and standards. Above ground storage tanks (ASTs) holding large quantities of DME are subject to local siting approval and generally should not be located near heavily populated areas. DME is a volatile organic compound that is stable but is extremely flammable and may form potentially explosive mixtures with air. Because the relative gas density of DME is heavier than air, vapors may collect in low lying areas such as ditches, sewers, basements, and can ignite at distances far from the source and flash back.

Undenatured DME has a strong, unpleasant, slightly sweet smell. There remains a need to explore consideration of whether there would be benefit to have DME possess an odor that is readily detectable but unique from natural gas and propane odorants.

Researchers have described the DME flame as nonluminous in cool flames, moderately luminous pale blue with low brightness, or luminous dark-blue in hotter flames. However, when a lubricant is added to improve lubricity, a rather strong, luminous flame might be detected. A flame that is not readily visible poses a safety problem for DME production plant workers, fire-fighters and first responders if an ignited leak occurs. During the evaluation of the luminosity of DME flames, a key issue will be what level of luminosity is required.

DME can be detected in air, soils, and water using routine US EPA sampling and analysis methods. As DME becomes more widely used as a transportation fuel, it is possible that DME will become more widely distributed into the environment including air and water resources. It may be prudent to include DME as one of the analytes of interest in the future.

9.1.6. DME Toxicity

The current literature provides sufficient information to assess the potential impacts of DME to human and ecological receptors. Dimethyl ether has a low order of toxicity on both an acute and chronic basis. The main physiological action of DME is that of “weak anesthesia” when inhaled at high levels. DME is extremely stable chemically and is essentially an inert chemical substance. Because DME was developed as an aerosol propellant that touches the human body directly, the safety of DME has been evaluated in detail.

Fossil fuel combustion for transportation has been associated with a number of criteria pollutants such as NO_x, SO_x, ozone, CO, particulate matter (PM), hydrocarbon (HC) emissions that lead to secondary PM, and some hazardous air pollutants such as benzene, aldehydes, and polycyclic aromatic hydrocarbons. The State of California and the U.S. EPA have identified diesel PM as a toxic compound. As a diesel substitute, DME combustion emissions during use phase must be assessed in terms of their emissions of criteria, air pollutants, and hazardous air pollutants. Preliminary work reveals a significant reduction of PM emissions relative to diesel when DME is used a diesel substitute.

9.1.7. DME Life-cycle Summary

A preliminary BioDME life-cycle assessment (LCA) was performed using CAGREET. Air emissions during each stage of the fuel life-cycle was determined, including cumulative emissions for carbon monoxide (CO), nitrogen oxides (NO_x), ozone, particulate matter, volatile organic compounds (VOCs) such as benzene, formaldehyde, and semi-volatile organic compounds (SVOCs) such as polycyclic aromatic hydrocarbons. During the preliminary BioDME LCA volatile organic compounds (VOCs), emissions from diesel engines using BioDME were found to be much lower compared to DME produced from natural gas. Carbon intensity of BioDME was also evaluated. The solid waste inventory for Oberon Fuels DME small scale fuel plants has been completed, and a catalyst recycling or disposal strategy has been developed.

9.2. Potential Benefits of Using DME as a Diesel Substitute

The use of DME as a diesel substitute in California offers several beneficial characteristics that will help California meet State renewable fuel goals. The key benefits identified in the Tier I study are summarized below.

Cleaner Burning Diesel Fuel

Preliminary assessments from the California Energy Commission (CEC, 2007) report that well-to-wheels (WTW) emissions of the criteria air pollutants NO_x, CO and PM10 from DME derived from natural gas are comparable and somewhat lower when compared on an energy basis to California diesel fuel. The CEC WTW analysis indicated that WTW emissions of hazardous air pollutants from natural-gas-derived DME are significantly lower than California diesel fuel, but there are concerns about higher levels of formaldehyde from DME use compared to California diesel fuel. Similar to LPG, The WTW modeling showed that DME fuel derived from natural gas could have VOC emissions higher than California diesel fuel, but these VOC emissions can be controlled (CEC, 2007). A preliminary life-cycle analysis of emissions from BioDME indicated that VOC emissions were much lower compared to DME produced from natural gas.

Reduced Carbon Intensity

BioDME can be produced from renewable biogas feedstocks. Carbon dioxide recycling during the production of BioDME is possible by using biogas feedstocks that are generated by the decomposition of agricultural waste and other biomass sources such as pulp and paper mill waste products.

Low DME Toxicity

DME toxicity has been examined in detail since it can safely be used as an aerosol propellant that touches the human body. The narcotic effects of DME are weak, but first-responders to DME releases must use respiratory protection. Skin contact with liquid DME may cause freezing of the skin.

Minimum Post Combustion Emission Controls Compared to ULSD

DME helps eliminate diesel engine after-treatment equipment that is costly and adds weight to trucks whose delivery capabilities are then decreased. DME burns cleanly with no soot. Compression ignition engines running on DME do not require diesel particulate filters to meet emissions standards for particulate matter.

Compared to diesel, DME has vastly superior cold starting, is literally smokeless, has quieter combustion, no fuel waxing in cold climates to clog fuel lines, low NO_x emissions, lower well-to-wheel greenhouse gas emissions, and potentially is a CO₂ absorber during its production. Conversion of a diesel engine to DME does not require modifications to diesel engine internal structures or components, e.g. head, block, pistons, cams, valves, manifolds, cooling pumps, turbo. The only modifications required are to the fuel system.

9.3. Key Information Gaps: Key Issues for Tier II Activities

Additional Combustion Emissions Testing – To evaluate emissions impacts of DME compared to California diesel fuel, engine testing must be conducted to characterize standard regulated emissions including PM, NO_x, CO, THC, CO₂, and unregulated (toxics) including TACs, PAHs, VOCs, and carbonyls. The development of DME Emissions Profiles will be part of Tier II

activities. Emissions data will be gathered by vehicle equipment manufacturers in conjunction with Oberon Fuels.

Additives – It is anticipated that DME used as a transportation fuel may require additives to meet several needs. These additives may include:

Odorant – Unodorized DME has a strong, unpleasant, slightly sweet smell. There remains a need to explore consideration of whether there would be benefit to have DME possess an odor that is readily detectable but unique from natural gas and propane odorants. An odorant is currently used in DME fuel in Europe, and the California Air Resources Board may also specify a need for an odorant. If an odorant is needed, then non-sulfur options for possible odorization of DME need to be explored.

Lubricity – It is generally recognized that DME use as a diesel transportation fuel requires a lubricity additive. Specific details regarding which chemicals and appropriate concentrations are being developed as part of the DME engine testing to be conducted by vehicle manufacturers in cooperation with Oberon Fuels.

Luminosity – The luminosity of DME flames can be variable. Researchers have described the DME flame as nonluminous in cool flames, moderately luminous pale blue with low brightness, or luminous dark-blue in hotter flames. However, when a lubricant is added to improve lubricity, a rather strong, luminous flame might be detected. A flame that is not readily visible poses a safety problem for DME production plant workers, fire-fighters and first responders if an ignited leak occurs. During the evaluation of the luminosity of DME flames, a key issue will be what level of luminosity is required. As part of Tier II activities, information on specific concentrations of any proposed additives needs to be specified.

Confirmation of DME Materials Compatibility

As DME is developed for the California transportation fuel market, Oberon Fuels, Inc. was actively involved in the development of ASTM standards for DME used as a transportation fuel. ASTM D7901, Standard Specification for Dimethyl Ether for Fuel Purposes, has been adopted and provides a list of elastomers that are known by industry to be compatible and perform well with DME.

Materials used in the storage, handling, and transfer of DME have to be compatible with and unaffected by DME. LPG infrastructures are widespread in the United States. Basic components of LPG storage and handling technology can be used for the storage and handling of DME, but substantial swelling of a variety of seal and gasket elastomers was observed with DME. Within the DME industry and ASTM, perfluoroelastomer, polytetrafluoroethylene, fluorosilicone, hydrogenated-nitrile-butadiene rubber, nitrile, and silicone elastomers as well as stainless steel have been found to perform well with DME. ASTM specification D7901 provides limited guidance on safety and handling of DME including elastomer selection for gaskets and seals.

The material compatibility information for seals and gaskets was obtained from a variety of sources, and these materials are commonly used within the DME industry including Oberon

Fuel's operational DME production facility in Brawley, California. During the implementation of DME production using the Oberon Fuels small scale production facility, materials compatibility will comply with the ASTM DME Standard and will be verified and documented with actual devices and production and storage systems to be used in California.

Development of Specifications for California Certification Fuel for DME

In order to complete its engine testing for DME, CARB must establish specification standards for the fuel used in the engine test ("test fuel"). The test fuel must fall in the range of specifications that CARB has selected. At this point, CARB has determined that the minimum requirement for the fuel specification would be ASTM specification D7901, and the maximum requirement has not yet been set. Therefore, the DME test fuel used for engine testing as part of the Multi-Media Assessment must fall within the ASTM specification range and will be compared to life-cycle analyses of natural-gas-derived DME, BioDME, and California diesel fuel.

DME Life-cycle Impacts

Modeling life-cycle emissions attributable to transportation fuels requires characterization of emissions factors during the life-cycle of the fuel including the production and operation of the vehicle. A preliminary life-cycle analysis for BioDME, DME produced from unscrubbed (60% methane) HSAD (High Solid Anaerobic Digestion) foodscraps and yard waste, shows promise in reducing VOC emissions and carbon intensity. As part of Tier II activities, the BioDME life-cycle analysis will be confirmed and documented using any new information resulting from the DME vehicle Emission Profile testing.

If DME becomes more widely used and below ground storage and piping infrastructure is used, then additional research into the subsurface transport of DME and potential impacts to groundwater resources may be needed.

Verification of DME Environmental Sampling and Analysis Methods

EPA does not give a specific method for the sampling and analysis of DME. EPA Standard Methods to sample and detect VOC such as MTBE in air and water should be applicable to DME. As part of Tier II activities, confirmation of the applicability of these methods needs to be conducted. These methods can then be used to monitor in air and surface and subsurface water as pilot production processes are demonstrated. As DME becomes more widely used as a transportation fuel, it is possible that DME will become more widely distributed into the environment, including air and water resources. It may be prudent to include DME as one of the analytes of interest in the future.

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11. Tier I Appendices

APPENDIX A

Legislative Incentives for Dimethyl Ether

DME can be explored as an “alternative fuel for vehicles” in some federal and state laws and regulations as explained in the following paragraphs. In August 2005, President George W. Bush signed into law the “Energy Policy Act of 2005” which covers some management issues for the future of America’s energy. This legislation mentions the need of supporting “alternative and renewable energy sources” and reducing “reliance on petroleum as an automobile fuel” (The White House 2005, EPAct 2005).

California has passed some climate change legislation applicable to vehicles that are common sources of releasing greenhouse gas (GHG) in the state (CARB & CEC, 2007); it has considered the “Fueling Alternatives” as a solution to reduce this negative effect of vehicles to the environment. Also in recent years, California has tried to reduce its dependency to petroleum both environmentally and economically.

In September 2005, the “California Energy Commission (CEC)” in cooperation with the “California Air Resources Board (CARB)” were required to develop and implement a “State Alternative Fuels Plan” based on the “Assembly Bill (AB) 1007” with the aim of increasing the use of alternative fuels (Nylund et al., 2008). Dimethyl Ether is among the alternatives fuels in AB 1007. A scenario was used for each fuel in this bill and some goals were developed for milestone years 2012, 2017, and 2022. Also, three case levels were defined for the scenarios: “business-as-usual”, “moderate”, and “aggressive”. The business-as-usual case assumes that the alternative fuel is in a market condition that cannot be competitive with the current fuels. The moderate case undertakes that the alternative fuel is available in the market and it is expected to have a growing market. The aggressive case assumes that all the barriers are removed, the production market of the new fuel is successful, and the conventional fuel is completely substituted with the new one (CARB & CEC, 2007). As of 2007, the maximum feasible use estimates in the moderate case reported by CARB (Table 1.1) show significant growth in the use of DME as an alternative fuel. In this table, “GGE” stands for “Gallons of Gasoline Equivalent”.

In September 2006, the “Assembly Bill (AB) 32” which is known as the “Global Warming Solutions Act of 2006” was signed by Governor Arnold Schwarzenegger and through this signature, the state of California was prepared to set goals for reducing the greenhouse gas emissions. Pursuant to AB32, the “Low Carbon Fuel Standard (LCFS)” program, considered as the greenhouse gas standard for vehicle fuels, was enacted by California’s Air Resources Board (CARB) in January 2007. According to this rule, the carbon amount of the passenger vehicle fuels in California will be reduced by at least 10% volumetric by 2020. This is estimated to manufacture at least 7 million “alternative fuel vehicles” or “hybrid vehicles” and substituting 20% of gasoline fuels with lower-carbon ones. Alternative fuels are introduced as the common

Table A.1. Maximum Feasible Alternative Fuel Use Results by Fuel (CARB & CEC, 2007).

Mile Stone Year	2012		2017		2022	
	Fuel Use	GHG	Fuel Use	GHG	Fuel Use	GHG
Propane	48	<0.1	173	0.1	282	0.2
Natural Gas	306	1.5	518	2.5	885	4.4
E10 (MW Corn)	1,394	3.8	1,354	3.8	1,327	3.6
E-85 (CA Poplar)	83	0.7	434	3.9	738	6.6
Hydrogen	40	0.3	80	0.6	440	4.4
Electricity	86	2.1	187	5.1	376	6.7
GTL, CTL, & PTL ²⁰	320	0	530	0	630	0
Renewable Diesel	130	1	310	2.4	530	4.2
Dimethyl Ether	13	0	62	0	101	0
Total	2,420	10	3,648	18	5,309	30

Fuel use measured in million GGE. For hydrogen and electricity, the petroleum displacement is greater than the fuel used due to the vehicle efficiency. GHG measured in MMT per year.

Source: California Energy Commission

sources of low carbon fuels for vehicles in this program. The fuel's full life-cycle which is known as the "well to wheels" or "seed to wheels" efficiency of vehicle fuels is considered by California LCFS as an effective factor in its evaluations (Nylund et al., 2008; <http://www.arb.ca.gov/cc/ab32/ab32.htm>; <http://www.arb.ca.gov/fuels/lcfs/lcfs.htm>, accessed on 7/24/13).

In August of 2014, the United States Department of Agriculture, the EPA, and the United States Department of Energy published the *Biogas Opportunities Roadmap, Voluntary Actions to Reduce Methane Emissions and Increase Energy Independence*, which states that the DOE will "strengthen programs that support the use of renewable natural gas from biogas ... as feedstock to develop other renewable vehicle fuels (e.g., hydrogen , DME, etc.)."

DME from Biogas Now Qualifies for RINS Credits. On August 18, 2014, the EPA published its approval of DME made from biogas by the Oberon process to qualify for RINS credits under the Renewable Fuel Standard. The EPA determined that bioDME produced from the Oberon process resulted in a 68% reduction in greenhouse gases when compared to baseline diesel.

The California Department of Food and Agriculture (CDFA) published proposed regulations to the California Regulatory Notice Register, which will provides a legal means to sell DME in California. Current DME sales are operating under a temporary waiver. The comment period for this regulation ends September 8, 2014, and once approved, these regulations will be published in the California Code of Regulations.

Appendix A References :

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California Air Resources Board (CARB), California Energy Commission (CEC). 2007. State Alternative Fuels Plan. (<http://www.energy.ca.gov/2007publications/CEC-600-2007-011/CEC-600-2007-011-CMF.PDF>).

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APPENDIX B

Summary of Current Market Forecast

Based on a report published on July 2013 named “Dimethyl Ether Market: Global Trends & Forecasts 2018 & 2023” provided by “Research and Markets” webpage, the DME market had remarkable improvements in recent years and it is expected to see faster progress during the next five years in many countries around the world. There is a competitive focus on developing the DME market in Asia-Pacific region especially in Japan, South Korea, Egypt, and Indonesia in addition to Sweden and Trinidad & Tobago. Currently, China is known as the main consumer of DME in the world; consuming more than 90% of the universal production in 2012. China has its own large fixed plants and facilities and produces DME locally. Additionally, a few DME production instruments are manufactured in Germany, The Netherlands, Japan, and the U.S. DME is at its “emerging stage” in these countries as they try to separate themselves from importing gas and oil.

DME is now blended with LPG in the above mentioned countries. This will be one of the continued DME applications in the future, which will grow. Additionally, DME has a great market in Western Europe as an aerosol propellant. DME’s function as an alternative diesel fuel and a power generation fuel may continue to grow on commercial scale in coming years. Still, there is a huge gap between demand and supply of DME. This may come from the absence of transaction standards and export foundations among the countries using DME. It is expected that countries like China, Papua New Guinea, and Saudi Arabia may remove these limitations and export DME to other countries by 2018²³.

²³ http://www.researchandmarkets.com/research/7fg4v7/dimethyl_ether).

Appendix C

Matheson Tri-Gas, Inc. Safety Data Sheet for Dimethyl Ether

**MATHESON**

ask. . .The Gas Professionals™

Safety Data Sheet

Material Name: DIMETHYL ETHER**SDS ID: 00244291**

* * * Section 1 - IDENTIFICATION* * *

Manufacturer Information

MATHESON TRI-GAS, INC.
150 Allen Road, Suite 302
Basking Ridge, NJ 07920

General Information: 1-800-416-2505
Emergency #: 1-800-424-9300 (CHEMTREC)
Outside the US: 703-527-3887 (Call collect)

Product Identifier: DIMETHYL ETHER**Trade Names/Synonyms**

Wood ether; Methyl oxide; Oxybismethane; Methyoxythane

Chemical Family

ethers, aliphatic

Product Use

industrial

Restrictions on Use

None known.

* * * Section 2 - HAZARDS IDENTIFICATION* * *

GHS Classification

Flammable gas, Category 1

Gas under pressure, Liquefied gas

Skin Corrosion / Irritation, Category 2

Eye Damage / Irritation, Category 2B

Specific Target Organ Toxicity - Single Exposure, Category 3 (central nervous system and respiratory system)

GHS LABEL ELEMENTS**Symbol(s)****Signal Word**

DANGER

Hazard Statement(s)

Extremely flammable gas

Contains gas under pressure; may explode if heated

Causes skin irritation

Causes eye irritation

May cause respiratory irritation

May cause drowsiness and dizziness

Safety Data Sheet

Material Name: DIMETHYL ETHER

SDS ID: 00244291

Precautionary Statement(s)

Prevention

Keep away from heat, sparks, open flame, and hot surfaces - No smoking. Avoid breathing gas. Wash thoroughly after handling. Wear protective gloves. Use only outdoors or in a well-ventilated area.

Response

Leaking gas fire: Do not extinguish, unless leak can be stopped safely. Eliminate all ignition sources if safe to do so. IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing. Call a POISON CENTER or doctor/physician if you feel unwell. IF ON SKIN: Wash with plenty of soap and water. If skin irritation occurs: Get medical advice/attention. Take off contaminated clothing and wash before re-use. IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. If eye irritation persists: Get medical advice/attention.

Storage

Store in a well-ventilated place. Protect from sunlight. Keep container tightly closed. Store locked up.

Disposal

Dispose of in accordance with applications with applicable regulations.

Other Hazards which do not Result in Classification

May cause frostbite upon sudden release of compressed gas.

* * * Section 3 - COMPOSITION / INFORMATION ON INGREDIENTS* * *

CAS#	Component	Percent
115-10-6	Dimethyl ether	100

* * * Section 4 - FIRST AID MEASURES* * *

Inhalation

If adverse effects occur, remove to uncontaminated area. Give artificial respiration if not breathing. If breathing is difficult, oxygen should be administered by qualified personnel. Get immediate medical attention.

Skin

If frostbite or freezing occur, immediately flush with plenty of lukewarm water (105-115 F; 41-46 C). DO NOT USE HOT WATER. If warm water is not available, gently wrap affected parts in blankets. Get immediate medical attention.

Eyes

Flush eyes with plenty of water for at least 15 minutes. Then get immediate medical attention.

Ingestion

If a large amount is swallowed, get medical attention.

Note to Physicians

For inhalation, consider oxygen.

Symptoms: Immediate

respiratory tract irritation, skin irritation, eye irritation, central nervous system depression, frostbite

Symptoms: Delayed

No information on significant adverse effects.

* * * Section 5 - FIRE FIGHTING MEASURES* * *

See Section 9 for Flammability Properties

Specific Hazards Arising from the Chemical

Severe fire hazard. Severe explosion hazard. The vapor is heavier than air. Vapors or gases may ignite at distant ignition sources and flash back. Vapor/air mixtures are explosive. Containers may rupture or explode if exposed to heat. Electrostatic discharges may be generated by flow or agitation resulting in ignition or explosion.

Safety Data Sheet

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SDS ID: 00244291

Extinguishing Media

carbon dioxide, regular dry chemical

Large fires: Flood with fine water spray.

Unsuitable Extinguishing Media

None known.

Protective Equipment and Precautions for Firefighters

Wear full protective fire fighting gear including self contained breathing apparatus (SCBA) for protection against possible exposure.

Fire Fighting Measures

Move container from fire area if it can be done without risk. Cool containers with water spray until well after the fire is out. Stay away from the ends of tanks. For fires in cargo or storage area: Cool containers with water from unmanned hose holder or monitor nozzles until well after fire is out. If this is impossible then take the following precautions: Keep unnecessary people away, isolate hazard area and deny entry. Let the fire burn. Withdraw immediately in case of rising sound from venting safety device or any discoloration of tanks due to fire. For tank, rail car or tank truck: Stop leak if possible without personal risk. Let burn unless leak can be stopped immediately. For smaller tanks or cylinders, extinguish and isolate from other flammables. Evacuation radius: 800 meters (1/2 mile). Do not attempt to extinguish fire unless flow of material can be stopped first. Flood with fine water spray. Cool containers with water spray until well after the fire is out. Apply water from a protected location or from a safe distance. Avoid inhalation of material or combustion by-products. Stay upwind and keep out of low areas. Evacuate if fire gets out of control or containers are directly exposed to fire. Evacuation radius: 500 meters (1/3 mile). Consider downwind evacuation if material is leaking.

Hazardous Combustion Products

Combustion: formaldehyde, oxides of carbon, peroxides

* * * Section 6 - ACCIDENTAL RELEASE MEASURES* * *

Personal Precautions

Wear personal protective clothing and equipment, see Section 8.

Environmental Precautions

Avoid release to the environment.

Methods for Containment

Leaking gas fire: Do not extinguish, unless leak can be stopped safely. Keep unnecessary people away, isolate hazard area and deny entry. Remove sources of ignition. Ventilate closed spaces before entering.

Cleanup Methods

Avoid heat, flames, sparks and other sources of ignition. Do not touch spilled material. Stop leak if possible without personal risk. Reduce vapors with water spray.

* * * Section 7 - HANDLING AND STORAGE* * *

Handling Procedures

Wash thoroughly after handling.

Storage Procedures

Store and handle in accordance with all current regulations and standards. Protect from physical damage. Store outside or in a detached building. Inside storage: Store in a cool, dry place. Store in a well-ventilated area. Avoid heat, flames, sparks and other sources of ignition. Subject to storage regulations: U.S. OSHA 29 CFR 1910.101. Keep separated from incompatible substances.

Incompatibilities combustible materials, halogens, oxidizing materials, strong acids

Safety Data Sheet

Material Name: DIMETHYL ETHER

SDS ID: 00244291

* * * Section 8 - EXPOSURE CONTROLS / PERSONAL PROTECTION* * *

Component Exposure Limits

Dimethyl ether (115-10-6)

Europe: 1000 ppm TWA; 1920 mg/m³ TWA

AIHA: 1000 ppm TWA

Component Biological Limit Values

There are no biological limit values for any of this product's components.

Engineering Controls

Ventilation equipment should be explosion-resistant if explosive concentrations of material are present. Provide local exhaust ventilation system. Ensure compliance with applicable exposure limits.

PERSONAL PROTECTIVE EQUIPMENT

Eyes/Face

Wear splash resistant safety goggles. Contact lenses should not be worn. Provide an emergency eye wash fountain and quick drench shower in the immediate work area.

Protective Clothing

For the gas: Wear appropriate chemical resistant clothing. For the liquid: Wear appropriate protective, cold insulating clothing.

Glove Recommendations

For the gas: Wear appropriate chemical resistant gloves. For the liquid: Wear insulated gloves.

Respiratory Protection

Under conditions of frequent use or heavy exposure, respiratory protection may be needed.

Respiratory protection is ranked in order from minimum to maximum.

Consider warning properties before use.

For Unknown Concentrations or Immediately Dangerous to Life or Health -

Any supplied-air respirator with a full facepiece that is operated in a pressure-demand or other positive-pressure mode in combination with an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive-pressure mode.

Any self-contained breathing apparatus that has a full facepiece and is operated in a pressure-demand or other positive-pressure mode.

* * * Section 9 - PHYSICAL AND CHEMICAL PROPERTIES* * *

Safety Data Sheet

Material Name: DIMETHYL ETHER

SDS ID: 00244291

Physical State:	Gas	Appearance:	Colorless gas
Color:	colorless	Physical Form:	liquefied gas
Odor:	sweet odor	Odor Threshold:	Not available
pH:	Not available	Melting/Freezing Point:	-142 °C
Boiling Point:	-24.8 °C	Flash Point:	-41 °C CC
Decomposition:	Not available	Evaporation Rate:	Not available
LEL:	3.4 %	UEL:	18 %
Vapor Pressure:	77 psia @ 20 °C	Henry's Law Constant:	0.00317683 atm-m3/mol
Vapor Density (air = 1):	1.6	Specific Gravity (water=1):	1.92 g/L @ 25 °C
Water Solubility:	7.6 %	KOW:	891.25 estimated from water solubility
Log KOW:	Not available	Coeff. Water/Oil Dist:	Not available
KOC:	1425.61 estimated from water solubility	Auto Ignition:	350 °C
Viscosity:	Not available	Molecular Weight:	46.08
Molecular Formula:	C ₂ H ₆ O		

Solvent Solubility

Soluble: alcohol, ether, chloroform, acetone, organic solvents

* * * Section 10 - STABILITY AND REACTIVITY* * *

Chemical Stability

May form explosive peroxides. Avoid prolonged storage or contact with air, light or storage and use above room temperature.

Conditions to Avoid

Avoid heat, flames, sparks and other sources of ignition. Minimize contact with material. Containers may rupture or explode if exposed to heat.

Possibility of Hazardous Reactions

Will not polymerize.

Incompatible Materials

combustible materials, halogens, oxidizing materials, strong acids

Hazardous Decomposition

Combustion: formaldehyde, oxides of carbon, peroxides

* * * Section 11 - TOXICOLOGICAL INFORMATION* * *

Acute and Chronic Toxicity

Component Analysis - LD50/LC50

The components of this material have been reviewed in various sources and the following selected endpoints are published:

Dimethyl ether (115-10-6)

Inhalation LC50 Rat 308.5 mg/L 4 h

Safety Data Sheet

Material Name: DIMETHYL ETHER

SDS ID: 00244291

RTECS Acute Toxicity (selected)

The components of this material have been reviewed, and RTECS publishes the following endpoints:

Dimethyl ether (115-10-6)

Inhalation: 93000 mg/m³/15 minute(s) Inhalation Mouse LC50; 72600 mg/m³/30 minute(s) Inhalation Mouse LC50
164000 ppm/4 hour Inhalation Rat LC50; 309 gm/m³/4 hour Inhalation Rat LC50; 308 gm/m³ Inhalation Rat LC50

Acute Toxicity Level

Dimethyl ether (115-10-6)

Slightly Toxic: inhalation

Immediate Effects

respiratory tract irritation, skin irritation, eye irritation, central nervous system depression, frostbite

Delayed Effects

No information on significant adverse effects.

Irritation/Corrosivity Data

No animal testing data available for skin or eyes.

RTECS Irritation

The components of this material have been reviewed and RTECS publishes no data as of the date on this document.

Local Effects

Dimethyl ether (115-10-6)

Irritant: inhalation, skin, eye

Target Organs

Dimethyl ether (115-10-6)

central nervous system

Respiratory Sensitizer

No data available.

Dermal Sensitizer

No data available.

Carcinogenicity

Component Carcinogenicity

None of this product's components are listed by ACGIH, IARC, NTP, OSHA or DFG.

Mutagenic Data

No data available.

RTECS Mutagenic

The components of this material have been reviewed, and RTECS publishes data for one or more components.

RTECS Reproductive Effects

The components of this material have been reviewed, and RTECS publishes the following endpoints:

Dimethyl ether (115-10-6)

200 mg/kg Intraperitoneal Hamster TD_{Lo} (pregnant 8 day(s)); 20000 ppm Inhalation Rat TC_{Lo} (pregnant 6-15 day(s))

Tumorigenic Data

No data available.

RTECS Tumorigenic

The components of this material have been reviewed, and RTECS publishes data for one or more components.

Specific Target Organ Toxicity - Single Exposure

respiratory system, skin, eye, central nervous system

Safety Data Sheet

Material Name: DIMETHYL ETHER

SDS ID: 00244291

Specific Target Organ Toxicity - Repeated Exposure

No data available.

Aspiration Hazard

Not applicable.

Medical Conditions Aggravated by Exposure

None known.

* * * Section 12 - ECOLOGICAL INFORMATION* * *

Component Analysis - Aquatic Toxicity

No LOLI ecotoxicity data are available for this product's components.

Persistence and Degradability

No data available.

Bioaccumulative Potential

No data available.

Mobility in Environmental Media

No data available.

* * * Section 13 - DISPOSAL CONSIDERATIONS* * *

Disposal Methods

Dispose in accordance with all applicable regulations. Subject to disposal regulations: U.S. EPA 40 CFR 262.

Hazardous Waste Number(s): D001.

Component Waste Numbers

The U.S. EPA has not published waste numbers for this product's components.

* * * Section 14 - TRANSPORT INFORMATION* * *

US DOT Information

Shipping Name: Dimethyl ether

UN/NA #: UN1033 **Hazard Class:** 2.1

Required Label(s): 2.1

IMDG Information

Shipping Name: Dimethyl ether

UN #: UN1033 **Hazard Class:** 2.1

* * * Section 15 - REGULATORY INFORMATION* * *

Component Analysis

U.S. Federal Regulations

None of this products components are listed under SARA Sections 302/304 (40 CFR 355 Appendix A), SARA Section 313 (40 CFR 372.65), CERCLA (40 CFR 302.4), TSCA 12(b), or require an OSHA process safety plan.

SARA 311/312 Hazardous Categories

Acute Health: Yes **Chronic Health:** No **Fire:** Yes **Pressure:** Yes **Reactive:** No

U.S. State Regulations

The following components appear on one or more of the following state hazardous substances lists:

Component	CAS	CA	MA	MN	NJ	PA
Dimethyl ether	115-10-6	No	Yes	Yes	Yes	Yes

Not regulated under California Proposition 65

Safety Data Sheet

Material Name: DIMETHYL ETHER

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Component Analysis - Inventory

Component	CAS	US	CA	EU	AU	PH	JP	KR	CN	NZ
Dimethyl ether	115-10-6	Yes	DSL	EIN	Yes	Yes	Yes	Yes	Yes	Yes

* * * Section 16 - OTHER INFORMATION* * *

NFPA Ratings: Health: 2 Fire: 4 Reactivity: 1

Hazard Scale: 0 = Minimal 1 = Slight 2 = Moderate 3 = Serious 4 = Severe

Key / Legend

ACGIH - American Conference of Governmental Industrial Hygienists; ADR - European Road Transport; AU - Australia; BOD - Biochemical Oxygen Demand; C - Celsius; CA - Canada; CAS - Chemical Abstracts Service; CERCLA - Comprehensive Environmental Response, Compensation, and Liability Act; CN - China; CPR - Controlled Products Regulations; DFG - Deutsche Forschungsgemeinschaft; DOT - Department of Transportation; DSL - Domestic Substances List; EEC - European Economic Community; EINECS - European Inventory of Existing Commercial Chemical Substances; EPA - Environmental Protection Agency; EU - European Union; F - Farenheit; IARC - International Agency for Research on Cancer; IATA - International Air Transport Association; ICAO - International Civil Aviation Organization; IDL - Ingredient Disclosure List; IMDG - International Maritime Dangerous Goods; JP - Japan; Kow - Octanol/water partition coefficient; KR - Korea; LEL - Lower Explosive Limit; LOLI - List Of Lists™ - ChemADVISOR's Regulatory Database; MAK - Maximum Concentration Value in the Workplace; MEL - Maximum Exposure Limits; NFPA - National Fire Protection Agency; NIOSH - National Institute for Occupational Safety and Health; NJTSR - New Jersey Trade Secret Registry; NTP - National Toxicology Program; NZ - New Zealand; OSHA - Occupational Safety and Health Administration; PH - Philippines; RCRA - Resource Conservation and Recovery Act; RID - European Rail Transport; RTECS - Registry of Toxic Effects of Chemical Substances®; SARA - Superfund Amendments and Reauthorization Act; STEL - Short-term Exposure Limit; TDG - Transportation of Dangerous Goods; TSCA - Toxic Substances Control Act; TWA - Time Weighted Average; UEL - Upper Explosive Limit; US - United States

Other Information

Matheson Tri-Gas, Inc. makes no express or implied warranties, guarantees or representations regarding the product or the information herein, including but not limited to any implied warranty or merchantability or fitness for use. Matheson Tri-Gas, Inc. shall not be liable for any personal injury, property or other damages of any nature, whether compensatory, consequential, exemplary, or otherwise, resulting from any publication, use or reliance upon the information herein.

End of Sheet 00244291

Appendix D

Estimation of Dimethyl Ether (DME) concentrations in water following the use of water spray to knock-down DME vapors.

To explore the potential for DME to reach groundwater, a hypothetical release scenario is proposed. The purpose of this calculation is to estimate the concentration of DME in water that may accumulate when a water spray is used to knock-down DME vapors as recommended by the Association of American Railroads (2005) and DME Safety Data Sheet (Appendix C).

The assumptions used are:

- There is a bulk DME release from a tanker truck transporting DME.
- The DME forms a cold, dense vapor cloud that migrates to a drainage ditch near the road. There is no water in the ditch at the time of the DME release. No wind is assumed.
- First responders determine that the DME air concentration in the ditch is 18%, which is above the Lower Flammable Limit of 3.4% and below the Upper Flammable Limit of 27%.
- Fearful that the DME vapors will find an ignition source, they decide to knock-down the vapors using a water spray. They spray 3000 gallons into the vapor cloud.
- Spray water interacts with the DME vapors according to Henry's Law. The dimensionless Henry's Law ratio K_{aw} is $\sim 0.3 \text{ mg/m}^3(\text{air})$ per $\text{mg/m}^3(\text{water})$ which means that K_{wa} is around $0.6 \text{ mg/m}^3(\text{water})$ per $\text{mg/m}^3(\text{air})$.
- Once the vapor is washed into the mixture of water and soil within the ditch it will begin slowly re-volatilizing but some DME contaminated water could penetrate deeper into the soil.

We consider the following highly simplified calculation as a rough yet conservative estimate of a potential groundwater concentration of DME that may originate from a spill of a given initial mass of DME. We assume the DME release creates a low-lying vapor cloud at a given initial concentration (g DME per m^3 of air/vapor), $C_a(t=0) = M_{air}(t=0)/V_{air}$. In the most conservative case, this initial concentration is equal to the density of pure DME vapor, that is $\sim 2.5 \text{ g/m}^3$.

We treat the “knock-down” strategy of spraying a fine mist of water through this cloud as a flow of water through the vapor cloud at rate Q_w and we assume complete mixing so that the washout water is in Henry's law equilibrium with the DME vapor cloud, *i.e.* the the air/vapor concentration of DME, C_{air} , is related to the aqueous concentration of DME, $C_{aqueous}$, by $C_{air} = K_H C_{aqueous}$. Alternatively, $C_{aqueous} = C_{air}/K_H$. The (dimensionless) Henry's law-based partitioning coefficient K_H is ~ 0.3 , similar to that of benzene. Note that maximum expected aqueous concentration $C_{aqueous}$ is equal to the maximum expected C_{air} divided by K_H , that is the density of pure DME vapor divided by K_H , that is $\sim 8.3 \text{ g/m}^3$. This value is below the reported solubility of DME ($\sim 71 \text{ g/m}^3$) so solubility limits are not expected to be reached.

We can estimate the way that the DME vapor/air cloud is washed out by treating the vapor/air volume as a constant and allowing the water flowing through this volume at rate Q_w to leave the volume with concentration equal to the Henry's law equilibrium concentration. In this case, the rate of loss of DME mass from the vapor cloud is equal to the flow rate of water multiplied by the concentration of DME in that water:

$$\text{rate} = -Q_w C_{\text{aqueous}}(t)$$

but the concentration of DME in the water $C_{\text{aqueous}}(t)$ is assumed always in equilibrium with the concentration of the DME in the vapor/air cloud $C_{\text{air}}(t)$, so

$$\text{rate} = -Q_w C_{\text{air}}(t) / K_H$$

and the definition of the vapor/air cloud concentration $C_{\text{air}}(t)$ is $M_{\text{air}}(t)/V_{\text{air}}$, so the rate is

$$\text{rate} = -[Q_w / (K_H V_{\text{air}})] M_{\text{air}}(t).$$

Thus the rate of loss of mass from the vapor/air cloud is analogous to the rate of radioactive decay, with decay or loss rate coefficient equal to $Q_w / (K_H V_{\text{air}})$. The corresponding solution states that the mass of DME remaining in the vapor/air cloud at time t is

$$M_{\text{air}}(t) = M_{\text{air}}(t=0) \exp[-Q_w / (K_H V_{\text{air}}) t]$$

then

$$M_{\text{aqueous}}(t) = M_{\text{air}}(t=0) (1 - \exp[-Q_w / (K_H V_{\text{air}}) t]).$$

Then the concentration in the water effluent pool is

$$C_{\text{aqueous}}(t) = M_{\text{aqueous}}(t)/V_w(t)$$

where the volume of water in the pool is $Q_w t$ (m^3).

The maximum aqueous concentration $C_{\text{aqueous}}(t)$ occurs at $t=0$ and this is $M_{\text{aqueous}}(0)/V_w(0)$ that can be shown to be

$$= M_{\text{air}}(t=0) / (K_H V_{\text{air}}).$$

Inserting the DME vapor density as the most conservative value of $M_{\text{air}}(t=0) / V_{\text{air}}$, and using the reported value for K_H of 0.3, the maximum concentration in the water pool that may reach groundwater is $\sim 8.33 \text{ g/m}^3$.

Because the maximum concentration of DME in the knock-down water occurs at the beginning of the knock-down spray, the longer the vapor/air cloud is sprayed, the more DME mass is contributed to the groundwater, but at an increasing overall dilution, with the result that longer sprays lead to lower overall concentrations in the source to groundwater.

The basic result is that the upper bound on the concentration assuming Henry's law equilibrium is that aqueous concentration in Henry's law equilibrium with pure DME vapor which gives $\sim 8\text{-}10 \text{ g/m}^3$.

Appendix E

DME Process Safety Management

Process Safety Management (PSM) Programs require facilities to do the following:

- (1) Develop and maintain written safety information identifying workplace chemical and process hazards, equipment used in the processes, and technology used in the processes;
- (2) Perform a workplace hazard assessment including, as appropriate, identification of potential sources of accidental releases, identification of any previous release within the facility that had a potential for catastrophic consequences in the workplace, estimation of workplace effects of a range of releases, and estimation of the health and safety effects of such a range on employees;
- (3) Consult with employees and their representatives on the development and conduct of hazard assessments and the development of chemical accident prevention plans and provide access to these and other records required under the standard;
- (4) Establish a system to respond to the workplace hazard assessment findings, which shall address prevention, mitigation, and emergency responses;
- (5) Review periodically the workplace hazard assessment and response system;
- (6) Develop and implement written operating procedures for the chemical processes, including procedures for each operating phase, operating limitations, and safety and health considerations;
- (7) Provide written safety and operating information for employees and employee training in operating procedures, by emphasizing hazards and safe practices that must be developed and made available;
- (8) Ensure contractors and contract employees are provided with appropriate information and training;
- (9) Train and educate employees and contractors in emergency response procedures in a manner as comprehensive and effective as that required by the regulation promulgated pursuant to section 126(d) of the Superfund Amendments and Reauthorization Act;
- (10) Establish a quality assurance program to ensure that initial process-related equipment, maintenance materials, and spare parts are fabricated and installed consistent with design specifications;
- (11) Establish maintenance systems for critical process-related equipment, including written procedures, employee training, appropriate inspections, and testing of such equipment to ensure ongoing mechanical integrity;
- (12) Conduct pre-startup safety reviews of all newly installed or modified equipment;

(13) Establish and implement written procedures managing change to process chemicals, technology, equipment and facilities; and

(14) Investigate every incident that results in or could have resulted in a major accident in the workplace, with any findings to be reviewed by operating personnel and modifications made, if appropriate.

As part of the PSM program, Standard Operating Procedures (SOPs) are developed which cover every aspect of operating the methanol plant. Each SOP includes the following steps and operating limits:

Steps for each operating phase:

- Initial startup;
- Normal operations;
- Temporary operations;
- Emergency shutdown, including the conditions under which emergency shutdown is required, and the assignment of shut down responsibility to qualified operators to ensure that emergency shutdown is executed in a safe and timely manner;
- Emergency operations;
- Normal shutdown; and
- Startup following a turnaround, or after an emergency shut down.

Operating limits:

- Consequences of deviation, and
- Steps required to correct or avoid deviation.
- Safety and health considerations:
- Properties of, and hazards presented by, the chemicals used in the process;
- Precautions necessary to prevent exposure, including engineering controls, administrative controls, and personal protective equipment;
- Control measures to be taken if physical contact or airborne exposure occurs;
- Quality control for raw materials and control of hazardous chemical inventory levels; and
- Any special or unique hazards.
- Safety systems (*e.g.*, interlocks, detection or suppression systems) and their functions.

Other requirements of PSM documentation include the following:

Information on the hazards of the highly hazardous chemicals in the process shall consist of at least the following:

- Toxicity,
- Permissible exposure limits,
- Physical data,
- Reactivity data,
- Corrosivity data, and

- Thermal and chemical stability data, and hazardous effects of inadvertent mixing of different materials.

Information on the technology of the process must include at least the following:

- A block flow diagram or simplified process flow diagram,
- Process chemistry,
- Maximum intended inventory,
- Safe upper and lower limits for such items as temperatures, pressures, flows or compositions, and
- An evaluation of the consequences of deviations, including those affecting the safety and health of employees.

Information on the equipment in the process must include the following:

- Materials of construction,
- Piping and instrument diagrams (P&IDs),
- Electrical classification,
- Relief system design and design basis,
- Ventilation system design,
- Design codes and standards employed,
- Material and energy balances for processes built after May 26, 1992, and
- Safety systems (e.g., interlocks, detection, or suppression systems).

More specific information on training is as follows:

Initial Training: OSHA believes that the implementation of an effective training program is one of the most important steps that an employer can take to enhance employee safety. Accordingly, PSM requires that each employee presently involved in operating a process or a newly assigned process must be trained in an overview of the process and in its operating procedures. The training must include emphasis on the specific safety and health hazards of the process, emergency operations including shutdown, and other safe work practices that apply to the employee's job tasks. Those employees already involved in operating a process on the PSM effective date do not necessarily need to be given initial training. Instead, the employer may certify in writing that the employees have the required knowledge, skills, and abilities to safely carry out the duties and responsibilities specified in the operating procedures.

Refresher Training: Refresher training must be provided at least every three years, or more often if necessary, to each employee involved in operating a process to ensure that the employee understands and adheres to the current operating procedures of the process. The employer, in consultation with the employees involved in operating the process, must determine the appropriate frequency of refresher training.

Training Documentation: The employer must determine whether each employee operating a process has received and understood the training required by PSM. A record must be kept

containing the identity of the employee, the date of training, and how the employer verified that the employee understood the training.

Appendix F

Airgas Material Safety Data Sheet (MSDS) for Dimethyl Ether

Material Safety Data Sheet



Dimethyl Ether

Section 1. Chemical product and company identification

Product name	: Dimethyl Ether
Supplier	: AIRGAS INC., on behalf of its subsidiaries 259 North Radnor-Chester Road Suite 100 Radnor, PA 19087-5283 1-610-687-5253
Product use	: Synthetic/Analytical chemistry.
Synonym	: dimethyl ether (dot); ether, dimethyl; ether, methyl; wood ether; methyl ether
MSDS #	: 001021
Date of Preparation/Revision	: 4/26/2010.
In case of emergency	: 1-866-734-3438

Section 2. Hazards identification

Physical state	: Gas. [COLORLESS LIQUEFIED GAS WITH A PLEASANT ODOR]
Emergency overview	: WARNING! FLAMMABLE GAS. MAY CAUSE FLASH FIRE. CAN CAUSE TARGET ORGAN DAMAGE. CONTENTS UNDER PRESSURE. Keep away from heat, sparks and flame. Do not puncture or incinerate container. Can cause target organ damage. Use only with adequate ventilation. Keep container closed. Contact with rapidly expanding gases can cause frostbite.
Target organs	: Causes damage to the following organs: skin, eyes.
Routes of entry	: Inhalation
Potential acute health effects	
Eyes	: Contact with rapidly expanding gas may cause burns or frostbite.
Skin	: Contact with rapidly expanding gas may cause burns or frostbite.
Inhalation	: Acts as a simple asphyxiant.
Ingestion	: Ingestion is not a normal route of exposure for gases
Potential chronic health effects	: CARCINOGENIC EFFECTS: Not available. MUTAGENIC EFFECTS: Not available. TERATOGENIC EFFECTS: Not available.
Medical conditions aggravated by over-exposure	: Pre-existing disorders involving any target organs mentioned in this MSDS as being at risk may be aggravated by over-exposure to this product.

See toxicological information (section 11)

Section 3. Composition, Information on Ingredients

Name	CAS number	% Volume	Exposure limits
Dimethyl Ether	115-10-6	100	AIHA WEEL (United States, 1/2009). TWA: 1000 ppm 8 hour(s).

Section 4. First aid measures

No action shall be taken involving any personal risk or without suitable training. If it is suspected that fumes are still present, the rescuer should wear an appropriate mask or self-contained breathing apparatus. It may be dangerous to the person providing aid to give mouth-to-mouth resuscitation.

- Eye contact** : Check for and remove any contact lenses. Immediately flush eyes with plenty of water for at least 15 minutes, occasionally lifting the upper and lower eyelids. Get medical attention immediately.
- Skin contact** : In case of contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. To avoid the risk of static discharges and gas ignition, soak contaminated clothing thoroughly with water before removing it. Wash clothing before reuse. Clean shoes thoroughly before reuse. Get medical attention immediately.
- Frostbite** : Try to warm up the frozen tissues and seek medical attention.
- Inhalation** : Move exposed person to fresh air. If not breathing, if breathing is irregular or if respiratory arrest occurs, provide artificial respiration or oxygen by trained personnel. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention immediately.
- Ingestion** : As this product is a gas, refer to the inhalation section.

Section 5. Fire-fighting measures

- Flammability of the product** : Flammable.
- Auto-ignition temperature** : 349.85°C (661.7°F)
- Flash point** : Closed cup: -41.15°C (-42.1°F).
- Flammable limits** : Lower: 3.4% Upper: 27%
- Products of combustion** : Decomposition products may include the following materials:
carbon dioxide
carbon monoxide
- Fire-fighting media and instructions** : In case of fire, use water spray (fog), foam or dry chemical.

In case of fire, allow gas to burn if flow cannot be shut off immediately. Apply water from a safe distance to cool container and protect surrounding area. If involved in fire, shut off flow immediately if it can be done without risk.

Contains gas under pressure. Flammable gas. In a fire or if heated, a pressure increase will occur and the container may burst, with the risk of a subsequent explosion.
- Special protective equipment for fire-fighters** : Fire-fighters should wear appropriate protective equipment and self-contained breathing apparatus (SCBA) with a full face-piece operated in positive pressure mode.

Section 6. Accidental release measures

- Personal precautions** : Immediately contact emergency personnel. Keep unnecessary personnel away. Use suitable protective equipment (section 8). Shut off gas supply if this can be done safely. Isolate area until gas has dispersed.
- Environmental precautions** : Avoid dispersal of spilled material and runoff and contact with soil, waterways, drains and sewers.
- Methods for cleaning up** : Immediately contact emergency personnel. Stop leak if without risk. Use spark-proof tools and explosion-proof equipment. Note: see section 1 for emergency contact information and section 13 for waste disposal.

Section 7. Handling and storage

- Handling** : Use only with adequate ventilation. Use explosion-proof electrical (ventilating, lighting and material handling) equipment. High pressure gas. Do not puncture or incinerate container. Use equipment rated for cylinder pressure. Close valve after each use and when empty. Keep container closed. Keep away from heat, sparks and flame. To avoid fire, eliminate ignition sources. Protect cylinders from physical damage; do not drag, roll, slide, or drop. Use a suitable hand truck for cylinder movement.

Dimethyl Ether

Storage

: Keep container in a cool, well-ventilated area. Keep container tightly closed and sealed until ready for use. Avoid all possible sources of ignition (spark or flame). Segregate from oxidizing materials. Cylinders should be stored upright, with valve protection cap in place, and firmly secured to prevent falling or being knocked over. Cylinder temperatures should not exceed 52 °C (125 °F).

Section 8. Exposure controls/personal protection

Engineering controls

: Use only with adequate ventilation. Use process enclosures, local exhaust ventilation or other engineering controls to keep worker exposure to airborne contaminants below any recommended or statutory limits. The engineering controls also need to keep gas, vapor or dust concentrations below any lower explosive limits. Use explosion-proof ventilation equipment.

Personal protection

Eyes

: Safety eyewear complying with an approved standard should be used when a risk assessment indicates this is necessary to avoid exposure to liquid splashes, mists or dusts.

Skin

: Personal protective equipment for the body should be selected based on the task being performed and the risks involved and should be approved by a specialist before handling this product.

Respiratory

: Use a properly fitted, air-purifying or air-fed respirator complying with an approved standard if a risk assessment indicates this is necessary. Respirator selection must be based on known or anticipated exposure levels, the hazards of the product and the safe working limits of the selected respirator.

The applicable standards are (US) 29 CFR 1910.134 and (Canada) Z94.4-93

Hands

: Chemical-resistant, impervious gloves complying with an approved standard should be worn at all times when handling chemical products if a risk assessment indicates this is necessary.

Personal protection in case of a large spill

: Self-contained breathing apparatus (SCBA) should be used to avoid inhalation of the product.

Product name

dimethyl ether

AIHA WEEL (United States, 1/2009).

TWA: 1000 ppm 8 hour(s).

Consult local authorities for acceptable exposure limits.

Section 9. Physical and chemical properties

Molecular weight : 46.08 g/mole

Molecular formula : C₂-H₆-O

Boiling/condensation point : -23.7°C (-10.7°F)

Melting/freezing point : -138.5°C (-217.3°F)

Critical temperature : 127°C (260.6°F)

Vapor density : 1.62 (Air = 1)

Specific Volume (ft³/lb) : 8.1833

Gas Density (lb/ft³) : 0.1222

Section 10. Stability and reactivity

Stability and reactivity : The product is stable.

Incompatibility with various substances : Highly reactive or incompatible with the following materials: oxidizing materials and metals.

Hazardous decomposition products : Under normal conditions of storage and use, hazardous decomposition products should not be produced.

Hazardous polymerization : Under normal conditions of storage and use, hazardous polymerization will not occur.

Section 11. Toxicological information

Toxicity data

Product/ingredient name	Result	Species	Dose	Exposure
dimethyl ether	LC50 Inhalation Vapor	Rat	309 g/m3	4 hours
	LC50 Inhalation Gas.	Rat	82000 ppm	1 hours

Chronic effects on humans : Causes damage to the following organs: skin, eyes.

Other toxic effects on humans : No specific information is available in our database regarding the other toxic effects of this material to humans.

Specific effects

Carcinogenic effects : No known significant effects or critical hazards.

Mutagenic effects : No known significant effects or critical hazards.

Reproduction toxicity : No known significant effects or critical hazards.

Section 12. Ecological information

Aquatic ecotoxicity

Not available.

Products of degradation : Products of degradation: carbon oxides (CO, CO₂) and water.

Environmental fate : Not available.

Environmental hazards : No known significant effects or critical hazards.

Toxicity to the environment : Not available.

Section 13. Disposal considerations

Product removed from the cylinder must be disposed of in accordance with appropriate Federal, State, local regulation.Return cylinders with residual product to Airgas, Inc.Do not dispose of locally.

Section 14. Transport information

Regulatory information	UN number	Proper shipping name	Class	Packing group	Label	Additional information
DOT Classification	UN1033	DIMETHYL ETHER	2.1	Not applicable (gas).		<p>Limited quantity Yes.</p> <p>Packaging instruction Passenger aircraft Quantity limitation: Forbidden.</p> <p>Cargo aircraft Quantity limitation: 150 kg</p> <p>Special provisions T50</p>

Dimethyl Ether

TDG Classification	UN1033	DIMETHYL ETHER	2.1	Not applicable (gas).		Explosive Limit and Limited Quantity Index 0.125 ERAP Index 3000 Passenger Carrying Ship Index Forbidden Passenger Carrying Road or Rail Index Forbidden
Mexico Classification	UN1033	DIMETHYL ETHER	2.1	Not applicable (gas).		-

"Refer to CFR 49 (or authority having jurisdiction) to determine the information required for shipment of the product."

Section 15. Regulatory information

United States

- U.S. Federal regulations** : **United States inventory (TSCA 8b):** This material is listed or exempted.
SARA 302/304/311/312 extremely hazardous substances: No products were found.
SARA 302/304 emergency planning and notification: No products were found.
SARA 302/304/311/312 hazardous chemicals: dimethyl ether
SARA 311/312 MSDS distribution - chemical inventory - hazard identification: dimethyl ether: Fire hazard, Sudden release of pressure
Clean Water Act (CWA) 307: No products were found.
Clean Water Act (CWA) 311: No products were found.
Clean Air Act (CAA) 112 accidental release prevention: dimethyl ether
Clean Air Act (CAA) 112 regulated flammable substances: dimethyl ether
Clean Air Act (CAA) 112 regulated toxic substances: No products were found.
- State regulations** : **Connecticut Carcinogen Reporting:** This material is not listed.
Connecticut Hazardous Material Survey: This material is not listed.
Florida substances: This material is not listed.
Illinois Chemical Safety Act: This material is not listed.
Illinois Toxic Substances Disclosure to Employee Act: This material is not listed.
Louisiana Reporting: This material is not listed.
Louisiana Spill: This material is not listed.
Massachusetts Spill: This material is not listed.
Massachusetts Substances: This material is listed.
Michigan Critical Material: This material is not listed.
Minnesota Hazardous Substances: This material is not listed.
New Jersey Hazardous Substances: This material is listed.
New Jersey Spill: This material is not listed.
New Jersey Toxic Catastrophe Prevention Act: This material is not listed.
New York Acutely Hazardous Substances: This material is not listed.
New York Toxic Chemical Release Reporting: This material is not listed.
Pennsylvania RTK Hazardous Substances: This material is listed.
Rhode Island Hazardous Substances: This material is not listed.

Dimethyl Ether

Canada

WHMIS (Canada)

- : Class A: Compressed gas.
- Class B-1: Flammable gas.
- CEPA Toxic substances:** This material is not listed.
- Canadian RET:** This material is not listed.
- Canadian NPRI:** This material is listed.
- Alberta Designated Substances:** This material is not listed.
- Ontario Designated Substances:** This material is not listed.
- Quebec Designated Substances:** This material is not listed.

Section 16. Other information

United States

Label requirements

- : FLAMMABLE GAS.
- MAY CAUSE FLASH FIRE.
- CAN CAUSE TARGET ORGAN DAMAGE.
- CONTENTS UNDER PRESSURE.

Canada

Label requirements

- : Class A: Compressed gas.
- Class B-1: Flammable gas.

Hazardous Material Information System (U.S.A.)

Health	*	1
Flammability		4
Physical hazards		1

National Fire Protection Association (U.S.A.)



Notice to reader

To the best of our knowledge, the information contained herein is accurate. However, neither the above-named supplier, nor any of its subsidiaries, assumes any liability whatsoever for the accuracy or completeness of the information contained herein.

Final determination of suitability of any material is the sole responsibility of the user. All materials may present unknown hazards and should be used with caution. Although certain hazards are described herein, we cannot guarantee that these are the only hazards that exist.

Appendix G

Dimethyl Ether Hazard Assessment for Oberon Fuels

January 18, 2013

HAZARD ASSESSMENT

for

OBERON FUELS
5451 Kershaw Road
Brawley, CA 92227

Prepared By:

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HAZARD ASSESSMENT COMPLIANCE MATRIX

Compliance Element	Corresponding Fed-EPA 40 CFR Section	Corresponding CalARP CCR Chapter 4.5 Section	Document Section
The owner or operator of a stationary source subject to this part shall prepare a worst-case release scenario analysis as provided below and complete the five-year accident history as provided. The owner or operator of a Program 2 and 3 process must comply with all sections below in this subpart for these processes.	§68.20	§2750.1	2,4
Offsite consequence analysis parameters: Endpoints.	§68.22(a)	§2750.2(a)	1
Toxics.	§68.22(a)(1)	§2750.2(a)(1-3)	N/A
Flammables.	§68.22(a)(2)	§2750.2(a)(4)	1
Explosion.	§68.22(a)(2)(i)	§2750.2(a)(4)(A)	1
Radiant heat/exposure time.	§68.22(a)(2)(ii)	§2750.2(a)(4)(B)	NA
Lower flammability limit.	§68.22(a)(2)(iii)	§2750.2(a)(4)(C)	1
Wind speed/atmospheric stability class.	§68.22(b)	§2750.2(b)	4
Ambient temperature/humidity.	§69.22(c)	§2750.2(c)	4
Height of release.	§68.22(d)	§2750.2(d)	N/A
Surface roughness.	§68.22(e)	§2750.2(e)	4
Dense or neutrally buoyant gases.	§68.22(f)	§2750.2(f)	N/A
Temperature of released substance.	§68.22(g)	§2750.2(g)	4
Worst-case release scenario analysis: The owner or operator shall analyze and report in the RMP:	§68.25(a)	§2750.3(a)	2
For Program 1 processes: One worst-case release scenario for each Program 1 process.	§68.25(a)(1)	§2750.3(a)(1)	N/A
For Program 2 and 3 processes: One worst-case release scenario that is estimated to create the greatest distance in any direction to an endpoint as previously defined resulting from an accidental release of regulated toxic substances from covered processes under previously defined worst-case conditions.	§68.25(a)(2) (i-ii)	§2750.3(a)(2) (A-B)	4

Compliance Element	Corresponding Fed-EPA 40 CFR Section	Corresponding CalARP CCR Chapter 4.5 Section	Document Section
Additional worst-case release scenarios for a hazard class if a worst-case release from another covered process at the stationary source potentially affects public receptors different from those potentially affected by the worst-case release scenario developed previously.	§68.25(a)(2)(iii)	§2750.3(a)(2)(C)	N/A
Determination of worst-case release quantity. The worst-case release shall be the greater of the following:	§68.25(b)	§2750.3(b)	2
For substances in a vessel, the greatest amount held in a single vessel, taking into account administrative controls that limit the maximum quantity	§68.25(b)(1)	§2750.3(b)(1)	4
For substances in pipes, the greatest amount in a pipe, taking into account administrative controls that limit the maximum quantity.	§68.25(b)(2)	§2750.3(b)(2)	N/A
Worst-case release scenario toxic gases.	§68.25(c)	§2750.3(c)	N/A
For regulated toxic substances that are normally gases at ambient temperature and handled as a gas or as a liquid under pressure, the owner or operator shall assume that the quantity in the vessel or pipe, as previously determined, is released as a gas over 10 minutes. The release rate shall be assumed to be the total quantity divided by 10 unless passive mitigation systems are in place.	§68.25(c)(1)	§2750.3(c)(1)	N/A
For gases handled as refrigerated liquids at ambient temperature: If the released substance is not contained by passive mitigation systems or if the contained pool would have a depth of 1 cm or less, the owner or operator shall assume that the substance is released as a gas in 10 minutes.	§68.25(c)(2)(i)	§2750.3(c)(2)(A)	N/A
If the released substance is contained by passive mitigation systems in a pool with a depth greater than 1 cm, the owner or operator may assume that the quantity in the vessel or pipe, as determined previously, is spilled instantaneously to form a liquid pool. The volatilization rate (release rate) shall be calculated at the boiling point of the substance and at the conditions previously specified.	§68.25(c)(2)(ii)	§2750.3(c)(2)(B)	N/A
Worst-case release scenario toxic liquids.	§68.25(d)	§2750.3(d)	N/A
For regulated toxic substances that are normally liquids at ambient temperature, the owner or operator shall assume that the quantity in the vessel or pipe, as previously determined, is spilled instantaneously to form a liquid pool.	§68.25(d)(1)	§2750.3(d)(1)	N/A

Compliance Element	Corresponding Fed-EPA 40 CFR Section	Corresponding CalARP CCR Chapter 4.5 Section	Document Section
The surface area of the pool shall be determined by assuming that the liquid spreads to 1 centimeter deep unless passive mitigation systems are in place that serve to contain the spill and limit the surface area. Where passive mitigation is in place, the surface area of the contained liquid shall be used to calculate the volatilization rate.	§68.25(d)(1)(i)	§2750.3(d)(1)(A)	N/A
If the release would occur onto a surface that is not paved or smooth, the owner or operator may take into account the actual surface characteristics.	§68.25(d)(1)(ii)	§2750.3(d)(1)(B)	N/A
The volatilization rate shall account for the highest daily maximum temperature occurring in the past three years, the temperature of the substance in the vessel, and the concentration of the substance if the liquid spilled is a mixture or solution.	§68.25(d)(2)	§2750.3(d)(2)	N/A
The rate of release to air shall be determined from the volatilization rate of the liquid pool.	§68.25(d)(3)	§2750.3(d)(3)	N/A
Worst-case release scenario flammables.	§68.25(e)	§2750.3(e)	4
Parameters to be applied.	§68.25(f)	§2750.3(f)	4
Consideration of passive mitigation.	§68.25(g)	§2750.3(g)	4
Factors in selecting a worst-case scenario:	§68.25(h)	§2750.3(h)	4
Smaller quantities handled at higher process temperature.	§68.25(h)(1)	§2750.3(h)(1)	N/A
Proximity to the boundary of the stationary source.	§68.25(h)(2)	§2750.3(h)(2)	N/A
Solids.	N/A	§2750.3(i)	N/A
Alternative release scenario analysis: The number of scenarios.	§68.28(a)	§2750.4(a)	4
Scenarios to consider.	§68.28(b)	§2750.4(b)	4
For each scenario required under the first part of this section, the owner or operator shall select a scenario:	§68.28(b)(1)	§2750.4(b)(1)	4
That is more likely to occur than the worst-case release scenario.	§68.28(b)(1)(i)	§2750.4(b)(1)(A)	4
That will reach an endpoint off-site, unless no scenario exists.	§68.28(b)(1)(ii)	§2750.4(b)(1)(B)	4
Release scenarios considered should include, but are not limited to, the following, where applicable:	§68.28(b)(2)	§2750.4(b)(2)	4
Transfer hose releases due to splits or sudden hose uncoupling.	§68.28(b)(2)(i)	§2750.4(b)(2)(A)	N/A

Compliance Element	Corresponding Fed-EPA 40 CFR Section	Corresponding CalARP CCR Chapter 4.5 Section	Document Section
Process piping releases from failures at flanges, joints, welds, valves and valve seals, and drains or bleeds.	§68.28(b)(2)(ii)	§2750.4(b)(2)(B)	4
Process vessel or pump releases due to cracks, seal failure, or drain, bleed, or plug failure.	§68.28(b)(2)(iii)	§2750.4(b)(2)(C)	N/A
Vessel overfilling and spill, or over-pressurization and venting through relief valves or rupture discs.	§68.28(b)(2)(iv)	§2750.4(b)(2)(D)	N/A
Shipping container mishandling and breakage or puncturing leading to a spill.	§68.28(b)(2)(v)	§2750.4(b)(2)(E)	N/A
Parameters to be applied.	§68.28(c)	§2750.4(c)	4
Consideration of mitigation.	§68.28(d)	§2750.4(d)	4
Factors in selecting scenarios.	§68.28(e)	§2750.4(e)	4
The five-year accident history as provided.	§68.28(e)(1)	§2750.4(e)(1)	1
Failure scenarios as identified.	§68.28(e)(2)	§2750.4(e)(2)	4
Defining off-site impacts to population: The owner or operator shall estimate in the RMP the population within a circle with its center at the point of the release and a radius determined by the distance to the endpoint previously defined.	§68.30(a)	§2750.5(a)	1,3,4
Population to be defined.	§68.30(b)	§2750.5(b)	1,3,4
Data sources acceptable.	§68.30(c)	§2750.5(c)	3
Level of accuracy.	§68.30(d)	§2750.5(d)	4
Defining off-site impacts to environment: The owner or operator shall list in the RMP environmental receptors within a circle with its center at the point of release and a radius determined by the distance to the endpoint previously defined.	§68.33(a)	§2750.6(a)	3
Data sources acceptable.	§68.33(b)	§2750.6(b)	3
Review and update: The owner or operator shall review and update the off-site consequence analyses at least once every five years.	§68.36(a)	§2750.7(a)	N/A
If changes in processes, quantities stored or handled, or any other aspect of the stationary source might reasonably be expected to increase or decrease the distance to the endpoint by a factor of two or more, the owner or operator shall complete a revised analysis within six months of the change and submit a revised risk management plan.	§68.36(b)	§2750.7(b)	N/A

Compliance Element	Corresponding Fed-EPA 40 CFR Section	Corresponding CalARP CCR Chapter 4.5 Section	Document Section
Documentation: The owner or operator shall maintain the following records on the off-site consequence analysis:	§68.39	§2750.8	4
For worst-case scenarios, a description of the vessel or pipeline and substance selected as worst-case, assumptions and parameters used, and the rationale for selection; assumptions shall include use of any administrative controls and any passive mitigation that were assumed to limit the quantity that could be released. Documentation shall include the anticipated effect of the control sand mitigation on the release quantity and rate.	§68.39(a)	§2750.8(a)	4
For alternative release scenarios, a description of the scenarios identified, assumptions and parameters used, and the rationale for the selection of specific scenarios; assumptions shall include use of any administrative controls and any mitigation that were assumed to limit the quantity that could be released. Documentation shall include the effect of the controls and mitigation on the release quantity and rate.	§68.39(b)	§2750.8(b)	4
Documentation of estimated quantity released, release rate, and duration of release.	§68.39(c)	§2750.8(c)	4
Methodology used to determine distance to endpoints.	§68.39(d)	§2750.8(d)	4
Data used to estimate population and environmental receptors potentially affected.	§68.39(e)	§2750.8(e)	3
Five-year accident history: The owner or operator shall include in the five-year accident history all accidental releases from covered processes that resulted in deaths, injuries, or significant property damage on site, or known off-site deaths, injuries, evacuations, sheltering in place, property damage, or environmental damage.	§68.42(a)	§2750.9(a)	2
Data required:	§68.42(b)(1)	§2750.9(b)	N/A
Date, time, and approximate duration of the release.	§68.42(b)(2)	§2750.9(b)(1)	N/A
Chemical(s) released.	§68.42(b)(3)	§2750.9(b)(2)	N/A
Estimated quantity released in pounds.	§68.42(b)(4)	§2750.9(b)(3)	N/A
The type of release event and its source.	§68.42(b)(5)	§2750.9(b)(4)	N/A
Weather conditions, if known.	§68.42(b)(6)	§2750.9(b)(5)	N/A
On-site impacts.	§68.42(b)(7)	§2750.9(b)(6)	N/A
Known offsite impacts.	§68.42(b)(8)	§2750.9(b)(7)	N/A

Compliance Element	Corresponding Fed-EPA 40 CFR Section	Corresponding CalARP CCR Chapter 4.5 Section	Document Section
Initiating event and contributing factors if known.	§68.42(b)(8)	§2750.9(b)(8)	N/A
Whether offsite responders were notified if known	§68.42(b)(9)	§2750.9(b)(9)	N/A
Operational or process changes that resulted from investigation of the release.	§68.42(b)(10)	§2750.9(b)(10)	N/A
Level of accuracy	§68.42(c)	§2750.9(c)	N/A

N/A: Not Applicable

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1.0 OVERVIEW

1.1 EXECUTIVE SUMMARY

This technical assessment was conducted to fulfill the requirements of the California Accidental Release Prevention (CalARP) Program for the Oberon Fuels Facility in accordance with the California Code of Regulations Title 19, Division 2, Chapter 4.5, Section 2750.

Oberon Fuels is located at 5451 Kershaw Road in Brawley, CA, which is approximately 1 mile north of County Highway S26 and 1 mile east of CA Highway 111. The area immediately surrounding the facility is rural. The facility location with respect to the surrounding area is shown in Figure 1-1.

The regulated substance of concern at the facility is dimethyl ether (DME), which is also referred to as methyl ether. The facility utilizes a methanol to DME conversion process to produce fuel grade DME in accordance with the IEA AMF standard for DME as a fuel for vehicles.

The endpoint requirements for determining the affected downwind distances for the postulated release scenarios for flammable substances are defined under 19 CCR Section 2750.2 (a)(4), Offsite Consequence Analysis Parameters, as follows:

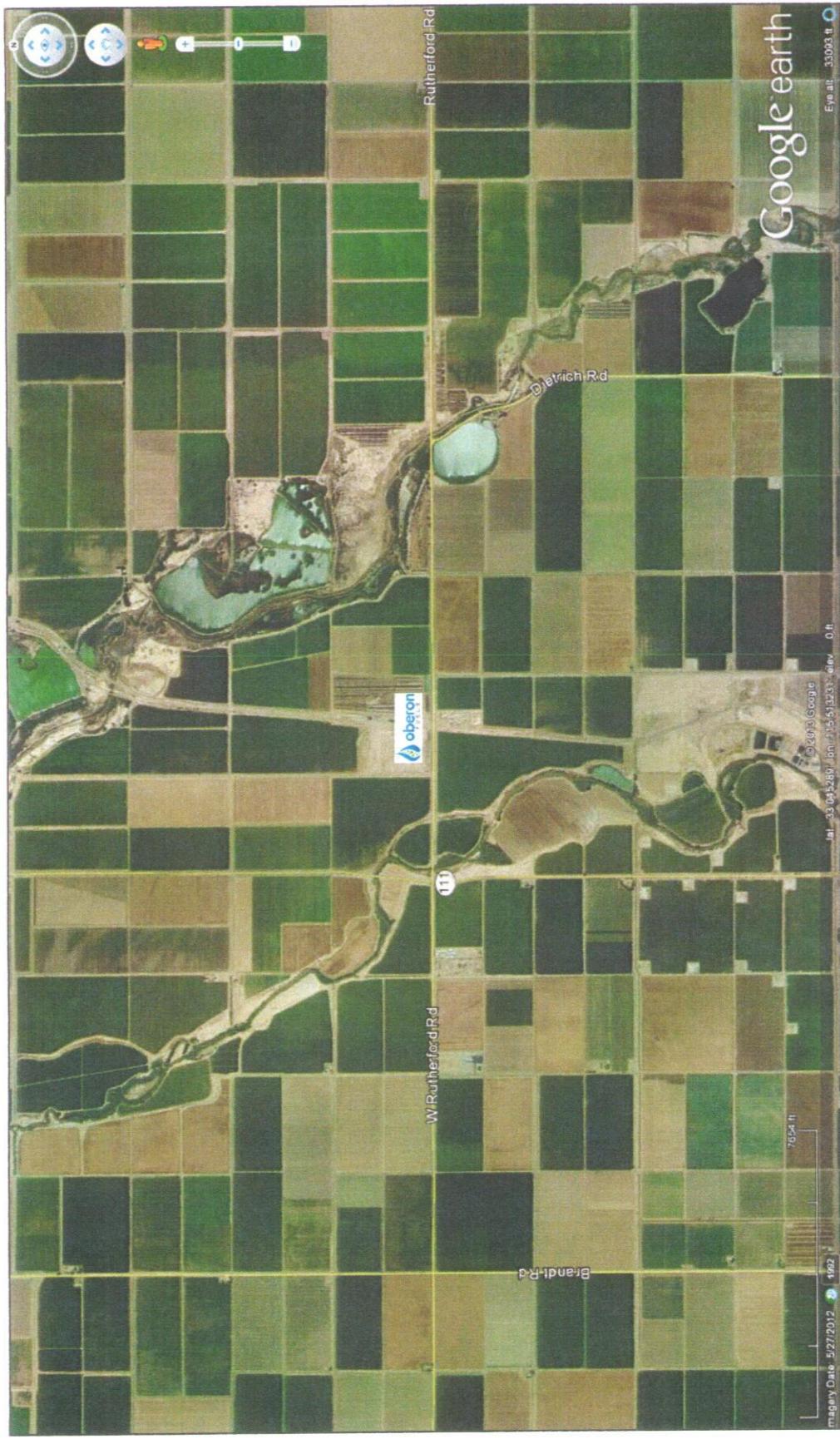
- (A) Explosion. An overpressure of 1 psi.
- (B) Lower Flammability Limit. A lower flammability limit as provided in NFPA documents or other generally recognized sources.

Table 1-1 summarizes the maximum downwind distances reached for the worst case and the alternative release scenarios and the estimated populations that are at risk to being exposed to the endpoints for each release. The at-risk population numbers are the estimated number of people within the radius of the maximum downwind distance reached by the plume in all wind directions.

TABLE 1-1 Summary of Maximum Downwind Distances and At-Risk Populations

Release Scenario	Endpoint	Maximum Downwind Distance to Endpoint	Residential Population at Risk
Worst Case Release	1 psi Overpressure	0.48 Miles	0
Alternative Case Release	Lower Flammability Limit (LFL)	0.10 Mile	0

FIGURE 1-1 Facility Location^[8]



1.2 DESCRIPTION OF CHEMICAL PROCESS AND OPERATING CONDITIONS

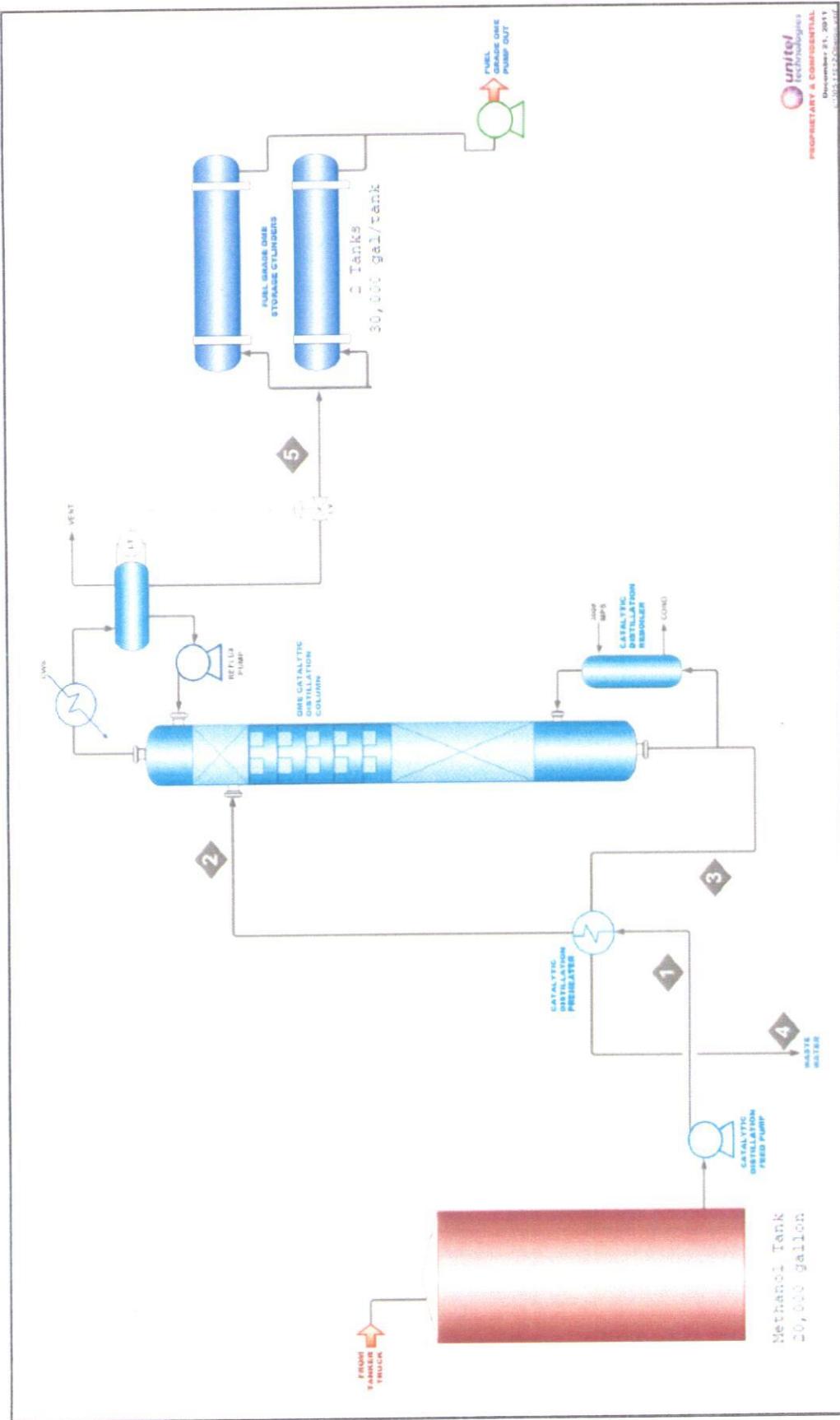
Methanol and dimethyl ether (DME) are used at the new Oberon Fuels facility in Brawley, CA. The process involves converting methanol to DME by means of a catalytic distillation column. The major equipment comprising the process includes a methanol storage tank, methanol pumps, a catalytic distillation (C-D) column, two DME storage vessels, and DME pumps. Typical operating conditions range from 0.1 - 120 psig on the methanol side of the system and from 120 – 140 psig on the DME side of the system.

Table 1-2 lists the Methanol to DME conversion process equipment and Figure 1-2 shows the process flow diagram.

TABLE 1-2 Methanol to DME Conversion Process Equipment

Equipment	Location	State
Methanol Storage Tank (T-100)	Methanol Feed Section	Liquid
Methanol Pumps (P-120A/B)	Methanol Feed Section	Liquid
Methanol Feed Interchanger (HE-140)	C-D Column Section	Liquid
C-D Column (C-200)	C-D Column Section	Liquid / Vapor
C-D Column Reboiler (HE-260)	C-D Column Section	Liquid / Vapor
C-D Column Condenser (HE-220)	C-D Column Section	Liquid / Vapor
C-D Column Reflux Drum (D-220)	C-D Column Section	Liquid
C-D Column Reflux Pumps (P-240A/B)	C-D Column Section	Liquid
DME Storage Tanks (D-400, D-420)	DME Storage Section	Liquid
DME Loading Pumps (P-460A/B)	DME Storage Section	Liquid

FIGURE 1-2 Methanol to DME Conversion Process Flow Diagram



1.3 DME PHYSICAL & CHEMICAL PROPERTIES^[1, 3]

At room temperature and pressure, dimethyl ether (DME) is an odorless, colorless, volatile, flammable gas. The Department of Transportation (DOT) classification for DME is a Class 2.1 Flammable Gas. Table 2-1 lists physical and chemical properties for DME.

TABLE 1-3 Physical & Chemical Properties for DME^[1, 3]

Molecular Symbol	C ₂ H ₆ O
CAS Registry Number	115-10-6
Boiling Point	-24.8°C (-12.7°F)
Melting Point	-141.5°C (-222.7°F)
Vapor Pressure	71.2 psig @ 25°C
Vapor Density (Air = 1)	1.621
Specific Gravity	1.612 @ 21.1°C

1.4 ACCIDENT HISTORY

The methanol to dimethyl ether conversion process at Oberon Fuels is of new construction at the time this Hazard Assessment was prepared (January 2013). System start up is scheduled for April 2013. Therefore, there have been no significant releases of methanol that exceeded the Federal Reportable Quantity of 5,000 pounds. Also, there have been no releases of methanol or DME that meet the state requirement mandating immediate reporting of any release or threatened release of a hazardous material in the past five years. In addition, there have been no injuries resulting from a methanol or DME release, nor any releases or “near misses” that warranted an internal incident investigation.

2.0 HEALTH EFFECTS

2.1 TOXICOLOGICAL PROPERTIES AND EFFECTS^[1]

There are four major exposure hazards associated with dimethyl ether: inhalation, skin contact, eye contact, and ingestion incidents. In all but very minor cases, the victim should be checked by qualified medical personnel as soon as possible. The hazards associated with dimethyl ether are as follows:

- Contact with liquid or cold vapor may cause frostbite or freeze burn;
- Vapor is not poisonous, but can cause asphyxia due to reduction of oxygen content in atmosphere;
- Vapor will ignite when mixed with air in concentrations of 3.4- 27% by volume in closed areas;
- Vapors may cause flash fire and burst violently when heated.

2.2 LEVELS OF CONCERN (LOCs)^[2, 4]

The endpoint requirements for determining the affected downwind distances for the postulated release scenarios for flammable substances are defined under 19 CCR Section 2750.2 (a)(4). The endpoints for the worst case release scenario and alternative release scenario are different as described below.

A worst case release is defined as the loss of the contents of the single largest vessel containing the regulated substance. For dimethyl ether and other flammable substances, the substance is assumed to explode and generate a pressure wave that can potentially damage people or structures in the event of a release. The endpoint for the worst case release scenario is an overpressure of 1 psi (at 1 psi, windows will break).

The alternative release scenario employed in this study is a 0.5" hole in a pipe. A release from the piping will lead to a vapor cloud fire. Causes of a break or rupture in the piping are related to liquid expansion as a result of valve failure, failure of relief devices, collision, or corrosion. The endpoint for this scenario (vapor cloud fire) is the Lower Flammability Limit (LFL), which is 64 mg/L for dimethyl ether.

3.0 OFF-SITE IMPACTS

3.1 AFFECTED POPULATION

In order to determine the impacted population around the facility, the potential for exposure to the flammable substance endpoint requirements was investigated. The endpoint requirements for determining the affected downwind distances for the postulated release scenarios for flammable substances are defined under 19 CCR Section 2750.2 (a)(4) as follows:

Worst Case:	Overpressure of 1 psi
Alternative:	Lower Flammability Limit (for Vapor Cloud Fires)

The furthest distance reached by an overpressure of 1 psi from the facility is 0.48 miles. The furthest distance reached by a pipe leak from a 0.5" hole is 0.10 mile. Figure 4-1 shows the potential off-site impacts on the community for the worst and alternate case release scenarios.

The population was estimated using 2010 census tract data with the CAMEO-MARPLOT Version 4.2.1 Mapping Software^[8]. When calculating population densities for large areas which encompass many tracts, the accuracy is rated as good; however, for small areas that encompass only two or three partial tracts, the population data may be skewed due to the unequal distribution within the tract. Table 3-1 displays the estimated populations that are at risk of being exposed in the event of the two release scenarios postulated. The “at risk” population represents the number of people within the radius of the maximum downwind distance reached by the plume in **all wind directions**. The data from CAMEO-MARPLOT Version 4.2.1 Mapping Software is included as Appendix A.

TABLE 3-1 Estimated Population Data^[9]

Scenario	Distance to Endpoint	Residential Population At Risk
Worst Case	0.48 Miles	0
Alternate Release	0.10 Mile	0

3.2 OFF-SITE RECEPTORS^[7, 8]

Population Receptors - Worst Case Release

The EPA RMP requirements state that sensitive populations such as schools, hospitals, day care centers, long term health care facilities, residential areas, public use parks/recreational areas, and major commercial facilities, located within the “at risk” area must be identified. There are no sensitive receptors located within the furthest endpoint of 0.48 miles from the Oberon Fuels facility. Information regarding sensitive receptors was gathered from the Yahoo! Yellow Pages^[7].

Population Receptors - Alternate Release

There are no population receptors within a 0.10 mile radius around the Oberon Fuels facility.

Environmental Receptors - Worst Case Release

The RMP requires that facilities also consider “Environmental Receptors”^[5] defined as: areas such as national or state parks, forests, or monuments; wildlife sanctuaries, preserves, refuges, or areas; and Federal wilderness areas. There are no “Environmental Receptors”, as defined above, located within a radius of 0.48 miles around the facility. Information regarding sensitive environmental receptors was gathered from CAMEO-MARPLOT Version 4.2.1 Mapping Software^[9] and Yahoo Yellow Pages^[7].

Environmental Receptors - Alternate Release

There are no environmental receptors within a 0.10 mile radius around the facility.

4.0 RELEASE SCENARIOS

The off-site consequence modeling consists of a worst case scenario and the alternative release scenario for the Waste Management facility. EPA's "Risk Management Program Guidance for Offsite Consequence Analysis" [2] (March 2009) was used as the primary source to determine the downwind distances for each scenario.

4.1 WORST CASE RELEASE SCENARIO^[2]

The worst case release scenario for flammable substance releases is defined by EPA as follows:

"The largest quantity of a regulated substance from a vessel or process line failure that results in the greatest distance to a specified endpoint. For the worst-case analysis, you do not need to consider the possible causes of the worst-case release or the probability that such a release might occur; the release is simply assumed to take place."

"For all regulated flammable substances, you must assume that the worst-case release results in a vapor cloud containing the total quantity of the substance that could be released from a vessel or pipeline."

"For the consequence analysis, the endpoint of a vapor cloud explosion of a regulated flammable substance is an overpressure of 1 pound per square inch (psi). This endpoint was chosen as the threshold for potential serious injuries to people as result of property damage caused by an explosion."

"For the analysis of the worst-case scenario, you must consider the largest quantity of a regulated substance handled on site in a single vessel at any one time. You also must consider the quantity that might be released if a pipeline were sheared."

Quantity Released

The worst case release scenario is a release of the largest quantity of a regulated substance from a vessel or process line failure that results in the greatest distance to a specified endpoint. The largest vessels in the system are the two DME Storage Tanks, which can each hold 30,000 gallons (165,000 lbs) of DME. The vessels are interconnected so the entire contents of the Storage Tanks (330,000 lbs) is assumed to be released in the worst case scenario. (Note: All vessels are located outside; therefore, the release that results in the greatest distance to the endpoint is a release from the largest vessel.)

Passive Mitigation Measures

If the largest vessel in the process is stored in an enclosure (building), the release rate to the outside atmosphere will be considerably less than if it were stored outside. In case of a release inside a building, the building can be considered to provide passive mitigation, unless^[2]:

- The building may fail as a result of the release. This is unlikely except in the case of a large vessel in a very small room. As a rough rule of thumb, if the room volume divided by the quantity of DME is less than the value of 0.1, there is a possibility that the release of DME will cause failures such as windows blowing out or doors blowing open.
- The release takes place facing an opening in the building (door or windows). In this case, the door or windows will be assumed to be open, and the DME will be released through these openings.

Since the DME Storage Tanks are located outside, a release from this vessel would not be mitigated by an enclosure. Thus, no passive mitigation effects of an enclosure were taken into account for the worst case scenario.

Release Rate

For a worst-case release of flammable gases and volatile flammable liquids, the release rate is not considered. The total quantity of the flammable substance in the largest vessel or process is assumed to be released as a vapor cloud explosion.

Meteorological Conditions

For the worst case scenario, a wind speed of 1.5 meters/second and stable conditions (F class stability) were used, based on EPA requirements.

Rural vs. Urban Topography

The local topography surrounding the facility was classified as **rural**. Urban means that there are many obstacles in the area immediately surrounding the release including skyscrapers, buildings, or trees. Rural means that there are few buildings or other obstacles in the immediate area.^[2] A facility's topography may be classified as urban by using the following guidance below:

If 50% of the landmass within a 1-mile radius can be described as indicated below, the area can be classified as urban:

- *Heavy industrial* (large chemical, other manufacturing facilities, 3-5 story building, flat roofs, grass and trees extremely rare); or

- *Light-to-moderate industrial* (rail yards, truck depots, warehouses, industrial parks, minor fabrication, 1-3 story buildings, flat roofs, limited grass and trees); or
- *Commercial* (offices and apartments, hotels 10-story heights, flat roofs, limited grass or trees); or
- *Compact residential* (single and some multiple family dwellings closely spaced, 2-story or less, alleys pitched or flat roofs, limited lawns and few old established trees, no driveways).

If none of the above apply, the area is classified as rural.

Estimation of Distance to a 1 Psi Overpressure

The following source was used to identify the distance to the overpressure endpoint of 1 psi, which uses EPA-approved reference tables:

- EPA's "Risk Management Program Guidance for Offsite Consequence Analysis", March 2009, Appendix C, Equation C-2^[2]. The RMP*Comp Model developed by the National Oceanic and Atmospheric Administration and EPA was used to prepare the data in this guidance document.

Equation C-2^[2] was used to calculate the distance to the Overpressure Endpoint for DME, for a total release of 330,000 pounds of DME from the methanol to DME conversion process, with an atmospheric stability class of "F", in a rural area, a wind speed of 1.5 meters per second, with no passive mitigation effects taken into account. In the worst case scenario the explosion efficiency is assumed to be 10 percent^[2]. The distance to an overpressure level of 1 psi is determined using the following equation, which is based on the TNT-equivalency method:

$$D_{mi} = 0.0081 \times (0.1 \times W_{lb} \times \frac{HC_f}{HC_{TNT}})^{1/3}$$

Where:	D_{mi}	=	Distance to the endpoint (miles)
	0.0081	=	Damage constant for 1.0 psi overpressure
	0.1	=	Explosion efficiency of 10%
	W_{lb}	=	Quantity of flammable substance released (pounds)
	HC_f	=	Heat of combustion of flammable substance (kilojoules per kilogram) (28,835 kJ/kg for dimethyl ether)
	HC_{TNT}	=	Heat of explosion of trinitrotoluene (TNT) (4,680 kilojoules per kilogram)

Therefore:

$$D_{mi} = 0.0081 \times (0.1 \times 330,000 \times \frac{28,835}{4,680})^{1/3} = 0.476 \text{ miles} \cong 0.48 \text{ miles}$$

The distance to the 1 psi overpressure endpoint in the worst case scenario is 0.48 miles. Table 4-1 shows the methodology and the results of a for a worst case release scenario described above.

TABLE 4-1 Worst Case Scenario Results

Reference	Input	Distance
EPA's Risk Management Program Guidance for Offsite Consequence Analysis, Appendix C, Equation C-2.	Quantity Released: 330,000 lbs	0.48 miles

The assumptions and results for this release scenario are included in Table 4-3 at the end of this section. The potentially impacted area surrounding the facility (based on the “Risk Management Program Guidance for Offsite Consequence Analysis” document) is shown as the outer yellow circle in Figure 4-1.

The circle represents the potentially impacted area in all wind directions. In the event of an emergency, awareness of the predominant wind direction along with the wind sock direction may aid in facility evacuation. The wind direction does not have any impact upon the determination of the downwind distances to the overpressure endpoint in this study.

4.2 ALTERNATIVE RELEASE SCENARIO^[2]

The criteria for selecting an alternative release scenario are as follows:

- The alternative release scenario should be more likely to occur than the worst case scenario; and
- The alternative release scenario should reach an endpoint offsite.

The alternative release scenario chosen for this facility is that of a 0.5 inch diameter orifice leading to an airborne release and a vapor cloud explosion. This is representative of a release from piping due to failure at flanges, joints, welds, valves, etc. For a conservative approach, it is assumed that this release is from the high side of the system, therefore at a maximum pressure of 120 psig. The release scenario is assumed to last approximately 30 minutes, which takes into account the system’s emergency shutdown capabilities. Passive mitigation was not considered for the release, since all equipment associated with the system is located outside.

Release Rate Calculation

For modeling the alternative release scenario, the RMP regulation allows typical meteorological conditions at the facility to be used. For the alternative release scenario, a wind speed of 3 meters/second and neutral conditions, D stability, were used. The release rate is derived using the following steps:

Area of the release orifice from a 0.5 inch diameter hole (D below) is calculated as follows:

$$HA = \frac{\pi D^2}{4} = \frac{\pi \times (0.5 \text{ in})^2}{4} = 0.196 \text{ in}^2$$

To estimate the release rate for flammable gases from hole size and storage conditions, the same method may be used as that for toxic gases. The equation for estimating the release rate of a gas from a hole in a tank is based on the equations for gas discharge rate presented in the Handbook of Chemical Hazard Analysis Procedures by the Federal Emergency Management Agency (FEMA), DOT, and EPA. The full equation can be found in the EPA's Risk Management Program Guidance for Offsite Consequence Analysis document, Appendix D. The simplified equation, as follows, can be found in Section 7.1 of the EPA's Risk Management Program Guidance for Offsite Consequence Analysis document:

$$QR = HA \times P_t \times \frac{1}{\sqrt{T_t}} \times GF$$

Where:

QR	=	Release rate (pounds per minute)
HA	=	Hole or puncture area (square inches)
P _t	=	Tank pressure (pounds per square inch absolute)
T _t	=	Tank temperature (K)
GF	=	Gas Factor, incorporating discharge coefficient, ratio of specific heats, molecular weight, and conversion factors (listed for each regulated flammable gas in EPA's Risk Management Program Guidance for Offsite Consequence Analysis Exhibit C-2, Appendix C) (22 for dimethyl ether)

At a pressure of 140 psig, the absolute pressure is calculated as:

$$P_t = 140 \text{ psig} + 14.7 = 154.7 \text{ psia}$$

The release rate can then be calculated as follows:

$$QR = 0.196 \times 154.7 \times \frac{1}{\sqrt{320}} \times 22 = 37.3 \text{ lbs/min}$$

The release rate is 37.3 pounds per minute. This release rate can then be used to determine the potential downwind distance to the Lower Flammability Limit (LFL) endpoint for the alternate release scenario.

Estimation of Distance to LFL Endpoint

The following source was used to identify the distance to the LFL endpoint of 64 mg/L for DME, which uses EPA-approved reference tables:

- EPA's "Risk Management Program Guidance for Offsite Consequence Analysis", March 2009, Reference Table 28^[2].

Table 4-2 shows the methodology and the results of a release of 1,118 pounds of DME from the system, with an atmospheric stability class of "D", in a rural area, a wind speed of 3.0 meters per second, with no passive mitigation effects taken into account. Because wind direction does not impact the downwind distance to the LFL endpoint in this study, the resulting plume is round. The table used to determine the distance to LFL Endpoint utilizes the release rate from the system divided by the LFL concentration in milligrams per liter. The ratio is calculated as:

$$\frac{\text{Release Rate}}{\text{LFL}} = \frac{37.3 \text{ lbs/min}}{64 \text{ mg/L}} = 0.58$$

Exhibit 6 from the EPA's Risk Management Program Guidance for Offsite Consequence Analysis is a reference table of distances for vapor cloud fires of flammable substances. Using the data for DME from Exhibit C-2 and the topography of the area surrounding the facility, Exhibit 6 indicates that EPA's Management Program Guidance for Offsite Consequence Analysis - Reference Table 28 is to be consulted for a neutrally buoyant gas released in a rural environment. Utilizing Reference Table 28 with an input of 20 [(lbs/min) / (mg/L)] provides a LFL endpoint distance of 0.1 mile.

TABLE 4-2 Alternative Case Release Scenario Results

Reference	Input	Distance
EPA's Risk Management Program Guidance for Offsite Consequence Analysis, Reference Table 28.	Release Rate/LFL: 0.58	0.1 mile

The input parameters and results for this release scenario are included in Table 4-3 at the end of this section and the potentially impacted area surrounding the facility is shown as the circle in Figure 4-1.

TABLE 4-3 Reference Table/Summary Sheet

	Worst-Case Scenario	Alternative Scenario
Input		
Total Release Quantity	330,000 lbs.	1,118 lbs.
Release Rate – total	N/A	37.3 lbs./min
Release Rate to Atmosphere	N/A	37.3 lbs./min
Release Time	10 minutes	30 minutes
Release Direction	Horizontal	Horizontal
Release Temperature (Daily Max. Temp. - WC)	100 °F	100 °F
Release Pressure	1 atm	1 atm
Ambient Temperature - Daily Max. Temp.	77 °F	77 °F
Ambient Pressure	1 atm	1 atm
Relative Humidity	50%	50%
Stability Class	F	D
Wind Speed	1.5 m/s	3.0 m/s
Surface Roughness	Rural	Rural
Averaging Time	10 minutes	30 minutes
Endpoint	1 psi Overpressure	LFL: 64 mg/L
Output		
Estimated Population Affected (Marplot Version 4.2.1)	0	0
Distance to Endpoint: Risk Management Program Guidance for Offsite Consequence Analysis	0.48 Miles	0.1 Mile

FIGURE 4-1 Worst and Alternate Case Release Scenarios (Distance to Endpoint: 0.48 & 0.1 Miles)^[8]



REFERENCES

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2. Risk Management Program Guidance for Offsite Consequence Analysis, EPA, March 2009.
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4. General Guidance on Risk Management Programs for Chemical Accident Prevention, EPA, March 2009.
5. California Accidental Release Prevention (CalARP) Program regulation, March 2009.
6. U.S. EPA, Federal Emergency Management Agency, U.S. DOT, Technical Guidance for Hazard Analysis - Emergency Planning for Extremely Hazardous Substances, Dec, 1987.
7. <http://yp.yahoo.com> Yahoo! Yellow Pages Website. Accessed January 18, 2013.
8. Images from Google™ Earth Pro (c) 2011.
9. CAMEO – MARPLOT Version 4.2.1 Mapping Software, U.S. EPA, Office of Emergency Management, and NOAA, Emergency Response Division, October 2011.

APPENDIX A

POPULATION DATA

WORST CASE RELEASE POPULATION DATA^[9]



ALTERNATE CASE RELEASE POPULATION DATA^[9]



APPENDIX B
EPA REFERENCE TABLES

Exhibit 6
Reference Tables of Distances for Vapor Cloud Fires of Flammable Substances

Applicable Conditions			Reference Table Number
Gas or Vapor Density	Topography	Release Duration (minutes)	
Neutrally buoyant	Rural	10 - 60	26
	Urban	10 - 60	27
Dense	Rural	10 - 60	28
	Urban	10 - 60	29

Reference Table 28
Dense Gas Distances to Lower Flammability Limit
Rural Conditions, D Stability, Wind Speed 3.0 Meters per Second

Release Rate (lbs/min)	Lower Flammability Limit (mg/L)									
	27	30	35	40	45	50	60	70	100	>100
	Distance (Miles)									
<1,500	#	#	#	#	#	#	#	#	#	#
1,500	<0.1	<0.1	#	#	#	#	#	#	#	#
2,000	0.1	0.1	<0.1	#	#	#	#	#	#	#
2,500	0.1	0.1	0.1	<0.1	#	#	#	#	#	#
3,000	0.1	0.1	0.1	0.1	<0.1	<0.1	#	#	#	#
4,000	0.1	0.1	0.1	0.1	0.1	0.1	<0.1	#	#	#
5,000	0.1	0.1	0.1	0.1	0.1	0.1	0.1	<0.1	#	#
7,500	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	<0.1	#
10,000	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	<0.1

< 0.1 mile (report distance as 0.1 mile)