TP 12998E Addendum

Safety Assessment of DME Fuel Addendum

Prepared for Transportation Development Centre Safety and Security Transport Canada M. Paas Consulting Ltd. April 1998

> Prepared by Madis Paas M. Paas Consulting Ltd.

This report reflects the views of the author and not necessarily those of the Transportation Development Centre.

Since some of the accepted measures are imperial, a combination of both metric and imperial units is used in this report.

Un sommaire français se trouve avant la table des matières.



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| 1. | Transport Canada Publication No. | 2. Project No. | | 3. Recipient's C | Catalogue No. | | |
|---|--|--|-------------------------|----------------------|-----------------------|---------------|--|
| | TP 12998E (Addendum) | 9322 | | | | | |
| | · · · · · | | | | | | |
| 4. | Title and Subtitle | | | 5. Publication E | Date | | |
| | Safety Assessment of DME Fuel – A | ddendum | | April 19 | 98 | | |
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| 7. | . Author(s) | | 8. Transport Ca | anada File No. | | | |
| | Madis Paas | | | 70014 | 35_675 | | |
| | | | | 200140 | 55-075 | | |
| 9. | Performing Organization Name and Address | | | 10. PWGSC File | No. | | |
| | M. Paas Consulting | | | XSD-7- | 01494 | | |
| | 70 McCallum Crescent | | | | | | |
| | Winnipeg, Manitoba | | | 11. PWGSC or 1 | Fransport Canada Co | ontract No. | |
| | R3R 2S6 | | | T8200-7 | 7-7562 | | |
| | | | | | | | |
| 12. | Sponsoring Agency Name and Address | | | 13. Type of Publ | lication and Period C | Covered | |
| | 800 René Lévesque Blvd West | (IDC) | | Final | | | |
| | 6th Floor | | | 14 Project Offic | er | | |
| | Montreal, Quebec | | | | | | |
| | H3B 1X9 | | | Roy S. | NISNIZAKI | | |
| 15. | Supplementary Notes (Funding programs, titles of related put | plications, etc.) | | | | | |
| | Funded by Program of Energy Resea | arch and Developme | nt (PERD) This | report is an add | endum to Sa | afetv | |
| | Assessment of DME Fuel, TP 12998 | E (TDC, April 1997). | | | | arety | |
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| 16. | i6. Abstract | | | | | | |
| | This report is an addendum to an earlier report TP 12998E. Safety Assessment of DME Fuel. Both reports | | | | | | |
| | provide a general assessment of the use of dimethyl ether (DME) as a transportation fuel for compression | | | | | | |
| | ignition engines. The goal was to determine issues that might impede the use of DME in this application and to | | | | | | |
| | identify equipment and standards requirements for the vehicle fuel system and for dispensing DME or mixtures of | | | | | r mixtures of | |
| | DME and propane into the vehicle. | | | | | | |
| | It was concluded that the safety concerns are similar to those for other liquefied cases that are beavier than air | | | | | | |
| | and flammable. Solubility of DME in water and vice versa may pose some special problems that are not | | | | | | |
| | encountered with other liquefied gas | ses. The specific vol | ume of liquid DN | ME varies with te | emperature | and the rate | |
| | of expansion and contraction is diffe | rent from that of othe | er liquefied gase | s. This must be | taken into ad | ccount when | |
| | selecting storage tanks and filling de | nsities. | | | | | |
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| 17. | Key Words | | 18. Distribution Statem | ent | | | |
| Dimethyl ether (DME), propane, safety, health, Limited number of copies a | | ailable from | the | | | | |
| environment, venicle tuel system, tuel dispensing | | | | | | | |
| | | | | | | | |
| 19. | Security Classification (of this publication) | 20. Security Classification (of | this page) | 21. Declassification | 22. No. of | 23. Price | |
| | Unclassified | Unclassified | | (date) | Pages x. 14 | _ | |
| | | Groussmen | | | apps | | |

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FORMULE DE DONNÉES POUR PUBLICATION

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| 1. | Nº de la publication de Transports Canada | N^o de l'étude | | N^o de catalo | gue du destinataire | | |
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| | | | | 6. N° de docum | nent de l'organisme e | exécutant | |
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| | | | | | | | |
| 7. | Auteur(s) | | | 8. N ^o de dossie | r - Transports Canad | da | |
| | Madis Paas | | | ZCD14 | 65-675 | | |
| 9. | Nom et adresse de l'organisme exécutant | | | 10. N ^o de dossie | r - TPSGC | | |
| | M Paas Consulting | | | XSD-7- | 01404 | | |
| | 70 McCallum Crescent | | スラレ-7-01494 | | | | |
| | Winnipeg, Manitoba | | | 11. Nº de contra | t - TPSGC ou Trans | ports Canada | |
| | R3R 2S6 | | | T8200- | 7-7562 | | |
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| 12. | Centre de développement des trans | norts (CDT) | | | blication et periode v | nsee | |
| | 800. boul. René-Lévesque Ouest | | | Final | | | |
| | 6 ^e étage | | | 14. Agent de pro | ojet | | |
| | Montréal (Québec) | | | Rov S. | Nishizaki | | |
| | H3B 1X9 | | | , | | | |
| 15. | Remarques additionnelles (programmes de financement, titre | es de publications connexes, etc.) | | | | | |
| | Parrainée par le Programme de rech | erche et développer | nent énergétique | es (PRDE). Ce d | locument est | t un | |
| | supplement au rapport Safety Asses | sment of DME Fuel, | TP 12998E (CD | 01, avril 1997). | | | |
| 16. | Résumé | | | | | | |
| | Ce rapport est un supplément au | rapport TP 12998F | Safety Assess | ment of DMF F | - uel Tous d | eux rendent | |
| | compte d'une analyse générale de l'utilisation du diméthyléther (DME) comme carburant de substitution pour les | | | | | | |
| | moteurs à allumage par compression dans les véhicules de transport. Le but visé était de déterminer les | | | | | | |
| | obstacles à cette utilisation, les équipements et les normes nécessaires concernant les circuits d'alimentation | | | | | | |
| | des véhicules et les pompes de distribution de DME pur ou mélangé avec du propane. | | | | | | |
| | La recherche a montré que, du point de vue de la sécurité, l'utilisation du DME soulève les mêmes questions que | | | | | | |
| | tout autre gaz inflammable plus lourd que l'air. La solubilité du DME dans l'eau, et vice-versa, risque d'entraîner | | | | | | |
| | des problèmes particuliers, que ne | posent pas les aut | res gaz liquéfié | s. Le volume m | assique du | DME liquide | |
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| | Non classifión | Non clossifiés | 0 - / | (date) | de pages | | |
| | | NULL CLASSINGE | | | ann. | | |

Executive Summary

The Canadian federal government has initiated studies and research into the use of dimethyl ether (DME) as an alternative to diesel fuel in compression ignition engines. These efforts are the result of concerns regarding the ability of diesel fuel to meet future emission regulations. At issue are the particulate and NO_x engine emissions. DME is being viewed as a potential solution.

Natural Resources Canada is supporting research into DME fuel system and engine development work. The Transportation Development Centre is complementing the engine development work with investigations into the safety, health, and environmental aspects of DME to determine issues related to the use of the fuel, the vehicle fuel system, and the dispensing system.

The Transportation Development Centre contracted with M. Paas Consulting Ltd. to conduct a preliminary safety assessment of DME fuel. The results were reported in TP 12998E, *Safety Assessment of DME Fuel*. Soon after this report was completed additional reference material was volunteered by Amoco Corporation and Akzo Nobel as part of an International Energy Agency undertaking. This addendum to the earlier report provides a review of that material as it pertains to the safety, health, and environmental aspects of the use of DME as an alternative transportation fuel.

Thirty-three new pieces of literature were submitted. Much of the information from Akzo Nobel dealt with the flammability of DME when used as an aerosol in indoor applications and therefore had limited use in this addendum. Akzo also provided information on the transport, storage, and handling of DME. This information confirmed that which appeared in the earlier report and expanded on the selection of elastomers for use in DME service. Amoco provided extensive information on the safety, health, and environmental properties of DME. This confirmed the statistics that appeared in the earlier report and provided new information, particularly in the areas of solubility in water and the very low risk of peroxide formation.

Extensive research has been conducted into the use of DME as an aerosol. It is, of course, flammable and has wide flammability limits. Various values are used for both the lower and upper flammability limits. DME is of low toxicity and is non-carcinogenic. It is extremely soluble in water and this may pose some problems with underground storage. The specific volume of DME changes with temperature and the rate of change falls between that of propane and that of normal butane in normal ambient conditions. When released into the atmosphere it is a photochemical oxidant and has low ozone-forming potential.

As in the earlier report, no major hurdles were identified in the use of DME as a fuel for compression ignition engines.

Sommaire

Le gouvernement du Canada a lancé des études sur l'utilisation du diméthyléther (DME) comme carburant de remplacement du diesel dans les moteurs à allumage par compression. Ces recherches sont nées d'inquiétudes quant à l'aptitude du carburant diesel à satisfaire aux réglementations futures concernant la pollution atmosphérique, notamment les émissions d'imbrûlés et de No_x. Le DME est une des solutions envisagées pour résoudre ce problème.

Ressources naturelles Canada a financé la recherche sur le développement technique d'un moteur brûlant du DME et sur le circuit d'alimentation correspondant. Pour leur part, Transports Canada et le Centre de développement des transports appuient la recherche sur le développement technique par des analyses de l'impact du DME sur la sûreté, la santé et l'environnement, afin de déterminer les enjeux reliés à l'utilisation de ce carburant, au circuit d'alimentation et aux pompes de distribution.

Le Centre de développement des transports a passé un contrat avec M. Paas Consulting Ltd. visant une analyse préliminaire de la sécurité du DME. Les résultats de cette analyse sont donnés dans le rapport TP 12998E, *Safety Assessment of DME Fuel*. Peu après la publication de ce rapport, les sociétés Amoco Corporation et Akzo Nobel divulguaient d'autres documents techniques en marge d'un programme de l'Agence internationale de l'énergie. Ce supplément au rapport déjà publié recense, parmi ces documents, ceux qui abordent les répercussions sur la sécurité, la santé et l'environnement de l'utilisation du DME comme carburant de substitution.

Trente-trois nouveaux écrits ont été soumis. Les articles proposés par Akzo Nobel traitaient pour la plupart de l'inflammabilité du DME lorsqu'il est utilisé comme aérosol dans certaines applications à l'intérieur de bâtiments et offraient donc peu d'intérêt aux fins du présent supplément. Akzo a également fourni diverses informations sur le transport, le stockage et la manutention du DME, qui confirmaient celles figurant dans le premier rapport. Elles comportaient toutefois des renseignements inédits pour le choix d'élastomères compatibles avec le DME. Quant aux documents fournis par Amoco, ils brossaient un tableau complet des propriétés du DME du point de vue de la sécurité, de la santé et de l'environnement. Là encore, les statistiques mentionnées dans le premier rapport se trouvaient confirmées, voire complétées, notamment pour ce qui a trait à la solubilité du DME et au risque très faible de formation de peroxyde.

Des recherches exhaustives sur l'utilisation du DME en tant qu'aérosol, il ressort qu'il s'agit, bien sûr, d'un produit inflammable, caractérisé par un domaine d'inflammabilité étendu. Diverses valeurs sont utilisées pour représenter les limites supérieure et inférieure d'inflammabilité. Le DME se révèle faiblement toxique et non cancérogène. Il est extrêmement soluble dans l'eau, ce qui peut rendre le stockage souterrain contre-indiqué. Le volume massique du DME varie avec la température et son coefficient de dilatation et de contraction est inférieur à celui du propane et du butane normal, dans des conditions ambiantes normales. En cas de fuite dans l'atmosphère, c'est un photooxydant qui présente un faible potentiel ozonogène.

Comme dans le rapport antérieur, on n'a rien observé de grave qui puisse compromettre l'utilisation du DME dans les moteurs à allumage par compression.

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Glossary of Abbreviations, Acronyms, Symbols, and Special Terms

| ACGIH | American Conference of Government Industrial Hygienists, Inc. |
|------------------|---|
| AET | Advanced Engine Technology Ltd. |
| AIHA | American Industrial Hygiene Association |
| °C | Degree Celsius |
| CAS | Chemical Abstracts Service |
| CI | Compression ignition |
| DME | Dimethyl ether |
| DOT | Department of Transportation (U.S.) |
| ETDM | Ethylene propylene |
| °F | Degree Fahrenheit |
| HMIS | Hazardous Material Information System |
| J | Joule |
| kg | Kilogram |
| kPa | Kilo Pascal |
| L | Litre |
| LC ₅₀ | Lethal concentration for 50% lethality |
| LPG | Liquefied petroleum gas |
| mJ | Millijoule |
| MSDS | Material Safety Data Sheet |
| N-Butane | Normal butane |
| NFPA | National Fire Protection Association |
| NO _x | Oxides of nitrogen |
| OSHA | Occupational Safety and Health Act |
| ppm | Parts per million |
| PTFE | Polytetrafluoroethylene |
| STEL | Short term exposure limit |
| TDG | Transport Dangerous Goods |
| TLV | Threshold limit value |
| TWA | Time weighted average |
| USWG | United States water gallon capacity |
| WHMIS | Workplace Hazardous Materials Information System |

1 INTRODUCTION

1.1 Background

The Canadian federal government has initiated studies and research into the use of dimethyl ether (DME) as an alternative to diesel fuel in compression ignition (CI) engines. These efforts are a result of concerns regarding the capability and cost of meeting future emission standards with diesel fuel and CI engines. Emission standards are being tightened to improve air quality and reduce the impact of emissions on health and the environment.

Transport Canada and Natural Resources Canada have taken an active interest in the use of DME. Natural Resources Canada is supporting DME research into fuel system design, CI engine development work, fuel mixtures, and production of DME. The Transportation Development Centre is complementing this work with their interest in the safety, health, and environmental aspects of the use of DME.

DME is not a naturally occurring product. Production is currently limited and would have to be increased substantially to meet the demand, if it were used as a vehicle fuel. DME is produced using methanol as the feedstock, but processes for direct synthesis from natural gas are being investigated. This could reduce the cost of DME. Canada has an abundant supply of natural gas and is well positioned to be the major producer of DME.

DME is rather benign and is used as a propellant in aerosol packaging. Prior to its use in that application, studies were done to determine the health and environmental aspects.

DME is an attractive alternative fuel for compression ignition engines because it has a high cetane value.

As part of a collaborative arrangement with Natural Resources Canada, the Transportation Development contracted with M. Paas Consulting Ltd. to conduct a preliminary safety assessment of DME fuel. The results were reported in TP 12998E, *Safety Assessment of DME Fuel*. No major hurdles were identified in the use of DME as a fuel for compression ignition engines. Soon after this report was completed additional reference material was volunteered by Amoco Corporation (Chicago, Illinois) and Akzo Nobel (Arnhem, Netherlands) as part of an International Energy Association undertaking.

This addendum to the original report provides a review of that material.

1.2 Project Objective and Tasks

The purpose was to review and analyse reference material supplied by Amoco and Akzo Nobel as it related to the safety of DME when used as a vehicle fuel. Refer to Appendix A for the list of the material (Material Safety Data Sheets, articles, internal correspondence, and company literature) supplied by each company. The project was broken down into four tasks:

Task 1 - Review of New Material on DME Review the material supplied by Amoco and Akzo Nobel.

Task 2 - Fuel System Requirements

Obtain and review the results of a DME fuel supply system audit conducted by DuPont at Advanced Engine Technology Ltd. (AET).

Task 3 - Analysis of Information from Tasks 1 and 2 Assess the implications for DME safety drawn from the new information and from the audit of the DME fuel delivery system setup at the AET engine test facility.

Task 4 - Prepare a report as an addendum to the previous report TP 12998E, *Safety Assessment of DME Fuel*, to identify new information or new issues.

2 APPROACH AND METHODOLOGY

The content of the addendum is based on reference material supplied by Amoco and Akzo Nobel. This material comprises internal reports, papers presented at conferences, magazine and trade journal articles, company literature, and various Material Safety Data Sheets (MSDSs) from a number of different companies.

The material was reviewed to determine whether it contained any new information that related to the safety, health, or environmental aspects of DME as a vehicle fuel. Much of the information in the new material had already been included in the earlier report. Four of the reports forwarded by Akzo Nobel dealt with the flammability and explosion risk of DME in indoor aerosol applications. Although very interesting, it had limited carryover to vehicle applications. Amoco supplied a broad array of material that dealt with different aspects of safety, health, and the environment.

The safety audit of the DME system installed at the AET facility was unique to the use of DME in a laboratory or testing type of environment and therefore didn't prove as useful as first thought. No further reference will be made to this in the addendum.

Only new information is included in the addendum.

3 DIMETHYL ETHER FUEL PROPERTIES

3.1 Safety

Detection

Either catalytic combustion or infrared adsorption detection systems can be used for sensing or detecting of DME vapours [1, 2].

Density and Specific Volume of Liquid DME

The density and specific volume of liquid DME vary with temperature. The graph in Figure 1 provides a comparison of saturated DME, propane, and normal butane (n-butane) in terms of specific volume versus temperature. As temperatures approach the critical temperature the rate of volume expansion increases dramatically. Table 1 provides critical temperatures for DME, propane, and n-butane [3].





| | Critical Temperature | Critical Volume | Critical Pressure | |
|----------|----------------------|-----------------|-------------------|--|
| | O° | L/kg | kPa absolute | |
| DME | 126.9 | 3.683 | 5 268.9 | |
| Propane | 96.8 | 4.438 | 4 266 | |
| N-Butane | 152.0 | 4.387 | 3 796.6 | |

| Table 1 | Critical Point | Values fo | r DMF | Propane | and N-Butane |
|---------|----------------|-----------|--------|-----------|--------------|
| | | values lo | \Box | r ropune, | |

The change in specific volume over a range of temperatures is important in determining maximum filling density of storage tanks, whether they be stationary or vehicle tanks. An internal company document raised a concern regarding the use of liquefied petroleum gas (LPG) storage for DME. The concern is that, as a result of the difference in liquid expansion rates for DME and LPG (propane and butane), it might be possible to overfill LPG storage tanks used for DME, based upon a filling level set for LPG.

Additional information is provided in Section 4.2, Maximum Permitted Filling Limits for Tanks.

Combustion

The majority of sources that provide the lower flammability limit in air list it as 3.4%. Others provide values that range from 3.0 to 3.5% [4]. DME burns with a more luminous flame than propane or butane, which could allow easier detection in case of a fire [5].

The minimum ignition energy for DME is 0.29 mJ as compared to propane at 0.25 mJ [6].

Chemical Stability

DME is a chemically stable compound at temperatures up to 400°C [5, 7, 8]. Polymerization does not occur under normal pressures and temperatures [9, 10, 11]. In aqueous solutions, DME is hydrolytically stable in neutral and dilute acid and alkali solutions [7].

Formation of Peroxides

Peroxides when exposed to friction, impact, or heating may explode. A number of MSDSs and other reference sources warn that explosive peroxides may be formed upon long exposure to air [10, 11, 12, 13, 14, 15, 16]. An article that appeared in Chimicaoggi in 1985 indicated that a number of experiments had been done by Union Kraftstoff and Aerofako to try to duplicate the formation of peroxides with DME, but with little success or little practical possibility [17]. The conditions needed to produce demonstrable amounts are UV light (i.e., only applicable to colorless and uncoated glass bottles), the presence of ethanol with a UV-absorber as a contaminant, and the availability of air. The article further pointed out that the risk involved would be extremely small due to the low concentration. In addition, many of the references stated that no cases of peroxide formation from the storage and use of DME had been reported [4, 18]. Amoco has indicated that adding a free radical inhibitor to the DME would probably remove any potential for problems [5].

3.2 Health

Workplace Exposure Limits

The maximum permitted level of exposure for materials that are considered hazardous in the workplace is set by government occupational health and safety regulations. Workplace exposure is normally associated with indoor air quality and is expressed in a threshold limit value (TLV). Frequently three values are provided - time weighted average (TWA) over a period of 8 hours, short term exposure limits (STEL) over a period of 15 minutes, and ceiling (C), which is the maximum level. Only a few governments have established a TLV for DME and those that have usually only provide the TWA value.

The review of the MSDSs and other literature provided the information in Table 2.

| Organization | TLV (TWA) ppm |
|---|------------------|
| British Columbia Occupational Health and Safety Regulation | 1 000 |
| American Industrial Hygiene Association (AIHA) | 1 000 |
| American Conference of Government Industrial Hygienists, Inc. (ACGIH) | none established |
| U.S. Occupational Safety and Health Act (OSHA) | none established |
| New Jersey Department of Health and Senior Services | none established |
| Germany - DFG MAK | 1 000 |
| Netherlands | 1 000 |

Table 2 Workplace Exposure in Threshold Limit Values for DME

Lethal Concentration

Several of the references listed the lethal concentration of DME in air for rats and mice. The concentration for 50% lethality (LC_{50}) in mice ranged from 49% by volume (v/v) of DME for 15 minutes down to 38% for 30 minutes [19]. The LC_{50} for rats is 16.4% by volume of DME for 4 hours [19].

Carcinogenicity

The new reference material provided additional confirmations of the low level of risk for DME as a carcinogenic agent. Analysis was done to determine whether a risk was associated with the formation of bischloromethylether from DME. Bischloromethylether is a strong carcinogenic. It was determined that the risk of formation was low [17, 20].

3.3 Environmental Factors

Evaporative Emissions

DME is a photochemical oxidant with a relatively short life. Its half life in the lower troposphere is 3 to 30 hours in bright weather and in the upper troposphere is 100 to 150 hours [17].

Testing done and reported in 1992 by the Swedish Environmental Research Institute on the photochemical ozone creation potential of seventy-five different organic compounds provided information indicating that DME had a lower ozone-forming potential than LPG or the hydrocarbons present in gasoline when released into the atmosphere [21].

Water Contamination

Studies have been conducted on fish in closed vessels, in which they were subjected to concentrations in water up to 4 g/L without mortality or toxic effect [18].

3.4 Operational Factors

DME Identifers

The Chemical Abstracts Service (CAS) number for DME is 115-10-6. This number is used specifically for DME and provides an identifier that is recognizable internationally. Other identifiers are provided in Table 3.

| Organization | Abbreviation | Identifier |
|--|--------------|---|
| Chemical Abstracts Service | CAS | 115-10-6 |
| Workplace Hazardous Materials Information (Canada) | WHMIS | A, B1 |
| Transport Dangerous Goods (Canada) | TDG | Shipping Name - Dimethyl Ether Classification - 2.1 Product Identification - UN1033 |
| Department of Transportation (U.S.) | DOT | Shipping Name - Dimethyl Ether Hazard Class - 2.1 Identification Number - UN1033 |
| National Fire Protection Association Rating | NFPA | Health 2 Fire 4 Reactivity 1 |
| Hazardous Material Information System Rating | HMIS | Heath - 1 Fire - 4 Reactivity - 1 |

Compatibility with Materials

Most elastomers are attacked by DME due to its high solvency. Selection of a suitable elastomer depends on the application it will be used in. Manufacturers recommend testing prior to use. Choices range from polytetrafluoroethylene (PTFE, Teflon®) and perfluoroelastomers (Kalrez®) to polyethylene. Use of two sealing systems, such as a layering, may expand the choices. Elastomers are available in different grades of polymer and can vary in compound ingredients.

Solubility in Water

DME is very soluble in water [22, 23] and vice versa. Refer to Figure 2 for information about the solubility at 20°C.

The high solubility is a concern with underground storage. Any leakage poses a risk as the DME can be picked up by the ground water supply and then later released.



Figure 2 Solubility of DME in Water [23]

DME can be picked up by surface water (DME is soluble to 5.7% by weight at 20°C and 1 atmosphere). Several studies indicate that the volatilization half life of DME under these conditions is about 3 hours from a river and about 30 hours from a pond.

Water is also soluble in DME. At 20°C and pressures of 380 kPa gauge DME can hold up to 5.5% by weight of water. There is a concern regarding phase separation at low temperatures, which might result in line freezing or plugging [22].

4 VEHICLE FUEL SYSTEM AND DISPENSING OF DME

A number of potential issues were identified.

4.1 Material Compatibility

Elastomers are attacked by DME due to its high solvency. Choice of materials depends on the application in which it is going to be used and the service life expected. Some elastomers, such as polyurethane, Buna N, neoprene, and butyl elastomers, tend to swell. Most literature states that materials should be tested prior to widespread use. See Appendix A for examples of some of the elastomers that Akzo Nobel uses for DME service in different applications (not meant as a recommendation but rather an example only).

4.2 Maximum Permitted Filling Limits for Tanks

An internal Amoco document raised an issue regarding the use of LPG storage tanks for DME service. The concern relates to the potential for overfilling of tanks.

CAN/CGA-B149.2 Propane Installation Code in Canada and NFPA 58 Standard for the Storage and Handling of Liquefied Petroleum Gases in the U.S. (that are adopted in government regulation) dictate the maximum fill level for LPG containers and tanks. NFPA 58 also provides some of the background on the setting of the maximum fill level. The maximum permitted filling limits are the maximum safe quantity that will ensure that the tank will not become liquid full when the liquid is at the highest anticipated temperature. For tanks or containers with a capacity of 1 200 USWG or less the temperature is assumed to be 54.4°C (130°F). For tanks with a capacity of 1 200 USWG or greater the temperature is assumed to be 46.1°C (115°F). If a fixed liquid level gauge is used during tank filling then the maximum fill level is calculated based on the temperature of the liquid being 4.4°C (40°F) [24]. The difference between the maximum permitted fill level (as if the liquid were at 4.4°C) and the liquid full level (at either 46.1°C or 54.4°C depending upon tank size) provides room for the expansion of liquid between those temperatures without activating the pressure relief valve of the tank.

Liquid DME, propane, and n-butane expand and contract at different rates. An example of the percent expansion using the temperatures in the previous paragraph is provided in Table 4.

| | 0 | | |
|--------------------------|---------|-----|----------|
| Temperature Change in °C | Propane | DME | N-Butane |
| From -15.6 to +46.1 | 21% | 15% | 12% |
| From -15.6 to +54.1 | 25% | 18% | 14% |

Table 4Liquid Expansion in %

Filling a tank with either propane or DME based on a maximum fill level specifically for nbutane would result in overfilling of the tank (if the temperature rose to the high end of the range).

4.3 Underground Storage Tanks

DME is soluble in water. This could be an issue with underground storage and piping, in that, if a leak develops, DME could be leached into the water and subsequently released into a confined area where a flammable mixture could be generated. Special precautions may be necessary when using underground tanks for storing DME.

4.4 Purging & Pressure Testing

Tank and line purging and pressure testing should be done with nitrogen.

5 CONCLUSIONS

5.1 DME Fuel Properties

DME is chemically stable at normal temperatures. The risk of forming peroxides while in storage and in the presence of air appears to be very low. Questions arise regarding the exact values of the lower and upper flammability limits but even the lowest value of the lower flammability limit is higher than many of the other liquefied gases.

DME is relatively benign. It has low toxicity and is non-carcinogenic. The LC_{50} for mice ranges from 38% to 49%. Only a few governments have established workplace threshold limit values.

DME is a photochemical oxidant with a relatively short life. Its ozone-forming potential is reported to be lower than that of LPG or gasoline.

DME is very soluble in water and special precautions would be required to keep it from coming into contact with water. DME is also a strong solvent and most elastomers are attacked by DME. Special care must be taken in the selection of elastomers to prevent premature failure of components using elastomers.

5.2 Vehicle Fuel System and Dispensing of DME

Due to the strong solvent action of DME special care must be taken in the selection of elastomers used for vehicle and dispensing components that come into contact with DME.

Although the maximum filling density of propane can be used for DME tanks, this may not give optimum tank loading.

Special precautions would be required for underground piping and storage of DME due to its high solubility in water.

6 RECOMMENDATIONS FOR FURTHER RESEARCH

The recommendations provided in the earlier report have not changed as a result of this addendum.

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APPENDIX A

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APPENDIX B

Examples of Elastomers Used in DME Service

Storage and Piping



Shut off Valve







Illustrations are supplied by Akzo Nobel Chemicals bv (not meant as recommendations).



PTFE Polytetrafluoroethylene EPDM Ethylene propylene