

GMM3.0

Green Maritime Methanol

Workplan WP 1.2: Safety – Operations with methanol





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1 Introduction

1.1 Project background

The maritime sector is facing a major challenge. While a globally growing economy leads to more demand for transport of goods, the goals from the Paris climate agreement and the subsequent agreement in IMO requires a 70% reduction of CO₂-emissions from maritime transport by 2050 compared to 2008. Several parties are working on the development of new fuel types for shipping, such as methanol, hydrogen, various biofuels and battery-electric. There is great uncertainty about the best option for the short and longer term, and what the best options are for different ship segments.

Within the Green Maritime Methanol 1 and 2 projects, sector wide consortia of respectively 30 and 37 partners have investigated the feasibility of application of methanol as a marine fuel. The main goal of the Green Maritime Methanol projects is to identify and remove barriers that stand in the way of methanol implementation.

For Green Maritime Methanol 3.0 the following objectives have been defined:

- Develop solutions for current safety issues when applying methanol.
- Broaden the knowledge on single methanol fuel solutions for powertrains on-board of ships.
- Understand the design barriers for different ship types by developing new ship design pilots.
- Understand the most important barriers (technology, economics and policy) towards investment decisions aimed at large scale adoption of methanol in shipping.

1.2 Aim of this document

The focus in WP1 lies on the safety aspects. Methanol is regarded as a hazard in its gaseous state. Due to the thermophysical properties of methanol, vapours can form at relatively low temperatures. Given that methanol is nearly odourless and colourless, it is difficult to detect. Nevertheless, its vapours pose a significant health risk and an explosion hazard.

It is therefore essential to understand the behaviour of methanol in case of leak and to extend the knowledge on its evaporation behaviour in confined spaces. Given the current insufficient knowledge on these topics, no clear guidelines that consider the risks of both toxicity and explosivity are available. Clear and unambiguous guidelines for methanol vapour risks are therefore needed. In order to obtain those, this WP aims to obtain clarity on the aforementioned safety aspects.

This document aims to inform the reader on the previous work done for the GMM project concerning the leakage and evaporation behaviour of methanol. And, to identify the knowledge gaps left between the previous work and the eventual goal: more insights in the risks caused by leakages of methanol, to support the development of guidelines for methanol propelled vessels. The eventual goal of this document is to present the intended activities to be done in the GMM 3.0 project, in order to reduce or eliminate the current knowledge gaps.

1.3 Revision table

Date	Description	Author	Reviewer	PM	Approver
7 May 2024	For external review	BRF	TGL	DEA	
31 July 2024	For internal review	BRF	DTS	DEA	
16 August 2024	Final			DEA	

2 Previous work

In this section, a summary of the previous work is given in order to inform and remind. First, a brief summary of the work by TNO is presented for GMM 2.0. Hereafter, an overview of the relevant input shared by partners is given.

2.1 GMM 2.0

For the GMM 2.0 project, calculations on the evaporation of methanol were done by TNO for different use cases, wherein in the case 'liquid spill in a confined space' is the most relevant case for GMM 3.0. For this use case, calculations were done for two extremes:

1. Spray release model: instantaneous evaporation with no pool formed, and
2. Pool evaporation model: all released methanol is added to the pool and evaporates from the pool.

The calculations were done following the methods of the *yellow book* [1].

The calculations in the *GMM 2.0, WP1 Development safety solutions* report [2] give a good representation of the order of magnitude and proportionality of the global methanol concentrations in a confined space in relation to room size, pipe pressure, hole size and modelling parameters. However, assumptions were made, which result in the inability to draw definitive conclusions based on the outcomes of the calculations presented in the *GMM 2.0 WP1* report. The main assumptions are:

1. The assumption of a non-boiling liquid. In reality, the assumption of a non-boiling liquid is not always valid. For example in the case of a (nearby) fire.
2. Instantaneous uniform distribution of the concentration methanol. Local concentrations are expected to be higher and therefore more critical.
3. Only 0.1 m/s venting speed above the pool is assumed, which is claimed to be highly conservative in the *GMM 2.0 WP 1 report*.
4. Models that take into account only instantaneous and complete evaporation or the forming of *only* a pool from which the methanol evaporates. Wherein reality, releases are expected to be characterised by a combination of these two.

In the case of pool evaporation, the confined space volume and pool size are the most influential parameters. Pipe pressure and response time have a more limited effect. In the case of a spray release, all parameters (i.e. pressure, space volume, response time and pipe diameter) are of significant matter.

Further on, the calculations gave insight into the methanol concentrations in the air for the two extremes, whilst varying the calculation parameters. The results showed that there is a very significant difference between the pool evaporation model and the spray release model. Hence, the *knowledge gap* left after this research was to investigate how a methanol leak releases and evaporates exactly, in order to get more clear insights in the methanol concentrations in a confined space.

The main recommendations of the GMM 2.0 WP1 report stated the following:

- Develop a simple calculation model on heat transfer towards methanol fuel tank when subjected to fire or sun radiation, in conjunction with fuel evaporation and vapor pressure build up.

- In the model only global concentrations of a space are considered, local concentrations are expected to be higher and therefore more critical.

2.2 Workshop

On Thursday, February 8th 2024, TNO hosted a workshop focused on Work Package (WP) 1.2 – Operations with Methanol. The event was well-attended, with 26 representatives from nearly all participants of GMM3.0 in attendance. Throughout the day, two brainstorming sessions were held to gather further insights into the knowledge gaps. A summary of the workshop and the results of the sessions can be found in the Memo ‘WP1 Safety aspects: Workshop task WP1.2 - Operations with Methanol’ [3].

The workshop revealed that the suggested problems and knowledge gaps provided by the participants had significant overlap and could be categorized into the following groups:

- Amount of methanol release/leakages
- Toxic area plans
- Sensor and equipment selection
- Evaporation of methanol
- Sizing of overflow tanks.

2.3 Partner input

Damen [4] performed calculations based on the TNO GMM 2.0 models [2] (see Appendix A), that contains both the TNO models for direct evaporation and pool release. Their main objective for these calculations was to find out if ventilation in a confined space could lower the concentration of methanol vapour enough to bring it below toxicity limits and the Lower Explosive Limit (LEL). The main difference between the calculations of Damen and the calculations presented in the TNO report, is that the model of Damen determines how much of the *leaked methanol is able to directly evaporate* with their parameters of interest, instead of calculating the actual direct evaporation. Besides, Damen looked into whether ventilation could be used to prevent a toxic cloud. As the GMM 2.0 report assumed an instantaneous uniform global distribution of the methanol concentration, Damen incorporated a hazardous area calculation based on IEC Standard 60079-10-1 Annex D [5]. Concluding, Damen states that it still remains unclear how much methanol will directly evaporate and it is recommended to look into this in a follow-up study.

Maersk already deploys a methanol-based vessel. In order to safely design their vessel, calculations on the evaporation and release of methanol were performed by Maersk [6]. They have shared some of their calculation methods, which include the following scenarios (see Appendix B):

- Evaporation from a pool with surface wind
- Evaporation from a pool due to sun radiation
- Evaporation from spray

Their calculation methods are mainly based on the IEC Standard 60079-10-1 Annex B [5]. The spray evaporation calculations already give a more clear idea on the actual release of methanol during a leak, but it is still based on the several (conservative) assumptions. The actual ratio of vapour and fog/rain that forms a pool after a leak remains unclear.

2.4 Chapter conclusion

For GMM 2.0, TNO performed calculations for the use case 'spill in confined space'. For this use case, calculations were done for two extremes: assuming only pool evaporation and assuming only a spray release. It remained unclear how methanol would be released from a leak and what the ratio between vapour and liquid would be in such release.

Both Damen and Maersk based some of their calculations on IEC standard 60079-10-1, although this standard is predominantly meant for classification of areas where flammable gas or vapour hazards may arise [5]. However, toxicity is not taken into account and in the case of methanol, toxicity is of higher relevance than flammability and explosivity, as the toxicity limits are below those.

What emerges from both the workshop and previous work, is that it remains unclear how methanol will evaporate and which concentrations will be present in a confined space. Whether it will flow out as a spray, vapour or a flow is of interest for the evaporation rate and forming of pools. And once there is a pool, the evaporation, also depending on ventilation and temperature, are to be clarified in order to quantify the risks for personnel and the integrity of the ship.

3 Workplan

The following section outlines the proposed research questions that aim to fill the existing gaps in knowledge, along with the activities to be done that will be used to address them.

3.1 Knowledge gaps

To close the gap between the work done and the remaining uncertainties, more insights need to be generated into the evaporation behaviour of Methanol. Therefore, the following research question were formulated:

- **How does methanol release in case of a leak?**
 - What is the influence of the pressure and/or orifice on the release? Orifice means here the shape of the opening, be it smooth or damaged.
 - Which phase changes occur between the start of the leak at the outlet and at velocity = 0 (at the pool, if it forms)?
- **What is the evaporation rate of methanol?**
 - What is the influence of temperature?
 - What is the influence of ventilation?
 - What is the influence of exposed surface/ volume ratio? This applies to droplets as well as the pool or drip tray.

3.2 Activities to be done

In order to answer the research questions mentioned in the previous paragraph, the following work is proposed:

- **What is the influence of the pressure and/or orifice on the release?**
 - Dispersion analyses (TNO)
 - Lab testing, simulate real leakage scenarios (TNO)
- **Which phase changes occur between the start of the leak at the outlet and at velocity = 0 (at the pool, if it forms)?**
 - CFD analyses (by partners in collaboration with TNO)
 - Literature review on relevant fluid dynamics/thermodynamics (TNO)
 - Lab testing, simulate real leakage scenarios recorded with High Speed Camera (TNO).
- **What is the evaporation rate of methanol depending on temperature, ventilation and surface/ volume ratio?**
 - CFD & thermodynamics (by partners in collaboration with TNO)
- **Rerun more realistic scenarios**
 - Retrieve feedback from partners
 - Lab testing for validation (TNO)

The aforementioned activities are considered as the core activities. These activities will be refined in consultation with the consortium partners and elaborated upon in separate documents (e.g., test plan).

4 References

- [1] C. J. H. van den Bosch, "Chapter 3 - Pool Evaporation," in *Methods for the calculation of physical effects - due to releases of hazardous materials*, VROM, 2005, pp. 202-329.
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- [3] F. Bziker, "GMM3.0 - WP1 Safety Aspects: Workshop task WP1.2 - Operations with Methanol," TNO, Delft, 2024.
- [4] S. Bierens, "Methanol dispersion in a ventilated space," Damen Shipyards, Research & Development, Gorinchem, 2024.
- [5] IEC 60079-10-1, "International Standard - Explosive Atmospheres - Part 10-1: Classification of areas - Explosive gas atmospheres," International Electrotechnical Commission (IEC), Geneva, 202.
- [6] Maersk, "Appendix B - Methanol evaporation estimates for design," Maersk, Copenhagen, 2023.
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- [8] "Explosive atmospheres - Part 10-1: Classification of areas - Explosive gas atmospheres (IEC 60079-10-1:2020;IDT)," NEN, 2021.
- [9] R. Kortenhorst, "Enabling safe and practicable storage of methanol as a ship's fuel by describing and mitigating venting risks," TU Delft/Damen, 2022.

Appendix A – Calculations Damen

([Hyperlink to PDF](#))

DAMEN

RESEARCH DEVELOPMENT & INNOVATION

MEMO

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to Pieter Spruijt
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from Sander Bierens
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subject Methanol dispersion in a ventilated space
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Introduction

All spaces containing equipment from which methanol could leak should be fully inerted with nitrogen or ventilated to dilute the concentration of methanol in the air below the Lower Explosive Limit (LEL) of 6 vol%. Ventilation is the most easy option, but if the LEL is reached, the outlet of the ventilation is considered a hazardous area. In this report, the concentration of methanol in the air will be determined at different leakage scenarios. This to gain insight if it is possible to dilute the methanol concentration inside a room during a hazard to safe levels and preventing the existence of a hazardous area by means of ventilation.

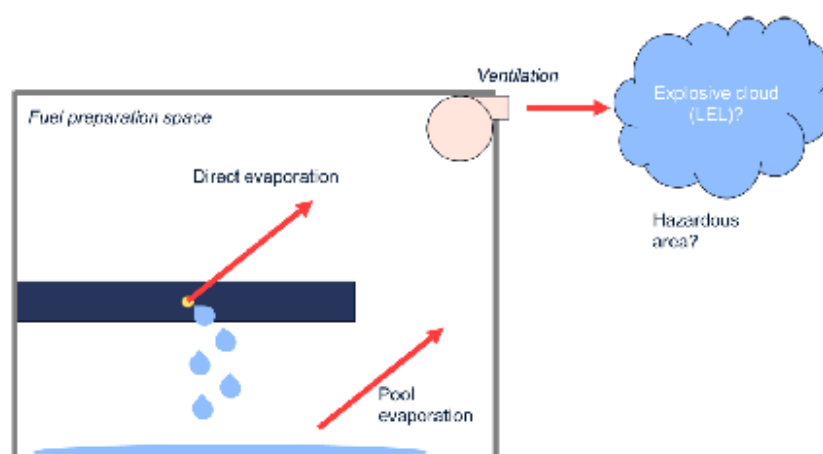


Figure 1: schematic overview of the case

Approach

Previously, TNO [1] has performed an evaluation of the MeOH concentration in the fuel preparation room using two different models: the first model assumes that all methanol would directly evaporate when it escapes the leaking pipe. The second model assumes that all the methanol will first form a pool and then evaporate. The first model will show a very conservative result, while the second model is too optimistic. The truth lies in between. To find this truth, a model has been developed that contains both the (optimized) models from TNO. Since spray evaporation is a very complex phenomenon and not fully well understood (which is assumed to be a main parameter in the dispersion calculations), the current model determines how much of the leaked methanol is allowed to directly evaporate with the current parameters instead of calculating the actual direct evaporation. The result can give a first indication and a sense of feeling if it is possible to ventilate the room without reaching LEL; e.g. if the model says that only 1% is allowed to directly evaporate before reaching LEL, it is unlikely that ventilation can be used. However, if the model says that 98% can directly evaporate before reaching LEL, it is very likely that ventilation is a good way to dilute the methanol concentration in the air.

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Appendix B – Calculations Maersk

([Hyperlink to PDF](#))

Appendix B Evaporation estimates

Appendix B Methanol evaporation estimates for design

This appendix provides guidance on methods to estimate expected evaporation rates from methanol in storage and as spills. These may be used during design for evaluating hazardous zones, selection of gas detector sensitivity, for gas dispersion studies, etc.

This appendix does not form a normative part of the design standard. It is intended to provide a convenient summary of available information and to facilitate selection of baseline design data, which should be agreed for each project specifically.

Introduction

When studying gas or vapour generation from liquid methanol with a temperature below boiling point there are two fundamentally different cases.

The first is methanol in storage in a confined space and covered with a gas cap. For this case a steady state concentration of vapour, governed by the vapour pressure of methanol, will develop that depends on the gas cap pressure and temperature in the tank.

The second case is the dynamic case where methanol is released into a previously methanol-free ventilated space, typically as a spill or a leak. In this case the governing parameter is the evaporation rate over time, which in combination with the ventilation or wind speed will give an indication of maximum attainable instantaneous concentrations.

Confined space steady state

This case is essentially analogous to water vapour in air and well documented. Basically, as the molecules in the liquid vibrate with heat, they will bump into each other, and some will be bumped to an energy state where they transfer to the gas phase. Meanwhile some molecules in gas phase will lose energy in collisions and transition to liquid phase. The more gas phase there is the more likely such collisions are. Thus, an equilibrium, the so-called vapour pressure, is eventually found, which is determined by the temperature in the tank, **but importantly not dependent on absolute pressure in the space¹**.

The vapour pressure is ranging from 4 to 35 kPa in the most interesting temperature range for stored methanol, 273 K (0 °C) to 313 K (40 °C). With the tank pressure in the range 100 to 120 kPa this means a volumetric fraction in the range of about 3% to 35%, the remainder being nitrogen.

As a worst case ~~35% concentration of~~ **0.44 kg methanol vapour per m³ released gas** could be assumed at the outlet when studying vent releases from the enclosed tanks. This occurs if the tank interior is around 40°C. Some of this methanol can then be expected to condense and fall out as dew if the ambient temperature around the vent is lower.

¹ This may appear somewhat counterintuitive. The explanation, simply put, is that the distance between molecules in a gas is large and different gases fit "between" each other, and pressure of one does not affect another's vapour concentration.