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## Green Maritime Methanol 2.0

WP1 Development safety solutions

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# Summary

Green Methanol is one of the feasible alternative energy carrier candidates for replacing fossil fuels on board ships. Unfortunately methanol is toxic to humans and it has a flashpoint of 12 °C which is well below the minimum required temperature of 60 °C , according SOLAS, hence also posing a fire risk. Therefore methanol needs to be regarded as hazardous. This report gives technical information regarding methanol on board and how methanol behaves when spilled. The other matter addressed is the concept of equivalent safety, which needs to be followed according IMO regulations when prescriptive regulations are not complied with. The aim is to increase the knowledge of designers, builders and crew. Finally, a list of knowledge gaps is given.

It is noted that quite a few matters have been identified which require further investigation. These will be addressed in a the next GMM project, GMM 3.0. Therefore for this report a 2nd version, based on the relevant findings of GMM 3.0, is already foreseen.

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# 1 Introduction

The maritime community has committed itself to move away from fuels which are pollutant or contributing to the greenhouse gas issue. This implies resorting to fuels other than heavy fuel oil (HFO), marine diesel oil (MDO) and marine gas oil (MGO) [1]. Candidate alternative fuels are (liquified) natural gas, hydrogen, ammonia and methanol. Unfortunately, all of these come with additional safety issues, because they are gaseous and/or have a low flash point. Moreover, ammonia and to a lesser extent methanol are toxic.

This report is only about methanol. Safety issues related to the use of methanol on board are addressed. However, the general approach towards safe use of methanol on board, as outlined in this report, is applicable to any hazardous fuel.

This report must be regarded as a 'living document' much useful information is given, however the authors realise that the data is not exhaustive, especially regarding methanol evaporation, methanol toxicity and failure frequencies. It is expected that a 2<sup>nd</sup> version of this document will be published in due cause. This will be done within the framework of the Green Maritime Methanol III project, currently under development.

Interim guidelines have been published by IMO on the use of methanol as fuel on board, known as MSC.1/Circular.1621 - Interim Guidelines for the Safety of Ships Using Methyl/Ethyl Alcohol as Fuel [2]. The guidelines follow a goal-based approach. The provisions for the design of the ship and its systems given in the guidelines are based on current operational experience. They aim at minimising the risk for the ship, its crew and the environment. A risk assessment is to be conducted to demonstrate that the risks arising from the use of methanol are properly addressed.

The guidelines contain prescriptive regulations. When these are complied with it is believed that sufficient safety is attained. For some ship types however, these guidelines prove to be too restrictive to make feasible designs. Fortunately the guidelines allow diverting from the prescriptive regulations through proposing alternative safety measures, provided convincing technical evidence is available to demonstrate the effectiveness of these measures. In such cases it has to be shown that the alternative measures provide safety which is equivalent to the safety attained with conventional fuels. How this works is explained in this report.

There are four main sections in this report:

1. An explanation on equivalent safety.
2. A description of typical safety characteristics related to methanol and behaviour of methanol when spilled on board.
3. An identification of incident / accident scenarios with methanol fuel on board, described through fault trees and event trees.
4. An identification of gaps in knowledge and know-how, regarding methanol behaviour on board in case of incidents / accidents.

Equivalent safety is addressed in chapter 2. Safety characteristics and behaviour of methanol when spilled are dealt with in chapter 3. Relevant incident / accident scenarios are described in chapter 4, while knowledge and know-how gaps are discussed in chapter 5. Conclusions and recommendations are given in chapter 6.

# 2 Equivalent safety according IMO and CESNI

## 2.1 Risk matrix and equivalent safety

Both IMO [3] and CESNI [4] regulations prescribe a risk-based approach to demonstrate that alternative fuels attain a safety level which is equivalent the level attained for conventional fuels. For this purpose, risk is expressed as a combination of the probability of occurrence of harm (likelihood) and the consequence of that harm (severity in terms of, amongst other things, injury or disease), as visualised in Figure 2.1. The diagram is referred to as a risk matrix approach of risk assessment.

Injury and Disease		Low level short-term subjective inconvenience or symptoms. No measurable physical effects. No medical treatment required.	Objective but reversible disability/impairment and/or medical treatment, injuries requiring hospitalization.	Moderate irreversible disability or impairment (<30%) to one or more persons.	Single fatality and/or severe irreversible disability or impairment (>30%) to one or more persons.	Short or long term health effects leading to multiple fatalities, or significant irreversible health effects to >50 persons.
		Low (1)	Minor (2)	Moderate (3)	Major (4)	Critical (5)
Likelihood	Almost Certain (E) Occurs 1 or more times a year	High	High	Extreme	Extreme	Extreme
	Likely (D) Occurs once every 1-10 years	Moderate	High	High	Extreme	Extreme
	Possible (C) Occurs once every 10-100 years	Low	Moderate	High	Extreme	Extreme
	Unlikely (B) Occurs once every 100-1000 years	Low	Low	Moderate	High	Extreme
	Rare (A) Occurs once every 1000-10000 years	Low	Low	Moderate	High	High

Figure 2.1: Typical risk matrix [5]

Regulatory authorities allow conventional (fossil) fuels on board, which implies that these fuels are considered sufficiently safe. This can be interpreted as that they are positioned in the green ‘Low’ or yellow<sup>1</sup> ‘Moderate’ area of the risk matrix. Hence, when a fuel system for an alternative fuel, e.g. methanol, is located in the green or yellow area of the risk matrix as well, its safety is equivalent to the safety of the fossil fuel. When hazardous events end up in the ‘High’ or ‘Extreme’ area, risk control measures have to be taken to reduce likelihood and / or consequence.

Calculating probabilities and consequences are essential for a meaningful risk assessment.

<sup>1</sup> In literature the yellow area is referred to as the ALARP area. See next page for an explanation.



The system then needs to be reassessed to demonstrate that reductions are sufficient to shift the hazardous events into the green ‘Low’ or yellow ‘Moderate’ area.

The yellow region represents a tolerable region defined by the concept of ALARP (As Low As Reasonably Practicable). The term reasonable is interpreted to mean cost-effective. To clarify, reducing the risk of a potentially hazardous event to the yellow “tolerable risk” region does not imply that the obligation to reduce the risk even further is no longer valid. So long as the costs in implementing risk reduction are not disproportionate to the benefits gained, it is strongly advised that further mitigation measures be taken. The green region implies that the identified risk is negligible and no risk reduction required.

Figure 2.2 pictures the risk assessment process.

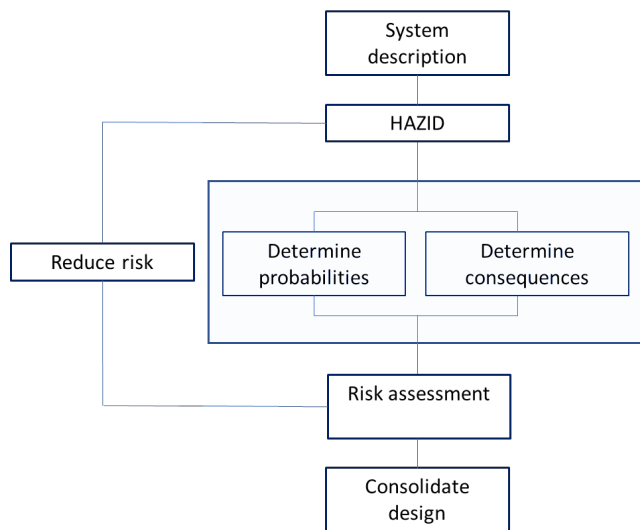


Figure 2.2: The risk assessment process

## 2.2 Determining probabilities and consequences

In order to determine probabilities and consequences, hazardous scenarios need to be identified, such as a leakage or loss of containment (LOC) of the fuel. Uncontrolled vapour venting is another example of a potentially hazardous event. Examples of leakages are those at flange connections, at faulty welds, at fatigue cracks and at corrosion spots. LOC will occur following a fuel tank rupture after a ship collision, when pressure relief venting occurs driven by a tank-adjacent fire, or when a pipe ruptures caused by dropped objects. For the identification of scenarios several techniques are available, for example: Hazard Identification (HAZID), Hazard and Operability Analysis (HAZOP), Failure Mode Effects (and Criticality) Analysis (FME(C)A), and Fault Tree Analysis. Standards and norms like ISO/IEC provide guidelines for a risk assessment [6].

For each scenario identified, both *probability of occurrence* and *consequences* have to be determined [6]. Several techniques are available for calculating the probabilities, such as Event Tree analysis (ETA), Fault Tree analysis (FTA), and Bayesian Belief Networks analysis (BBN). These techniques require values for probabilities of the basic events constituting the scenario. Basic event probabilities can be obtained from literature e.g. [7] and [8], through statistics (data analysis and calculation), through testing, or, if no data is available, through relying on expert opinions. Chapter 4 gives a further explanation.

Consequences of incidents with methanol for people are injuries, disease or death due to exposure to combusting methanol or the toxic effects of its vapour. The related harmful properties of the fuel are flammability (resulting in fire) and toxicity. The extent of the hazardous zone, in case of an incident, can be determined by applying analytical expressions from, for example, ISO and IEC standards (e.g. [9]) or computer codes, such as PHAST [10], Safeti-NL [11] or EFFECTS [12]. In situations where local effects are dominant, CFD analyses or tests are more suitable, e.g. Kameleon FireEX [13], FLACS-CDF [14], or Fluent [15].

## 2.3 Required technical and statistical evidence

The technical and statistical evidence required to calculate probabilities and consequences has to be based on natural sciences, i.e. physics, chemistry, and biology and reliable data sources. Data, calculation models and experimental facilities to obtain this evidence are available. Typical data examples are component and machine failure statistics (e.g. [7, 16]), collision statistics (e.g. using Automatic Identification System (AIS) data or [17]) and atmospheric dispersion datasets (e.g. a compilation from [18]). Typical examples of numerical analyses required to calculate conditional probabilities are mechanical fatigue calculations, accidental limit state analysis, crash analyses, fire exposure/ solar exposure calculations, and blast calculations. Several methods can be used for these analyses, e.g. analytical models, finite element analyses (LS-DYNA, Abaqus) or fire dynamics simulator. In specific cases, additional experiments will be required to validate the models and attain sufficient confidence in the predictions. These experiments will involve lab-scale and full-scale testing covering phenomena such as cloud dispersion, leakage and loss of containment, tank fracture, crash, and fire.

## 2.4 Risk reduction

When the initial design of an alternative fuel system shows an ‘extreme’, a ‘high’ or a ‘moderate’ risk, risk control measures have to be taken. Two control options are available: reducing the probability of a hazardous scenario actually taking place and mitigating consequences of the scenario when it takes place. Typical measures to reduce probability are: designing for crashworthiness, monitoring of system state, applying pressure relief valves or applying double-walled fuel lines. Typical mitigating measures are: providing ventilation, use of protective clothing, and maintaining overpressure in accommodation or work spaces. The effect of these measures needs to be quantified by calculating the decrease in either the probability of occurrence or the consequences of these scenarios, or both if possible. Provided the risk of the scenario in question can be lowered to an acceptable category (at most “moderate”), the risk assessment can then be updated to demonstrate equivalent safety.

## 2.5 Opportunities

As has been said, calculating probabilities and consequences is pivotal for the risk-based approach to demonstrate equivalent safety. This requires both supporting technical evidence as well as identifying and assessing risk control measures.

Following the approach as outlined in this document, gives the following advantages:

1. An increased design freedom based on firm technical evidence, especially when deviation from prescriptive regulations may be desirable.
2. The possibility to introduce fuels not (yet) covered by prescriptive regulations, such as ammonia and hydrogen.
3. The possibility to apply alternative design solutions supported by technical evidence.
4. The potential to provide technical evidence for formulating prescriptive regulations.

# 3 Methanol safety characteristics spill behaviour

## 3.1 Introduction

This chapter describes typical methanol behaviour on board ships during potentially unsafe situations, in terms of 'ball park' figures. This is done by using first principle methods aiming for simplified calculations to recognise trends and identify areas for further research which may require experimental investigation.

The result is an improved understanding of the behaviour of methanol on board, which can be used as background for fault trees and event trees that will be developed in stage 2 (chapter 4) as well as the more detailed scenario analysis in stage 3 (chapter 5).

Together with the GMM partners, five scenarios were selected for the initial analyses in stage 1:

1. Methanol vapour release on deck (venting scenario above the waterline), which is discussed in section 3.3.
2. Methanol vapour release below the waterline (venting scenario), which is discussed in section 3.4.
3. Methanol liquid spill in a confined space (e.g. the technical space, from a fuel line or a day tank appendage), which is discussed in section 3.5. The framework of this calculation could also be applied to a leak in the cofferdam, considering this is a liquid spill in a confined space.
4. Methanol liquid spill on the quay (contents of the bunker hose spilled), which is discussed in section 3.6.
5. Methanol liquid spill on water (e.g. following a collision or structural malfunction), which is discussed in section 3.7.

It should be noted that the above list is not exhaustive.

Before studying these separate scenarios, a summary is given of relevant data of methanol (section 3.2).

## 3.2 Methanol data

Methanol is a clear, colourless liquid that is soluble in water and is biodegradable [19]. Methanol is both flammable and toxic. Some of its most important physical properties are given in Table 3.1.

Table 3.1: General properties of methanol. Taken from [19], [20]

Description	Value/classification
Name	Methanol
Chemical formula	CH <sub>3</sub> OH
Molar mass [kg/kmol]	32.04
Freezing point [°C]	-98
Flash point [°C]	12
Boiling point [°C]	64.6
Critical point [°C], [MPa]	239, 8.084
Explosive/Flammable limits in air (v/v%)	6 (LEL/LFL) – 36 (UEL/UFL) 6.7 (LEL/LFL)
Solubility: Methanol in water/ Water in methanol	100%/100%
Flammable vapour above methanol/water mixture	100wt% methanol – 25wt% methanol
Conversion factors	1 ppm = 1.33 mg/m <sup>3</sup> ; 1 mg/m <sup>3</sup> = 0.76 ppm

Another parameter of importance is the vapour pressure as a function of temperature. This parameter is important as the temperature inside a fuel tank is not constant and therefore the amount of methanol that is found in the gas cap above the methanol liquid inside the fuel tank will vary with temperature.

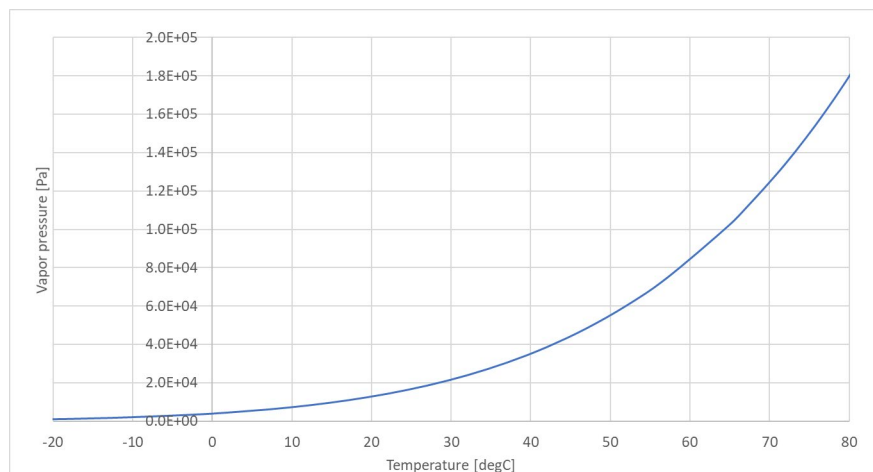


Figure 3.1: Methanol vapour pressure as a function of temp. [21]

For toxicity several numbers can be found in literature, see Table 3.2. The TWA value is considered a safe value for which no adverse effects will occur for an exposure of 8 hr/day, 40 hr/wk. The EEGL is most often used for submarine design to indicate emergency exposure levels below which no irreversible effects occur.

“An EEGL is defined as a ceiling concentration that will not cause irreversible harm or prevent performance of essential tasks, such as closing a hatch or using a fire extinguisher, during a rare emergency situation usually lasting 1-24 hours.” [22]

Table 3.2: Toxicity numbers for methanol.

Description	Value
TWA (Time weighed average)	200 ppm (260 mg/m <sup>3</sup> ) [23]
EEGL (Emergency Exposure Guidance Levels) <sup>2</sup>	800 ppm for 10 minutes, 400 ppm for 30 minutes, 200 ppm for 1 hour, 10 ppm for 24 hours [23]
IDLH (Immediate danger to life and health)	6 000 ppm [23]

The National Institute of Occupational Safety and Health (NIOSH) defines an immediately dangerous to life or health condition as a situation "that poses a threat of exposure to airborne contaminants when that exposure is likely to cause death or immediate or delayed permanent adverse health effects or prevent escape from such an environment." The IDLH limit represents the concentration of a chemical in the air to which healthy adult workers could be exposed (if their respirators fail) without suffering permanent or escape-impairing health effects. Until 1994, an exposure duration of 30 minutes was associated with the IDLH. However, the current definition has no exposure duration associated with it; workers should not be in an IDLH environment for any length of time unless they are equipped and protected to be in that environment.” [24]

## 3.3 Methanol vapour release on deck

One of the hazards that is identified in the GMM2.0 project is the release of a mixture of methanol vapour and nitrogen when the pressure relief valve is opening due to overpressure during; refuelling, a fire in an adjacent compartment, or a tank volume reduction following a collision. This release is referred to as the “venting event”.

### 3.3.1 Introduction

Three hazards are identified as the most stringent, related to this venting event:

1. Flammability/explosivity of the methanol vapour.
2. Toxicity.
3. Asphyxiation property of CH<sub>3</sub>OH-N<sub>2</sub> mixture.

The third hazard is called inert gas asphyxiation and refers to the case where the physiologically inert gas (in this case nitrogen) acts as a diluent that reduces the oxygen concentration in the air that is breathed in. This hazard was not studied in stage 1, assuming that the short duration of the venting event will not cause a long-term deficiency of oxygen. However, it is strongly suggested that a dispersion-code, such as EFFECTS, is used to quantify the hazard associated with a nitrogen release. The NEN-EN-IEC 60079-10-1 [9] indicates results based on dispersion-calculations that can be used for hazardous zone classifications.

<sup>2</sup> These relatively low values for the EEGL are for a background base concentration that should be safe in normal working conditions. It should not be applied to anomaly events such as studied in this report.

The goal of this section is to get a feeling for the safety distances, related to the flammability and toxicity hazards, that should be applied when venting methanol above deck.

### 3.3.2 Method

For the calculations of safety distances NEN-EN-IEC 60079-10-1 [9] is used. It is “concerned with the classification of areas where flammable gas or vapour hazards may arise and may then be used as a basis to support the proper design, construction, operation and maintenance of equipment for use in hazardous areas [...]” [25]. Typical prevention in the process industry comprises elimination of open flames, cigarettes and sparks [26] in the hazardous area.

The IEC standard provides a classification of the severity of the explosion risk per area, as a function of the properties of the surroundings and the gas. That is, to classify hazardous areas and to indicate important considerations in the design of a process plant. In this report it is assumed that a tank from which a methanol/nitrogen mixture is vented can be considered as (part of) a process plant. The applicability of the IEC is justified by the statement that “It (i.e. the IEC standard) is intended to be applied where there may be an ignition hazard due to the presence of flammable gas or vapour, mixed with air [...]” [9].

The IEC standard does not explicitly enable the analysis of a safety zone in relation to toxicity. However, considering the nature of the IEC calculation (which is based on CFD (Computational Fluid Dynamics) simulations of various venting events), which defines the zones based on gas concentration, the same principles would apply to the lower concentration that corresponds with a toxic environment. The IEC calculation, providing the validity bounds are not exceeded, is applied to study the safety zones for toxicity.

Lastly, to study the effect of the assumptions (see section 3.3.3), a parameter variation study is performed for both the explosivity and toxicity hazard.

### 3.3.3 Assumptions

The ranges for which the calculations in this section are performed are:

- Pressure relief valve (PRV) set pressure between 5 kPa and 20 kPa.
- Temperature between -15 and 35 degrees Celsius.
- Valve diameter of 50, 100 and 150 mm.

These values are selected to represent scenario's for a variety of vessels and operating conditions. Moreover methanol is assumed to behave in the considered outflow scenarios as a diffusive gas. It should be noted that the results will differ for a high velocity PRV, in that case a jet release can be more suitable.

The IEC standard distinguishes three gas types: heavy, jet and diffusive. The considerations are as follows:

- The mixture of methanol and air is not to be considered as a heavy gas. The mixture is considered as a heavy gas if the density of the mixture is at least 1.1 times the air density. Physically, a mixture of methanol vapour and nitrogen should, for a temperature of 20 degrees Celsius, consist of at least 95% methanol to reach this density. This is not a realistic situation.

- A jet release is not deemed realistic. A jet release is typically a choked release, which is not likely with the low overpressure level in the tank. This corresponds to the 30 m/s outflow velocity required by regulations [2] for methanol pressure relieve valves, which is much smaller than the sonic velocity in air (343 m/s).

The diffusive release is therefore considered as the most realistic scenario. The presence of a ship is assumed to justify a calculation for obstructed areas, which determines the ventilation velocity in the IEC. The relevant toxicity limit is assumed to be the IDLH (Immediate Danger to Life and Health), which is the limit for which the toxicity safety distances are calculated.

For a diffusive gas the IEC standard limits the applicability to characteristic release rates between 0.06 and 30 m<sup>3</sup>/s (see figure D.1 in NEN-EN-IEC 60079-10-1:2021). For the calculation this means that the minimum allowable valve diameter (full diameter) is, dependent on the PRV set pressure and operating temperature as given in Table 3.3. The explanation of these numbers is given in Appendix B. If the valve diameter is below this value, CFD simulations are required to arrive at reliable estimates of the required safety zone.

Table 3.3: Minimum valve diameter (full diameter) of the PRV, per PRV set pressure and operating temperature, to remain within the IEC validity bounds

	-15 °C	17 °C	35 °C
5 kPa	0.127 m	0.055 m	0.033 m
20 kPa	0.123 m	0.053 m	0.033 m

The volume percentage of methanol in the methanol-nitrogen mixture is a function of the pressure and temperature in the tank (see Figure 3.2). The corresponding formula is [21]:

$$\%_{CH_3OH} = \frac{\exp\left(82.718 - \frac{6904.5}{T} - 8.8622 \cdot \ln T + 7.47(10^{-6}) \cdot T^2\right)}{p_{tank}},$$

in which

$\%_{CH_3OH}$  Volume percentage methanol in the vapour  
 $T$  Temperature in the tank in K  
 $p_{tank}$  Absolute tank pressure in Pa



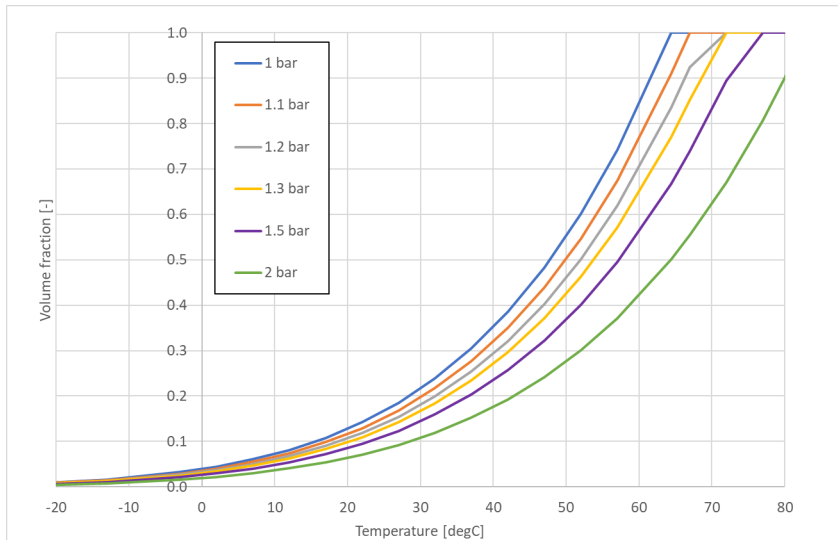


Figure 3.2: Volume fraction in methanol tank as a function of temperature and absolute pressure inside tank.

In the IEC standard, methanol should be considered as “A liquid with an associated release of flammable vapour.” (6.3.1); placing it within the scope of the standard. The proposed analysis for such a liquid is the “source of release approach” (Annex F).

Please refer to 3.3.6 (Discussion) where relief pressures and venting pipe diameters are discussed in hind sight.

### 3.3.4 Results: example case

The steps of this approach, according to the IEC standard, are followed in Appendix C for illustration purposes. The assumptions in this example case are a PRV opening at 5 kPa (50 mbar), vapour-nitrogen temperature 17 °C and a valve diameter of 100 mm.

The properties of methanol for this example case are summarized in the IEC format in Table 3.4. The resulting hazardous distances are presented in Table 3.5.

Table 3.4: Input parameters and classifications for the IEC calculation

Category	Description	Value/classification
Flammable substance	Name	Methanol (CH <sub>3</sub> OH)
	Molar mass [kg/kmol]	32.04
	Relative density gas/air	1.11 [27]
	Polytropic index of adiabatic expansion	1.2 <sup>3</sup>
	Flash point [° C]	11
	Ignition temperature [° C]	464
Volatility	Boiling point [° C]	64.7
	Vapour pressure at 20 [° C] [kPa]	16.9
LFL/UFL	Vol %	6/36
	kg/m <sup>3</sup>	
Source of release	Description	Pressure relief
	Location	On deck
	Grade of release	P – Primary
	Rate of release [kg/s]	0.019
	Release characteristic [m <sup>3</sup> /s]	0.21
Flammable substance	Operating temperature	20 [°C]
	State	G – Gas
Ventilation	Type	N – natural
	Degree of dilution	Medium
	Availability	Good

Table 3.5: Hazardous distance for an explosion risk for the example case (PRV limit of 5 kPa, 100 mm PRV diameter, 17 degrees Celsius in the tank), indicated for each gas type, resulting from the IEC calculation. The column of a diffusive gas is highlighted to indicate the relevant gas scenario for a methanol vapour release on deck.

Case study results	Heavy gas	Diffusive gas	Jet
Zone type	Zone 1 or 2	Zone 1 or 2	Zone 1 or 2
Zone extent vertical [m]	-	1.9	1.0
Zone extent horizontal [m]	4.1	1.9	1.0

To apply the model of the IEC to toxicity, the critical concentration was adjusted. The exposure limit that is used in this calculation is the IDLH (Immediate Danger to Life and Health) of 6000 ppm. This IDLH of methanol (methyl alcohol) is based on acute inhalation toxicity data in animals [28]. “This may be a conservative value due to the lack of relevant acute toxicity data for workers exposed to concentrations between 1,000 and 30,000 ppm.” [23].

<sup>3</sup> For an ideal gas assumption Mayer’s relation can be applied. This relation is  $\gamma = c_p/c_v$ . For methanol at 20 degrees Celsius  $c_p = 2.5$  kJ/kgK and  $c_v = 2.08$  kJ/kgK, yielding  $\gamma \approx 1.20$ .

6000 ppm methanol in air corresponds to a concentration of approximately 0.6% (volume percentage)<sup>4</sup>. For these concentrations the dilution level according to the IEC standard is also (just like the flammability analysis) **medium**. The analysis provides for safety distances as indicated in Table 3.6.

Table 3.6: Hazardous distance for a toxicity risk for the example case (PRV limit of 5 kPa, 100 mm PRV diameter, 17 degrees Celsius in the tank), indicated for each gas type, resulting from the application of the IEC framework to a toxic limit of 6000 ppm  $\approx$  0.6%. The column of a diffusive gas is highlighted to indicate the relevant gas scenario for a methanol vapour release on deck.

Case study results	Heavy gas	Diffusive gas	Jet
Zone extent vertical [m]	-	6.4	3.3
Zone extent horizontal [m]	13.6	6.4	3.3

### 3.3.5 Parameter study

As was indicated in section 3.3.3, the ranges for which the calculations in this section are performed are:

- Pressure relief valve (PRV) set pressure between 5 kPa and 20 kPa.
- Temperature between -15 and 35 degrees Celsius.
- Valve diameter of 50, 100 and 150 mm.

The influence of all three parameters is studied by performing the calculations for the outer limits of the parameters. The results are presented in Table 3.7. The parameter study scenarios indicate a temperature, pressure and size that respectively indicate the temperature in the tank, the pressure in the tank and the diameter of the PRV.

The cells which are highlighted in orange fall outside of the validity domain of the IEC curves. The validity and amount of (un)conservatism in this domain is unknown.

<sup>4</sup>This is because the molar mass and density of methanol vapor and air are relatively close. The relative density of methanol is approximately 1.1 times that of air and the molar mass is respectively 32.04 and 28.97 g/mol for methanol and dry air.

Table 3.7: Results of the parameters study for the safety radii (m) in relation to an explosive and toxic atmosphere, according to the IEC calculation. Cells that are highlighted in orange fall outside of the validity domain of the IEC curves.

Parameter study results	Explosive atmosphere (IEC)	Toxicity
Unit	[m]	[m]
Zone type	Zone 1 or 2 <sup>5</sup>	IDLH
-15 degC, 5 kPa, 50 mm	0.4	1.4
35 degC, 5 kPa, 50 mm	1.6	5.2
-15 degC, 20 kPa, 50 mm	0.4	1.4
35 degC, 20 kPa, 50 mm	1.6	5.4
-15 degC, 5 kPa, 100 mm	0.8	2.8
35 degC, 5 kPa, 100 mm	3.1	10.4
-15 degC, 20 kPa, 100 mm	0.9	2.8
35 degC, 20 kPa, 100 mm	3.2	10.8
-15 degC, 5 kPa, 150 mm	1.2	4.1
35 degC, 5 kPa, 150 mm	4.6	15.5
-15 degC, 20 kPa, 150 mm	1.3	4.2
35 degC, 20 kPa, 150 mm	4.8	16.1

The parameter study shows that, for the IEC calculation, the following trends and relations can be observed:

- The PRV set pressure has a negligible effect on the safety distances.
- The safety distance is approximately proportional with the diameter of the pressure relief valve. It should be noted that this is due to the time-independent nature of the IEC calculation. In reality a smaller diameter of the valve will result in a longer duration of each venting event and a higher flow velocity.
- The temperature in the tank has a significant effect on the safety distances: operating in a warmer environment significantly increases the percentage of methanol in the vapour (see also Figure 3.2) and thereby the required safety distance. It should be noted that the temperature in the tank can differ from ambient conditions due to differences in the temperature of the bunkered methanol and ambient conditions.
- For low temperatures and small (i.e. below 100 mm, see the results in Table 3.7) valve diameters, the IEC curves are not valid and tests or CFD simulations are required.

### 3.3.6 Discussion

In hind sight, some of the assumptions seem to be ‘out of range’. This go in particular for the smallest venting pipe size (d 50mm) and prv settings (5 kPa). Venting pipe diameter of at least 100 mm seems much more realistic while prv settings are bound to be in the range of 50 kPa (500 mbar), because of the vapour pressure of methanol at elevated temperatures (e.g. 56 kPa @ 50 C).

<sup>5</sup> If a vapor return is present during bunkering, the classification is zone 2. Otherwise, the classification is zone 1.

The IEC indicates a time-independent zone classification. This means that, without a vapour return during bunkering, a significant zone of the vessel should be considered as zone 1. When the venting release can be reduced to a secondary release (which is achieved if the venting event is not part of the normal operation) – this is reduced to a zone 2 classification. In both situations the classification is time-independent, which means that it is not only during e.g. bunkering.

To prevent ignition, sparks (also from static electricity) should be eliminated. “Due to the flammability of methanol vapour, static electricity may ignite it. Therefore, grounding and bonding should always be applied when there is a potential for static electricity, and is required for all equipment.” [29].

The application of the IEC with toxicity concentrations in addition to flammability concentrations is justified by considering that the curves on hazardous distances are based on reputed CFD simulations of various ventilation events and thus focus on the spreading of gas rather than the exclusive applicability for flammability. Thereby it is assumed that the ventilation velocity studies by which the developers of the IEC have generated their graphs can as well be extended to toxicity.

A note from the IEC is that “Extrapolation of the curves beyond the chart area shown should not be undertaken due to other factors that will affect the assessment beyond the limits indicated [...]” [9]. For a diffusive gas this limits the applicability to characteristic release rates between 0.06 and 30 m<sup>3</sup>/s. The calculations in this chapter are within these limits.

### 3.3.6.1 Limitations

Three main limitations are identified with regards to the presented analysis:

- There is no time component. For a ship this is not convenient as the hazardous zone should be available for other operations when venting does not occur.
- In the calculation of the toxic safety distance, local effects are not taken into account. The released volume of methanol is non-uniformly distributed within the cylinder, which means that -during a venting event- close to the vent opening a much higher concentration could occur. Also, the vented vapour may spread in a specific direction, depending on many factors such as wind speed and direction. In all situations it is advisable to not enter the zone within the indicated perimeter without additional precautions.
- The hazard of inert gas asphyxiation is not considered in this analysis, whereas neglecting this hazard in the design and analyses could provide for an unsafe environment. It is recommended to study this hazard using more advanced methods than first principle calculations, e.g. by applying integrated models (e.g. EFFECTS [12]) or CFD simulations.

### 3.3.6.2 Mitigation techniques

Amongst the mitigation techniques is the creation of a jet outflow. This could be achieved by reducing the orifice area at the outflow and provides for a hazardous area with a halved radius. A second option could be to add extra ventilation during venting. Considering venting as a passive safety mechanism, this is not deemed a desirable mitigation technique. However, increased air movement will increase mixing and thereby reduce the concentration. Depending on the threshold values this could result in a smaller effect

distance, but it will always reduce the respective concentrations. Another option is to provide for a vapour return line from the receiving tank to the delivering tank, which already a common and well-established technology for LNG and chemical tankers. This will avoid venting and hence the development of a hazardous zone on deck.

### 3.3.6.3 Comparison of results to prescriptive rules in the interim guidelines MSC.1-Circ. 1621

The IMO interim guidelines for the safety of ships using methyl/ethyl alcohol as fuel states:

- Regulation 6.4.7 in MSC.1-Circ. 1621 [2]:
- *Fuel tank vent outlets should be situated normally not less than 3 m above the deck or gangway if located within 4 m from such gangways. The vent outlets are also to be arranged at a distance of at least 10 m from the nearest air intake or opening to accommodation and service spaces and ignition sources. The vapour discharge should be directed upwards in the form of unimpeded jets.*

The text from MSC.1-Circ. 1621 is further analysed below.

***Fuel tank vent outlets should be situated normally not less than 3 m above the deck or gangway if located within 4 m from such gangways.***

The placement of the vent outlets several meters above deck could relate to the fact that methanol vapour is slightly heavier than air. Furthermore, the calculations in this section do not allow for verification of these values due to the horizontal instead of vertical classification in this section.

***The vent outlets are also to be arranged at a distance of at least 10 m from the nearest air intake or opening to accommodation and service spaces and ignition sources.***

The venting outlet in relation to accommodation and service spaces is interpreted as a formulation in relation to toxicity. The outlet location in relation to ignition sources should than relate to the flammability/explosivity safety distance. The required safety distance of at least 10 meters for both hazards is considered as an over-simplification of the situation. In the least favourable scenario from Table 3.7, the safety distance is 16.1 m for toxicity (assuming a diffusive outflow). This would be approximately 8 m for a jet outflow. The related safety distance for flammability, for this same jet-type outflow worst case scenario, would be approximately 2.5 m. The indicated safety distances in MSC.1-Circ. 1621 are thereby deemed conservative.

***The vapour discharge should be directed upwards in the form of unimpeded jets.***

The required vapour discharge directed upwards in the form of an unimpeded jet would approximately half the safety distances compared to a diffusive outflow (see Appendix A for the fraction of the safety distances for a diffusive and jet-type outflow for each of the 12 scenarios from Table 3.7, the average fraction is 2.0 [-]). This is in line with the suggested first mitigation technique of creating a jet outflow in section 3.3.6.2.

## 3.3.7 Conclusion

The goal of this section was to get a feeling for the safety distances, related to the flammability and toxicity hazards, that should be applied when venting methanol above deck.

The conclusion is that, when applying the IEC standard, significant safety distances are required for both the flammability and toxicity hazard. In the most severe case (35 degrees Celsius, PRV diameter of 150 mm, 20 kPa PRV limit) the safety distances go up to 4.8 m for flammability and 16.1 for toxicity. In most ship designs these large safety zones cannot be accommodated.

From the parameter study it is observed that the valve diameter and temperature in the tank have the most influence on the safety distance. Considering that the temperature is a property that will not be a design parameter, only the valve diameter can be modified (i.e. reduced) to arrive at smaller safety distances (within the IEC) if required. The safety distance is approximately proportional with the valve diameter.

Besides that, it is concluded that for low temperatures and smaller valve diameters the characteristic release rate is below the validity domain of the IEC curves. For those specific scenarios (characteristic release rate below  $0.06 \text{ m}^3/\text{s}$ ), which will have relatively small safety zones due to the reduced concentration of methanol in the vapour at low temperatures, CFD simulations are required. It is possible that the required hazardous zone becomes negligibly small for those release rates.

To arrive at a feasible solution, further research is required. The suggestion is to study the topic of venting above deck further and to start with including a time component that accounts for the duration and frequency of the venting event, as well as by performing CFD analyses. The significantly sized hazardous zone classification could then only be required for short durations or even be reduced.

## 3.4 Methanol vapour release below waterline

This section covers analytical calculations for methanol vapour release below the waterline. The purpose of these calculations is to get a sense of scale and provide input to possible experiments to investigate the feasibility of methanol venting below the waterline.

The calculations in this section give estimates of the amount of methanol-nitrogen mixture released per venting event, the duration of a venting event and the interaction time of the gas bubbles with the water. Based on these calculations, recommendations for further (experimental) investigations to be performed are given (stage 3 of the GMM II project or possibly new follow-up project).

### 3.4.1 Introduction

This section describes two aspects of underwater venting:

- Volume outflow from the tank.
- Flow of methanol/nitrogen mixture through the water column.

The idea of underwater venting is that:

1. Part of methanol in the released gas stream is dissolved in the water, reducing the concentration of the methanol vapour escaping the water surface.
2. The methanol released from the water surface into the air will remain below deck level of the ship(s) involved.

These mechanisms are then supposed to be sufficient to avoid hazardous methanol concentrations on deck.

If dissolution doesn't lead to concentrations below the LEL or the toxicity levels, the approach used for normal venting, section 3.3, can give an indication of the area affected by the release of methanol-nitrogen mixture. In the case of underwater release, the release velocity from the water will be low and the diffusive approach should be used.

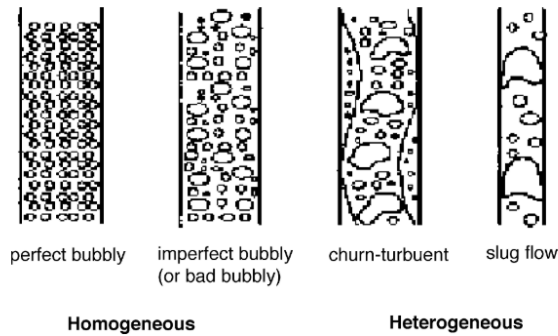


Figure 3.3: Regimes of operation for bubble columns. [30, 31]

The process of underwater venting is similar to what happens in a bubble column which is used in the chemical industry to dissolve gasses in liquids. For a proper interaction, i.e. in this case dissolution of methanol vapour in water, several parameters are of importance e.g. bubble size, bubble rise velocity, interaction time. For a bubble column 4 regimes of operation are distinguished: perfect bubbly, imperfect bubbly, churn-turbulent, and slug flow, see Figure 3.3. For the case of underwater venting the situation of slug flow will not occur due to the absence of walls constraining the flow.

The most efficient exchange occurs in a homogeneous bubbly flow, i.e. both perfect and imperfect bubbly, see Figure 3.3. This occurs for low superficial gas velocities below 0.05 m/s (5 cm/s), see Figure 3.4. The regime of churn turbulent is also able to give sufficient exchange. The calculation shown in the current chapter will give an indication of which regime underwater venting is in.

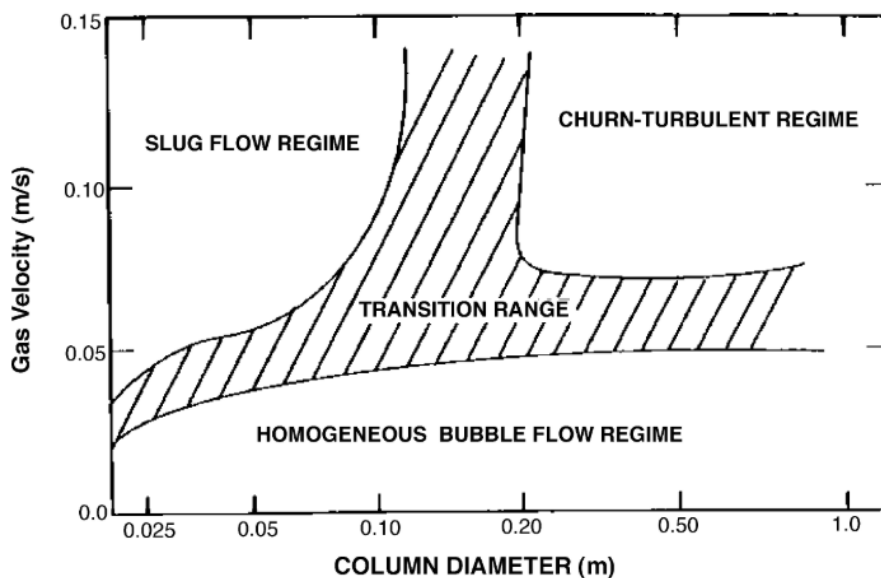


Figure 3.4: Flow regime map for bubble columns. [30, 32]



### 3.4.2 Method

For both questions, outflow and flow through the water column, a simple, analytical approach is chosen.

### 3.4.3 Assumptions

For reference purposes a typical general cargo ship was selected with a length of 114 m.

With this ship in mind the following assumptions are made:

- Bunker 200 m<sup>3</sup>.
- Bunker rate: 100 m<sup>3</sup>/hr  
(= 0.028 m<sup>3</sup>/s = 0.04 kg/s @ 10 kPa overpressure in tank).
- Vent line diameter: 50 – 150 mm.
- PRV setpoint: 1 – -0 kPa (overpressure in tank).
- Release @ 1m water depth.
- Gas phase is modelled as only nitrogen.

### 3.4.4 Model description

Figure 3.5 shows the principle lay out.

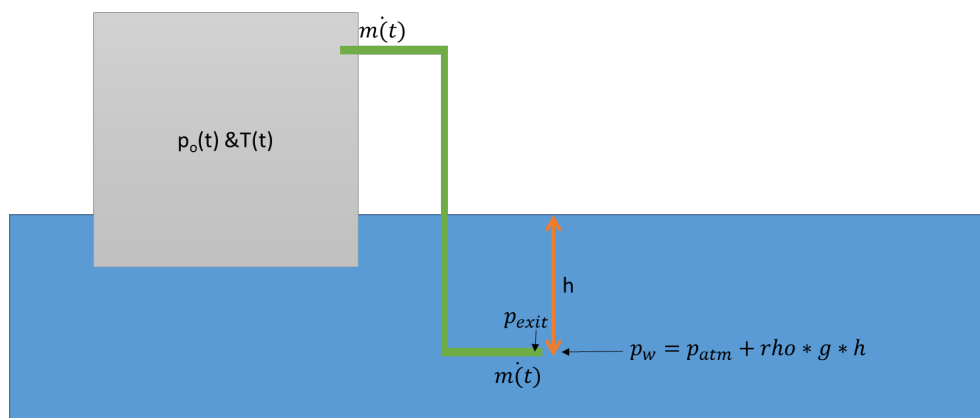


Figure 3.5: Schematic overview of underwater venting system.

The outflow of the tank during venting is modelled using the equations in ‘Yellow book’ section 2.5.2.4 [33]. The mass flow rate is based on the pressure difference between the pressure inside the tank  $p_o$  and the pressure at the outlet  $p_w$ . The latter pressure depends on the depth  $h$  of the water column above the outlet.

The calculation is in five steps:

1. Estimate an initial value for  $p_{exit}$  ( $p_o > p_{exit} > p_w$ ).
2. Calculate the flow through the pipe (dependent on  $p_o$  and  $p_{exit}$ ).
3. Calculate the flow at the exit of the pipe (dependent on  $p_{exit}$  and  $p_w$ ).
4. Iterate  $p_{exit}$  so that calculated flows become identical (conservation of mass).
5. Update the tank conditions.

These steps are repeated for each time step.

The mass flow rate through the pipe is calculated as follows:

$$\dot{m}(t) = A_p * \sqrt{\frac{2 * \int_{p_o}^{p_{exit}} \rho(p) dp}{4f_F * l_p / d_p}}$$

In which the pressure integral can be approximated by:

$$\int_{p_o}^{p_{exit}} \rho(p) dp = p_o * \rho_o * (\zeta / 1 + \zeta) * ((p_{exit} / p_o)^{((1+\zeta)/\zeta)} - 1)$$

The mass flow rate at the exit is calculated as:

$$\dot{m}(t) = C_d * A_p * \psi * \sqrt{(\rho_o * p_o * \gamma * (2/\gamma + 1)^{(\gamma+1)/(\gamma-1)})}$$

With for unchoked flow:

$$\psi^2 = (2/(\gamma - 1)) * ((\gamma + 1)/2)^{(\gamma+1)/(\gamma-1)} * (p_w/p_{exit})^{2/\gamma} * (1 - (p_w/p_{exit})^{(\gamma-1)/\gamma})$$

For each time step the value of  $p_{exit}$  is varied until the mass flow rate through the pipe is equal to the mass flow rate at the exit. The mass inside the tank is decreased by the mass flow rate, which results in a new  $p_o$  and  $\rho_o$ . These parameters are used in the next time step to calculate the changing mass flow rate.

Table 3.8: List of used symbols.

Symbol	Property	Value	Unit
$p_o$	Pressure inside tank	varied	Pa
$p_{exit}$	Pressure at exit of pipe	calculated	Pa
$p_w$	Pressure in water	Calculated	Pa
$h$	Water height	1	m
$\rho_w$	Density of water	1000	kg/m <sup>3</sup>
$\rho_o$	Density of gas inside tank	calculated	kg/m <sup>3</sup>
$g$	Gravitational constant	9.81	m/s <sup>2</sup>
$A_p$	Cross sectional area of pipe	Depends on diameter	m <sup>2</sup>
$d_p$	Diameter of pipe	Varied: 0.05-0.10-0.15	m
$l_p$	Length of pipe	20	m
$f_F$	Fanning friction factor	0.04	
$C_D$	Discharge coefficient	1	-
$\zeta$	Compressibility factor	1	-
$\gamma$	Ratio between $C_p$ and $C_v$	1.4	-
$\psi$	Outflow coefficient	calculated	-
$v_{bubble}$	Superficial bubble velocity	calculated	m/s
$A_{bubble}$	Cross sectional area of bubble rise column	varied	m <sup>2</sup>

The resulting mass flow rate is then converted to a volume flow rate. And based on the cross-sectional area of the column that the vapour flow occupies, the superficial bubble velocity is calculated:

$$v_{bubble} = (m/\rho(p_w))/A_{bubble\ column}$$

A high bubble velocity leads to a small residence time of the gas in the water. This leads to a very limited exchange of methanol vapour between the gas phase and water. A bubble velocity of 0.05 m/s is adopted as the limit of efficient interaction (Figure 3.4).

### 3.4.5 Parameter study

For the outflow calculations the following parameters have been varied:

- Outflow/pipe diameter.
- Overpressure inside tank.

The resulting tank pressures (left) and mass flow rates (right) as a function of time are shown in

Figure 3.6. The continuous venting scenario is shown as the dashed line in the right-hand figures. The maximum time in the graphs is 60 s.

For an outflow diameter of 50 mm 60 sec is too short to complete the venting operation. In addition, for small overpressure (1 and 2 kPa) the outflow rate is smaller than the continuous outflow rate, these are not valid options.

Using the same values for overpressure and increasing the outflow diameter to 100 or 150 mm the pressure inside the tank reduces to the outside pressure within the 60s for most initial pressures. The outflow process starting at an overpressure of 10kPa takes longer than the outflow process starting at an overpressure of 1kPa.

The maximum obtained mass flow rates for the various combinations of allowed overpressure and outflow diameter are reported in Table 3.9. Mass flow ranges from 0.02 kg/s to 1.15 kg/s.

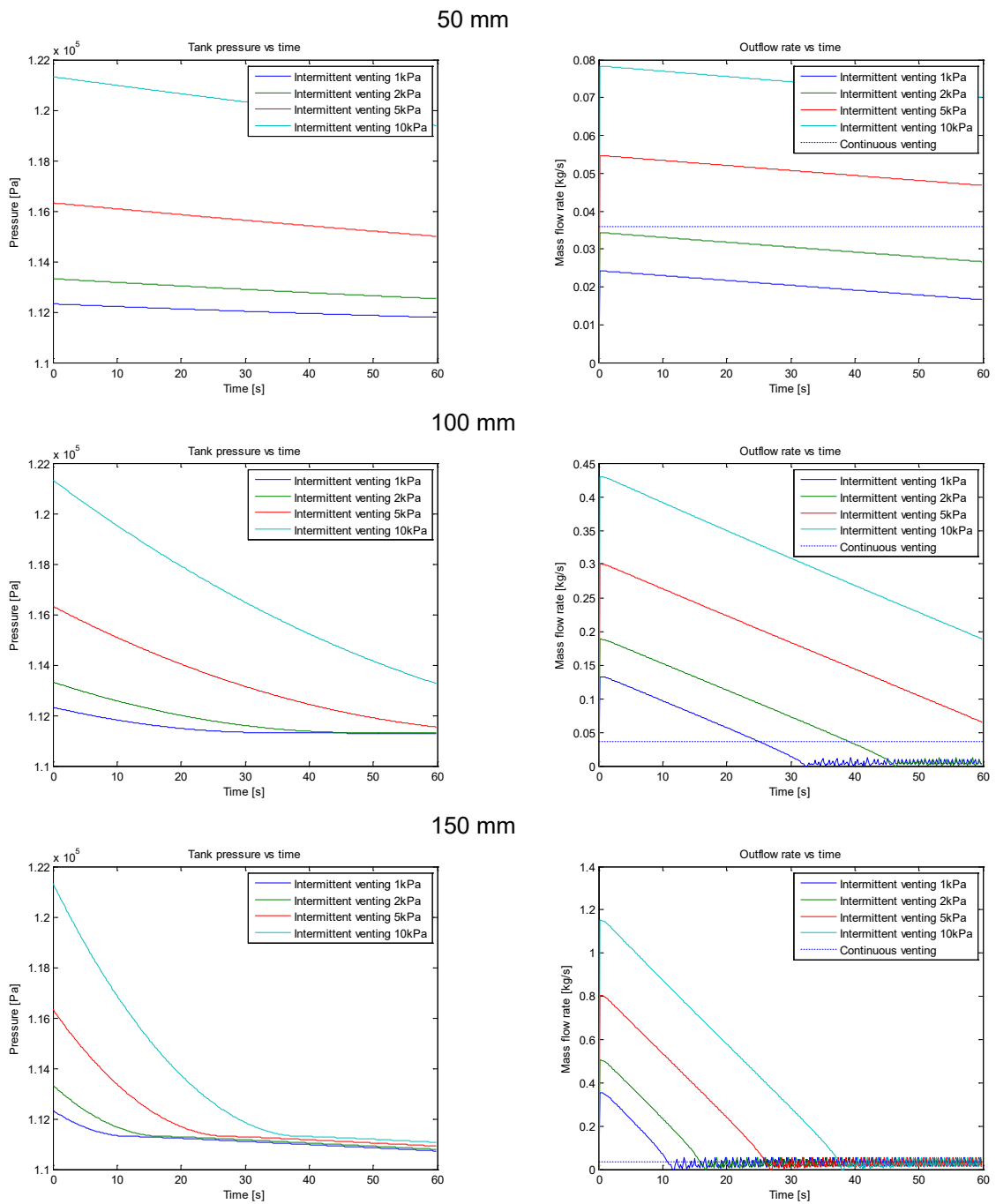


Figure 3.6: Tank pressure (Pa) and mass flow rate (kg/s) for 50, 100, and 150 mm outflow diameter and 1, 2, 5, and 10 kPa overpressure setpoints for opening of PRV. As a reference the continuous venting scenario with a flow rate of 0.04 kg/s is shown as the dashed line in the outflow rate plot on the right-hand side.

Table 3.9: Maximum mass flow rate (kg/s) for varying outflow diameter and tank overpressure. (Continuous venting results in a mass flow rate of 0.04 kg/s.)

	50 mm		100 mm		150 mm	
	Mass flow rate (kg/s)	Venting time (s)	Mass flow rate (kg/s)	Venting time (s)	Mass flow rate (kg/s)	Venting time (s)
<b>1kPa</b>	0.02	>60	0.13	32	0.36	11
<b>2kPa</b>	0.03	>60	0.19	46	0.50	16
<b>5kPa</b>	0.05	>60	0.30	>60	0.80	27
<b>10kPa</b>	0.08	>60	0.43	>60	1.15	38

The mass flow rates from Table 3.9 are taken as the starting point for the gas flow through the water. Three values are taken: 0.04 kg/s (continuous venting), 0.19 kg/s (intermittent venting, mid-range), 1.15 kg/s (maximum intermittent venting). The properties of interest are the bubble velocity and connected to this the time bubbles need to rise to the water surface.

The bubble rise velocity depends on the diameter of the bubble column. No exact number for the bubble column diameter is known, this depends on the outflow configuration. The width of the bubble column is estimated to be one to two times the outflow diameter. Tests will have to give confirmation of this estimate. The calculation of bubble rise velocity has been performed for diameters of 0.05m to 2.0m. The results for the bubble rise velocity are given in Table 3.10.

Increasing the bubble column diameter leads to lower bubble velocities. The value of 0.05 m/s is only reached for the 0.04 kg/s and 0.19 kg/s mass flow rates with bubble column diameters of 1.0 m and 2.0 m respectively.

Based on the bubble rise velocity the bubble residence time is calculated, see Table 3.11. The numbers show that the residence time for most cases is rather small. It is too small to have significant exchange of methanol vapour between gas phase and water.

Table 3.10: Bubble rise velocity (m/s) for a variation of mass flow rate and bubble column diameter.

	0.05m	0.10m	0.15m	0.20m	0.50m	1.00m	2.00m
<b>0.04kg/s</b>	16	4	1.8	1.0	0.16	0.04	0.01
<b>0.19kg/s</b>	-	19	8.5	4.8	0.76	0.19	0.05
<b>1.15kg/s</b>	-	-	51	29	4.6	1.2	0.29

Table 3.11: Bubble residence time (s) for a variation of mass flow rate and bubble column diameter.

	0.05m	0.10m	0.15m	0.20m	0.50m	1.00m	2.00m
<b>0.04kg/s</b>	0.06	0.25	0.56	1.00	6.23	24.9	100
<b>0.19kg/s</b>	-	0.05	0.12	0.21	1.31	5.25	21
<b>1.15kg/s</b>	-	-	0.02	0.03	0.22	0.87	3.5

### 3.4.6 Discussion and conclusions

Some of the values listed in Table 3.10 and Table 3.11 are unrealistic. Clearly some of the assumptions are outside the range of reality, e.g. a 50 mm diameter venting pipe is too small. This will need to be dealt with in the next update of this report.

Still some conclusions can be drawn.

When considering a methanol fuel tank of 200 m<sup>3</sup>, the flow of methanol-nitrogen mixture during a venting event, caused by a blocked vapour return during bunkering, is too high to obtain an efficient interaction between the gas mixture and the water for the methanol to dissolve. Hence most of the methanol vapour will be released to the air.

Decreasing the outflow rate is one direction for a solution, however, the required reduction is too high to keep an acceptable bunker rate. Another solution is to increase the diameter of the bubble column.

One aspect that has not been taken into account is that the vapour cools down when it enters the water and it may condensate. Liquid methanol dissolves easily in water and may therefore not pose a risk above water when mixed in these quantities.

Additional study must be done to address these topics.

In case of much larger fuel tanks (10000 – 15000 m<sup>3</sup>) sufficient dissolution of vapour during a venting event is unrealistic. Therefore, the *'venting below the water line'* option would seem irrelevant for such fuel tanks. However large fuel tanks have large vapour spaces where pressure will build up when sailing from cold latitudes to tropical latitudes. In such cases excess blanket gas must be vented. For this scenario the *'vapour venting below'* is considered to be very attractive.

The outcome of these calculations gives input for a test plan to further study the process of underwater venting.

The tests can be divided into two steps:

1. Qualitative: what does outflow look like? Is it possible to reach bubbly flow?
2. Quantitative: how much methanol reaches above the water line and how does it disperse?

The proposed tests are described in more detail in chapter 5.

## 3.5 Methanol liquid spill in a confined space

This section describes the calculation of the effects of a liquid spill of methanol in a confined space. A spill in the technical space is considered as a use-case, whereas in all cases where the following assumptions are justified, the calculation can be applied. The main assumption is the instantaneous uniform distribution of the concentration over the volume in each time step. This is mostly valid for small rooms.

The calculation is both for ventilated and non-ventilated spaces. When applying the calculation to a non-ventilated space, the amount of air-changes per hour should be set to 0. The results in this section are all presented for a ventilated room.

### 3.5.1 Introduction

The case description of this scenario is:

Due to damage of piping and/or seals, methanol is leaking into the a confined room. Either a spray release occurs or a pool of liquid methanol develops on the bottom, after which it evaporates.

The increased concentration of methanol particles in the air poses a risk related to:

1. Explosion of the methanol.
2. Poisoning of the crew due to the toxic effects of methanol vapour.
3. Ignition of the liquid methanol pool.

In this calculation the first two events are considered. The third is considered in section 3.6. For a complete assessment of the risk, the risk of a pool fire should be considered separately.

The goal of this section is to get a feeling for the order of magnitude and proportionality of the global methanol concentration in a confined space in relation to room size, pipe pressure, hole size and modelling parameters.

The calculations are performed to estimate the global concentration of methanol in relation to the LEL (Lower Explosion Limit of 6.7% [34]) and the toxicity levels (IDLH, EEGl for 10, 30 and 60 minutes, see section 3.2). The goal of this part of the project is to provide input to the experimental part of the GMM2.0 project, and to investigate options to mitigate the consequences related to a methanol spill in a confined space.

**It is important to note that this section provides a first range of ballpark figures by considering two extremes. The reality, and thereby the real consequences will differ from the results of both extreme cases and should be considered with care.**

### 3.5.2 Method

To estimate the concentration of methanol in the air of the confined space, a model has been built based on pool evaporation and instantaneous uniform distributions of gasses throughout a room.

This model considers both of two extremes, being:

1. Either all released methanol evaporates instantaneously and no pool is formed, which could occur for a nozzle outflow.
2. or all released methanol is added to the pool and evaporates from the pool.

In reality there will be a combination of both processes, and thereby a concentration in between both extreme boundaries.

### 3.5.3 Assumptions

The ranges for which the calculations in this section are performed are indicated in this section. Scenario parameters to study different layouts and response protocols:

- Room volume between 236 m<sup>3</sup> (small inland waterway vessel) and 2000 m<sup>3</sup> (large short sea ship).
- Pipe pressure between 1 and 10 barg.
- The response time to stop a leak is assumed to be either 30 seconds or infinity (no response).
- Methanol pool areas of 1 and 5 m<sup>2</sup>.
- Pipe DN16 and DN32<sup>6</sup>.

Fixed assumptions that are deemed applicable to most vessel types:

- Hole size: 100% of the cross sectional area of the pipe<sup>7</sup>.
- Plate thickness of the steel plating in the confined space: 10 mm.
- Ventilation rate: 30 air renewals per hour<sup>8</sup>.
- Temperature of the air in the confined space: 30 degrees Celsius.
- Temperature of the steel plate on which the methanol is spilled: 30 degrees Celsius.
- Temperature of the spilled methanol: 20 degrees Celsius.

Calculation-specific parameters are:

- Venting speed (“wind speed”) above the pool<sup>9</sup>: 0.10 m/s. This assumption is highly conservative, however, without CFD calculations that account for the confined space geometry and pool location a less conservative estimate is not possible.

Underlying assumptions are:

- All generated methanol vapour in each timestep is, in this model, assumed to instantaneously and uniformly spread throughout the confined space. This assumption is further commented upon in the subsection on “Limitations” (3.5.7.1).
- The pressure in the pipe will not drop due to the methanol release. The spill rate remains unchanged during the spill, until the leak is stopped (i.e. accounting for the response time). This will provide for a conservative analysis, as in reality less methanol will be released than what is accounted for.
- The temperature of the steel surface is assumed constant. In practice this will cool down due to the evaporative cooling of the methanol pool. This assumption results in a possible overestimation of the mass flux through evaporation, by which the assumption is deemed slightly conservative.

<sup>6</sup> DN32 is the inner pipe diameter in the room in the P&ID of the Hunteborg [58]

<sup>7</sup> This is the least favorable assumption from the BEVI handleiding [36], which states the requirement to perform the calculations for hole sizes of 10 and 100% of the cross section of the pipe.

<sup>8</sup> “13.6.1 Fuel preparation rooms, shall be fitted with effective mechanical ventilation system of the under pressure type, providing a ventilation capacity of at least 30 air changes per hour.” IGF-Code [3]

<sup>9</sup> The value of 0.10 is the minimum velocity for “obstructed areas” in the NEN-EN-IEC 60079-10-1:2015 [9]. Besides that, 0.1 m/s is indicated as “may be used as the assumed internal air velocity in some simple heat transfer calculations” in [59] as well as indicated in the ASHRAE standard 55-2017 [60] – both are for buildings and are thereby considered as conservative estimates for the air velocity in technical spaces, where ventilation rates are typically higher.



- The temperature of the air in the confined space is assumed constant. Providing this temperature is close to the temperature of the spilled methanol this is assumed to have a negligible effect on the results.

### 3.5.4 Model description

This model is based on the descriptions from the ‘Yellow book’ [33]. The model for non-boiling liquids is used. Methanol starts boiling at 64.7 °C (338 K). It is assumed that the floor of the confined space does not exceed this temperature, by which the model for non-boiling liquids is deemed valid.

A heat and mass balance is derived for the methanol pool to assess the mass flow through evaporation. Figure 3.7 presents a schematic overview of both the system and the heat and mass fluxes on the methanol pool.

**Heat and mass balance – liquid spill of methanol in engine room**

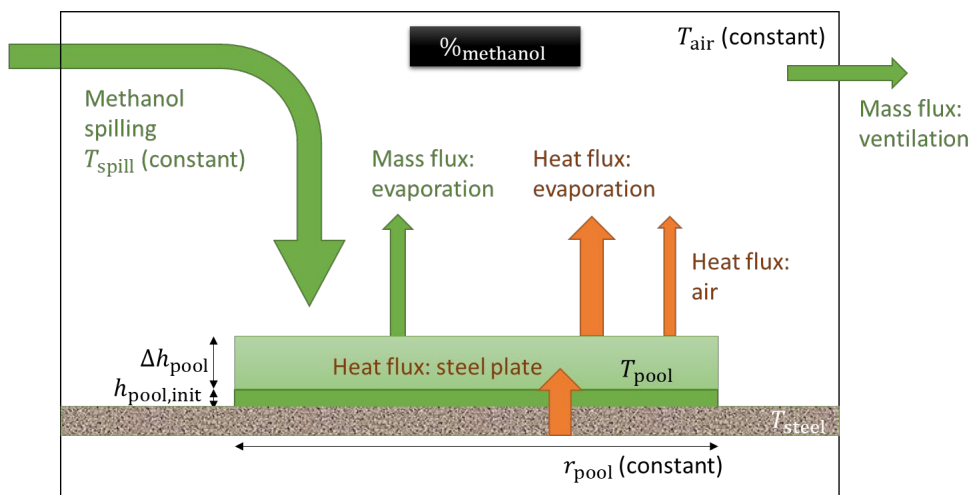


Figure 3.7: Diagram of heat and mass flows in the system to consider the effects of a liquid spill of methanol in a confined space, which in this case is the engine room. The initial pool height  $h_{pool,init}(t = 0) = 0$ .

The input values in the model are presented in Table 3.12.

Table 3.12: Input parameters for the model of the liquid spill in the confined space

Property	Unit	Explanation
$\Delta t$	[s]	Timestep
$T_{air}$	[K]	Temperature of the room
$T_{spill}$	[K]	Temperature of the spilled methanol
$T_{steel}$	[K]	Temperature of the steel surface
$t_{plate}$	[m]	Thickness of the steel plate
$n_{renew}$	[1/hr]	Amount of air renewals per hour
$u_{w,10}$	[m/s]	Ventilation velocity above the pool
$A_{hole}$	[m <sup>2</sup> ]	Hole diameter
$A_{pool}$	[m <sup>2</sup> ]	Pool area
$p_{pipe}$	[Pa]	Pressure in the pipe (absolute)

The output of the model is the global concentration of methanol vapour in the air, for each timestep.

### 3.5.4.1 Model formulation

Three colours are used:

- Black parameters are input parameters that specify the scenario
- Green parameters are calculated using formulas elsewhere in the document
- Blue parameters indicate fixed properties (e.g. properties of methanol or empirical values)

There is a spill of methanol, of which the spill rate is given, using Bernoulli, by:

$$q_s = A_{hole} \cdot \sqrt{\frac{p_{pipe}}{\rho_{m,L}}}, \tag{3.4.1}$$

in which

$q_s$	Spill rate in [m <sup>3</sup> /s]
$A_{hole}$	Hole area through which the methanol is spilled in [m <sup>2</sup> ]
$p_{pipe}$	Pipe pressure in [Pa]
$\rho_{m,L}$	Density of liquid methanol in [kg/m <sup>3</sup> ] = 792

The mass flux from the evaporation is expressed by equation (3.13) from [33]:

$$q''_{v,(i)} \approx k_m \cdot P_{v,(i)}(T_{ps,(i)}) \cdot \frac{\mu_i}{R \cdot T_{ps,(i)}}, \tag{3.4.2}$$

in which

$q''_{v,(i)}$	Evaporation mass flux in [kg/(m <sup>2</sup> s)]
$k_m$	Mass transfer coefficient in [m/s], see equation (3.4.4)
$P_{v,(i)}$	Vapour pressure as a function of the temperature in [N/m <sup>2</sup> ], empirically fitted to the Clapeyron relation, yielding:  $P_{v,(i)} \approx \frac{23730}{\exp\left(\frac{H_{vap}}{R} \cdot \left(-\frac{1}{304.79} + \frac{1}{T_{ps,(i)}}\right)\right)}, \tag{3.4.3}$ in which  $H_{vap}$ Molar enthalpy of vaporization of methanol in [J/mol] = 35270
$T_{ps,(i)}$	Temperature at the pool surface, assumed to be equal to the pool temperature in [K] = $T_{pool,(i)}$ see equation (3.4.10)
$\mu_i$	Molecular mass of methanol in [kg/mol] = 0.03204
$R$	International gas constant in [J/(molK)] = 8.3145

The mass transfer coefficient (for evaporating non-boiling liquids) is calculated using equation (3.24) from [33], which is formulated based on a well validated empirical model by Kawamura and MacKay [35]:

$$k_m = C_{m\&m} \cdot u_{w,10}^{0.78} \cdot (2r_p)^{-0.11} \cdot Sc^{-0.67}, \tag{3.4.4}$$

in which

$k_m$	Mass transfer coefficient in [m/s]
$C_{m\&m}$	Empirical factor in [m <sup>0.33</sup> /s <sup>0.22</sup> ] [33] = 0.004786
$u_{w,10}$	Wind speed at 10 meters height in [m/s]
$r_p$	Radius of the liquid pool in [m] which is calculated from the pool area assuming a circular pool
$Sc$	Schmidt number in [-], which in general for gases and vapours = 0.8 [33]

The evaporation rate is given by equation (3.141) from [33]:

$$q_{v,(i)} = q''_{v,(i)} A_{pool}, \tag{3.4.5}$$

in which

$q_{v,(i)}$	Evaporation rate in [kg/s]
$q''_{v,(i)}$	Evaporation mass flux in [kg/(m <sup>2</sup> s)] see equation (3.4.2)
$A_{pool}$	Pool area in [m <sup>2</sup> ]

If there is a pool, there is pool evaporation which results in both a change in temperature and height of the pool for each timestep:

Pool height is based on equation (3.143a) from [33]:

$$\begin{aligned} \Delta h_{pool,(i)} &= \Delta t \cdot (\Delta h_{pool,spill(i)} + \Delta h_{pool,evap(i)}) \\ &= \Delta t \cdot \left( \frac{q_s}{A_{pool}} \right) - \Delta t \cdot \left( \frac{q''_{v,(i)} A_{pool}}{\rho_{m,L}} \right), \end{aligned} \tag{3.4.6}$$

in which

$\Delta h_{pool,(i)}$	Change in pool height in one time step in [m]
$\Delta t$	Time step in [s]
$\Delta h_{pool,spill(i)}$	Change in pool height due to the spill in one time step in [m]
$\Delta h_{pool,evap(i)}$	Change in pool height due to evaporation in one time step in [m]
$q_s$	Spill rate in [m <sup>3</sup> /s] see equation (3.4.1)
$A_{pool}$	Pool area in [m <sup>2</sup> ]
$q''_{v,(i)}$	Evaporation mass flux in [kg/(m <sup>2</sup> s)] see equation (3.4.2)
$\rho_{m,L}$	Density of liquid methanol in [kg/m <sup>3</sup> ] = 792

By which the pool height in total yields (see also equation (3.143b) from [33]):

$$h_{pool(i)} = h_{pool,(i-1)} + \Delta h_{pool,(i)}, \tag{3.4.7}$$

in which

$h_{pool(i)}$	Pool height in the current step in [m]
$h_{pool,(i-1)}$	Pool height in the previous step in [m], $h_{pool,(i=0)} = 0$
$\Delta h_{pool,(i)}$	Change in pool height in one time step in [m] see equation (3.4.6)

The pool temperature (see also equation (3.77) from [33]) is expressed by:

$$\Delta T_{pool,(i)} = \Delta t \cdot \left( \frac{\sum H_{(i)} - q''_{v,(i)} \cdot L_v}{h_{pool,(i)} \rho_{m,L} C_{p,L}} + \frac{q_s}{\rho_{m,L} h_{pool,(i)} A_{pool}} (T_{spill} - T_{pool,(i)}) \right), \quad (3.4.8)$$

in which

$\Delta T_{pool,(i)}$	Temperature change in one time step in [K]
$\Delta t$	Time step in [s]
$\sum H_{(i)}$	Total heat flux (excluding evaporation) in [J/(m <sup>2</sup> s)] see equation (3.4.9)
$q''_{v,(i)}$	Evaporation mass flux in [kg/(m <sup>2</sup> s)] see equation (3.4.2)
$L_v$	Latent heat of vaporization of methanol in [J/kg] = 1 100 000
$h_{pool,(i)}$	Methanol pool height in [m], see equation (3.4.7)
$\rho_{m,L}$	Density of liquid methanol in [kg/m <sup>3</sup> ] = 792
$C_{p,L}$	Specific heat of liquid methanol in [J/(kgK)] = 2530
$q_s$	Spill rate in [m <sup>3</sup> /s] see equation (3.4.1)
$A_{pool}$	Pool area in [m <sup>2</sup> ]
$T_{spill}$	Temperature of the spilled methanol in [K]
$T_{pool,(i)}$	Temperature of the methanol pool in [K] see equation (3.4.10)

The total heat flux (see also equation (3.4) from [33]) is given by:

$$\sum H_{(i)} = H_{air,(i)} + H_{steel,(i)} = k_{H,air} (T_{air} - T_{pool,(i)}) + k_{H,steel} (T_{steel} - T_{pool,(i)}), \quad (3.4.9)$$

in which

$\sum H_{(i)}$	Total heat flux (excluding evaporation) in [J/(m <sup>2</sup> s)]
$H_{air,(i)}$	Heat flux to the air in [J/(m <sup>2</sup> s)]
$H_{steel,(i)}$	Heat flux to the steel plate in [J/(m <sup>2</sup> s)]
$k_{H,air}$	Heat transfer coefficient to the air in [J/(m <sup>2</sup> sK)] = 162
$k_{H,steel}$	Heat transfer coefficient to the steel plate in [J/(m <sup>2</sup> sK)] which is given by $k_{H,steel} = \lambda_{steel} / t_{plate}$ in which $\lambda_{steel}$ Thermal conductivity of steel in [J/(Kms)] = 45 $t_{plate}$ Thickness of the steel plate in [m]
$T_{air}$	Temperature of the air in the confined space in [K]
$T_{pool,(i)}$	Temperature of the methanol pool in [K] see equation (3.4.8)
$T_{steel}$	Temperature of the steel plate in [K]

By which the pool temperature after this step yields:

$$T_{pool(i)} = T_{pool,(i-1)} + \Delta T_{pool,(i)}, \quad (3.4.10)$$

in which

$T_{pool(i)}$	Pool temperature in the current step in [K]
$T_{pool,(i-1)}$	Pool temperature in the previous step in [K], $T_{pool,(i=0)} = T_{spill}$
$\Delta T_{pool,(i)}$	Change in pool temperature in one time step in [K] see equation (3.4.8)

### 3.5.4.2 Output: global concentrations [vol/vol]

First, an initial estimate of the global concentration of methanol, without the effects of the ventilation:

$$\%_{CH_3OH,est.,(i)} = \frac{V_{m,(i)}}{V_{room} + V_{m,(i)}}, \quad (3.4.11)$$

in which

$\%_{CH_3OH,est.,(i)}$	Initial estimate of the methanol concentration based on previously calculated methanol volume in the confined space in [vol/vol]
$V_{m,(i)}$	Volume of methanol in the confined space based on current data, $V_{m,(i=1)} = 0$ in [m <sup>3</sup> ]
$V_{room}$	Volume of the confined space in [m <sup>3</sup> ]

The influence of the ventilation system is accounted for in a second step:

$$\Delta V_{(i)} = \begin{cases} \Delta h_{pool,evap(i)} \cdot A_{pool} & , \text{ if pool evaporation governing} \\ \Delta t \cdot q_s & , \text{ if spray release governing} \end{cases} \quad (3.4.12)$$

$$\Delta V_{ventilation(i)} = \%_{CH_3OH,est.,(i)} \cdot Q_v, \quad (3.4.13)$$

$$V_{m,(i+1)} = V_{m,(i)} + \Delta V_{(i)} - \Delta V_{ventilation(i)}, \quad (3.4.14)$$

$$\%_{CH_3OH,(i)} = \frac{V_{m,(i+1)}}{V_{room} + V_{m,(i+1)}}, \quad (3.4.15)$$

in which

$\Delta V_{(i)}$	Methanol volume that is evaporated in this timestep in [m <sup>3</sup> ]
$\Delta h_{pool,evap(i)}$	Change in pool height due to evaporation in one time step in [m]
$A_{pool}$	Pool area in [m <sup>2</sup> ]
$\Delta t$	Time step in [s]
$q_s$	Spill rate in [m <sup>3</sup> /s] see equation (3.4.1)
$\Delta V_{ventilation(i)}$	Methanol volume that is removed from the room through ventilation in this timestep in [m <sup>3</sup> ]

$\%_{CH_3OH,est.,(i)}$	Initial estimate of the concentration of methanol in the confined space, not accounting for the ventilation in the current time step in [vol/vol] see equation (3.4.11)
$Q_v$	Ventilation rate in [m <sup>3</sup> /s], calculated using $Q_v = \frac{n_{renew} \cdot V_{room}}{3600}, \quad (3.4.16)$ in which $n_{renew}$ Amount of air renewals per hour [1/hr] $V_{room}$ Volume of the confined space in [m <sup>3</sup> ]
$V_{m,(i+1)}$	Volume of methanol in the confined space, including the effect of ventilation in [m <sup>3</sup> ]
$V_{m,(i)}$	Volume of methanol in the confined space based on current data, $V_{m,(i=1)} = 0$ in [m <sup>3</sup> ]
$\%_{CH_3OH,(i)}$	Estimate of the concentration of methanol in the confined space, accounting for the effect of ventilation in the current time step in [vol/vol]
$V_{room}$	Volume of the confined space in [m <sup>3</sup> ]

### 3.5.4.3 Output: global toxicity levels [ppm]

For the translation of volume percentage methanol to ppm:

$$ppm_{(i)} = 10^6 \cdot \frac{\frac{V_{m,(i)} \cdot \rho_{m,g}}{\mu_i}}{\frac{V_{room} \cdot \rho_{air}}{\mu_{air}} + \frac{V_{m,(i)} \cdot \rho_{m,g}}{\mu_i}}, \quad (3.4.17)$$

in which

$ppm_{(i)}$	Initial estimate of the methanol concentration based on previously calculated methanol volume in the confined space in [vol/vol]
$V_{m,(i)}$	Volume of methanol in the confined space based on current data, $V_{m,(i=1)} = 0$ in [m <sup>3</sup> ] see equation (3.4.14)
$\rho_{m,g}$	Density of gaseous methanol in [kg/m <sup>3</sup> ], (see Appendix D) given by $\rho_{m,g} = 0.0697e^{0.0473(T_{air})}, \quad (3.4.18)$ in which $T_{air}$ Temperature of the air in the confined space in [K]
$\mu_i$	Molecular mass of methanol in [kg/mol] = 0.03204
$V_{room}$	Volume of the confined space in [m <sup>3</sup> ]
$\rho_{air}$	Density of air in [kg/m <sup>3</sup> ], given by: $\rho_{air} = \frac{\rho_{m,g}}{RD}$ in which

	$\rho_{m,g}$	Density of gaseous methanol in [kg/m <sup>3</sup> ] see equation (3.4.18)
	$RD$	Relative density of methanol over air in [-] = 1.11
$\mu_{air}$		Molecular mass of air in [kg/mol] = 0.03000

### 3.5.5 Parameter study

As was indicated in section 3.5.3, the values for which the calculations in this section are performed are:

- Confined space volume between 236 m<sup>3</sup> (small inland waterway vessel) and 2000 m<sup>3</sup>.
- Pipe pressure between 1 and 10 bar (overpressure).
- The response time to stop a leak is 30 or 60 seconds.
- Methanol pool area of 1 and 5 m<sup>2</sup>.
- Pipe DN16 and DN32.

The influence of all five parameters is studied by performing the calculations for the outer limits of the parameters. The results are presented in this section.

The parameter study scenarios indicate a pressure, a time and a volume that respectively indicate the overpressure in the pipe, the response time (i.e. duration of the leak) and the volume of the confined space. The plots of the concentration development (for a DN32 pipe with a hole area equal to 100% of the pipe area) over time are included, for all 8 scenarios (varying confined space volume, pipe pressure and response time) are included in Appendix E).

#### 3.5.5.1 Assuming pool evaporation governs

Table 3.13 presents the results of the parameter study with the assumption that pool evaporation is governing, which is presented in the form of the concentration after 2 hours of the start of the spill. After approximately 2 hours, for the considered scenarios, the concentration in the air has stabilised with the venting rate. The assumption that pool evaporation is governing is deemed valid for small hole sizes with relatively low discharge velocities.

It should be noted that Table 3.13 does not indicate the pipe diameter. This is because for this scenario the influence of the pipe diameter is negligible. The only effect of the pipe diameter (and related outflow velocity) is the small reduction of the pool temperature with, for the considered scenarios, negligible effect on the maximum concentration and development thereof.



Table 3.13: Results of the parameter study under the assumption that pool evaporation is governing over a spray release instantaneous evaporation. The indicated results are expressed by the concentration in the air 2 hours after the spill.

Parameter study results	A pool = 1 m <sup>2</sup>		A pool = 5 m <sup>2</sup>	
	[vol/vol]	[ppm]	[vol/vol]	[ppm]
2 bara, 60s, 236 m <sup>3</sup>	0.04%	464	1.01%	10618
2 bara, 60s, 2000 m <sup>3</sup>	0.01%	55	0.12%	1253
11 bara, 60s, 236 m <sup>3</sup>	0.04%	464	1.01%	10618
11 bara, 60s, 2000 m <sup>3</sup>	0.01%	55	0.12%	1253
2 bara, 30s, 236 m <sup>3</sup>	0.04%	464	1.01%	10618
2 bara, 30s, 2000 m <sup>3</sup>	0.01%	55	0.12%	1253
11 bara, 30s, 236 m <sup>3</sup>	0.04%	464	1.01%	10618
11 bara, 30s, 2000 m <sup>3</sup>	0.01%	55	0.12%	1253

The parameter study shows that, for the assumption that pool evaporating is governing, the following trends and relations can be observed:

- The influence of the confined space volume is significant. The resulting maximum concentration after two hours is approximately inversely proportional with the confined space volume.
- In this simplified model, the influence of the pool size is significant. The resulting maximum concentration after two hours  $\propto \sqrt{f}^{-0.11} \cdot f^2$ , which is a factor 22.9 higher for a factor 5 increase in pool size.
- The pipe pressure and response time have limited effect because if a pool is formed its evaporation can take up to several hours to evaporate.

### 3.5.5.2 Assuming spray release evaporation governs

Table 3.14 presents the results of the parameter study with the assumption that no pool is formed and all methanol is evaporated immediately, which is presented in the form of the time between the initial spill and the moment when the concentration value drops below the critical concentration to safe levels. It should be noted that the concentration is considered as uniformly distributed throughout the volume.

Please note that Table 3.14 does not indicate a pool diameter because in the spray release scenario there is no pool.

Table 3.14: Results of the parameter study under the assumption that no pool is formed due to immediate evaporation of the spray release. The results are expressed by the number of minutes to exceeding the threshold levels to safe regimes.

Parameter study results	DN32		DN16	
	LEL	IDLH	LEL	IDLH
Scenario				
2 bara, 60s, 236 m <sup>3</sup>	27.5	32.7	11.5	16.7
2 bara, 60s, 2000 m <sup>3</sup>	7.7	12.9	3.5	8.6
11 bara, 60s, 236 m <sup>3</sup>	53.2	58.4	19.1	24.3
11 bara, 60s, 2000 m <sup>3</sup>	12.2	17.3	5.8	11.0
2 bara, 30s, 236 m <sup>3</sup>	17.2	22.3	7.8	12.9
2 bara, 30s, 2000 m <sup>3</sup>	5.1	10.3	1.6	6.7
11 bara, 30s, 236 m <sup>3</sup>	30.8	36.0	12.4	17.6
11 bara, 30s, 2000 m <sup>3</sup>	8.2	13.4	3.6	8.8

Considering the non-linear nature of the analysis, results no further than the comparison between the calculated extremes can be presented.

The parameter study shows that the following observations can be made:

- Pressure: 11 bara factor 1.5 to 2 times longer time than 2 bara.
- Volume: 2000 m<sup>3</sup> factor 0.2 to 0.3 shorter than 236 m<sup>3</sup>.
- Response time: 60 seconds factor 1.5 to 1.7 longer than 30 seconds.
- Pipe diameter: DN16 factor 0.3 to 0.5 shorter than DN32.

### 3.5.6 Conclusion

The goal of this section was to get a feeling for the order of magnitude and proportionality of the global methanol concentration in a confined space in relation to room size, pipe pressure, hole size and modelling parameters.

The main conclusion is that the hazards related to methanol vapour in an enclosed space are significant and should be considered as such, both for larger and smaller confined spaces. It should be noted that this model only considers the global concentrations. The local concentrations are expected to be higher and thereby more critical.

#### 3.5.6.1 Order of magnitude

There is a very significant difference between the pool evaporation model and the spray release model (in which no pool is formed). In reality the situation will be composed of a combination of both models, by which the global concentration is somewhere between both extremes. The results are presented in Table 3.15.

The main conclusions to draw from this comparison are:

- For the pool evaporation model;
  - The global concentration levels do not exceed the LEL, both for the 1 m<sup>2</sup> and 5 m<sup>2</sup> pool size,
  - The global toxicity levels do not exceed the EEGL limit for 10 minutes if the pool size is 1 m<sup>2</sup>. They do however exceed the EEGL limit for 30 minutes,

- The global toxicity levels do exceed the IDLH if the pool size is 5 m<sup>2</sup> for the small confined space. If the confined space is larger the EEGL 10 is exceeded but the global level remains below the IDLH.
- For the immediate spray release model, the concentration is excessive and up to 95% methanol in the air (for the first few minutes after the spill). After that, in all scenarios the concentrations reduce to below the critical levels within several hours.

Table 3.15: Results of the global concentrations in the confined space. These numbers are a combination of the results in Table 3.13 and Tabel 3.14.

Scenario	Immediate spray release		Pool Evaporation
	DN32		A = 5m <sup>2</sup>
	Time to below LEL [min]	Time to below IDLH [min]	Global concentration after 2 hours [ppm]
2 bara, 60s, 236 m <sup>3</sup>	27.5	32.7	10618
2 bara, 60s, 2000 m <sup>3</sup>	7.7	12.9	1253
11 bara, 60s, 236 m <sup>3</sup>	53.2	58.4	10618
11 bara, 60s, 2000 m <sup>3</sup>	12.2	17.3	1253
2 bara, 30s, 236 m <sup>3</sup>	17.2	22.3	10618
2 bara, 30s, 2000 m <sup>3</sup>	5.1	10.3	1253
11 bara, 30s, 236 m <sup>3</sup>	30.8	36.0	10618
11 bara, 30s, 2000 m <sup>3</sup>	8.2	13.4	1253

It can thereby be concluded that, globally speaking, the small confined space will have a toxic environment (exceeding the IDLH) for all scenarios. In the most beneficial case the spray release approach is justified, by which this situation will exist for 20 to 60 minutes (for the considered scenarios). In the least beneficial scenario the pool evaporation model is justified, by which the IDLH is exceeded in the stabilised situation and will last for several hours.

The larger confined space will, globally speaking, have a toxic environment (exceeding the EEGL 10-min) for all scenarios. In the most beneficial case, the spray release approach is justified, by which this situation will exist for 10 to 18 minutes (for the considered scenarios). In the least beneficial scenario the pool evaporation model is justified, by which the EEGL 10-min is exceeded in the stabilised situation and will last for several hours.

The LEL will (globally) only be exceeded, assuming the spray release, for several minutes after the release. For scenario 3 (high pressure, long response time, small confined space) this is up to 54 minutes. For scenario 6 (low pressure, short response time, large confined space) this is up to 6 minutes. Under the assumption that pool evaporation is governing, the LEL is not exceeded for either of the considered cases.

The local effects (that is, near the outlet and in close proximity of the methanol pool) will be more severe than the global estimates that are presented in this section.

### 3.5.6.2 Proportionality

The results of the parameter study, that indicate the sensitivity of the results to the assumed parameters and design choices, are presented in Table 3.16.

Table 3.16: Results of the parameter study that indicate the proportionality of the results.

	Pool evaporation (maximum concentration)	Spray release model (time to below IDLH)
Larger room	Proportional: $\frac{1}{f}$ (f = the increase factor)	Dangerous period is shorter
Smaller pool size	Proportional: $\sqrt{f}^{-0.11}$ . $f^2$	N.a.
Lower pipe pressure	Negligible	Dangerous period is shorter
Shorter response time	Negligible	Dangerous period is shorter
Smaller pipe diameter	Negligible	Dangerous period is shorter

### 3.5.6.3 Concluding Remarks

In reality, a methanol leakage or spill will consist of a combination of a spray release and pool evaporation. The dominant mode depends on the nature of release, e.g. how big the hole is, or on properties such as the flow pressure of methanol, where higher pressure tends to favour spray release. The size of the confined space, ventilation rate, and the response time play a key role in mitigating the consequences of a leak.

## 3.5.7 Discussion

For each release, it should be carefully considered which model (pool evaporation or spray release) is the best fit. For high pressure releases, the spray release with immediate evaporation is most suitable, for low pressure releases the pool evaporation model is most suitable. It should be kept in mind that in reality releases can be characterised by a combination of the two models.

The model simulates the simplified distribution of evaporated methanol throughout the confined space, based on thermodynamic properties of the methanol pool. The case study for the confined space of a small inland waterway vessel has indicated the severity of the risk related to a methanol spill in the confined space, both in terms of an explosive and toxic environment. For piping in enclosed spaces, such as the confined space, IMO formulates the following provision:

*Provision 5.7.4.1: "Fuel piping that passes through enclosed spaces in the ship should be enclosed in a pipe or duct that is gas and liquid tight towards the surrounding spaces with the fuel contained in the inner pipe." [2]*

Other mitigating measures such as sufficient ventilation and leakage detection systems are also presented in the IMO interim guidelines, as follows from the following requirement:

Functional requirement 3.2.2: *“The probability and consequences of fuel-related hazards should be limited to a minimum through arrangement and system design, such as ventilation, detection and safety actions. In the event of fuel leakage or failure of the risk reducing measures, necessary safety actions should be initiated.”*[2]

After each timestep all methanol that is evaporated is uniformly distributed throughout the confined space volume. It should be noted that, when applying this assumption, the local concentrations could be significantly higher due to non-uniformly distributed concentrations in the real-world case. This makes the calculation non-conservative for local effects, but useful for to study the global concentration (both the proportionality and order of magnitude).

### 3.5.7.1 Limitations

The model contains no information on the concentration distribution over the confined space, as it only considers the global uniform concentrations. Especially the distribution over the height is of interest, providing this affects the toxicity hazard at 1.5m height. Besides that, the local concentration is of relevance to quantify the risk of local ignition (when the LEL is locally exceeded). To calculate these local effects, dispersion modelling is required, which is not part of the scope of the current project.

### 3.5.7.2 Mitigation techniques

Based on the model that was developed, three mitigation techniques are suggested (in random order):

1. Reducing the maximum pool size. This slows the evaporation process down, which in combination with the ventilation increases the time to the maximum concentration as well as reduces the maximum concentration itself. This reduction can be attained by separating the floor area in compartments.
2. Increasing the ventilation rate. This has the same type of effect as the reduction of the maximum pool size. This can be done by installing a different ventilation system.
3. Reducing the response time. If the spill is stopped after a shorter time, the total amount of methanol in the confined space is reduced which in turn provides for lower concentrations. The response time is strongly linked to the detection systems, which require separate attention, but are not within the scope of this project.

## 3.6 Methanol liquid spill on quay

This section describes the calculation of the effects of a liquid spill of methanol on the quay.

### 3.6.1 Introduction

The scenario to be studied here is the outdoor spill of liquid methanol on a solid surface like a quay. This can occur during bunkering when the hose connecting the tank truck to the ship either is not properly connected or has a (small) hole, see Figure 3.8 for a schematic representation of the system.

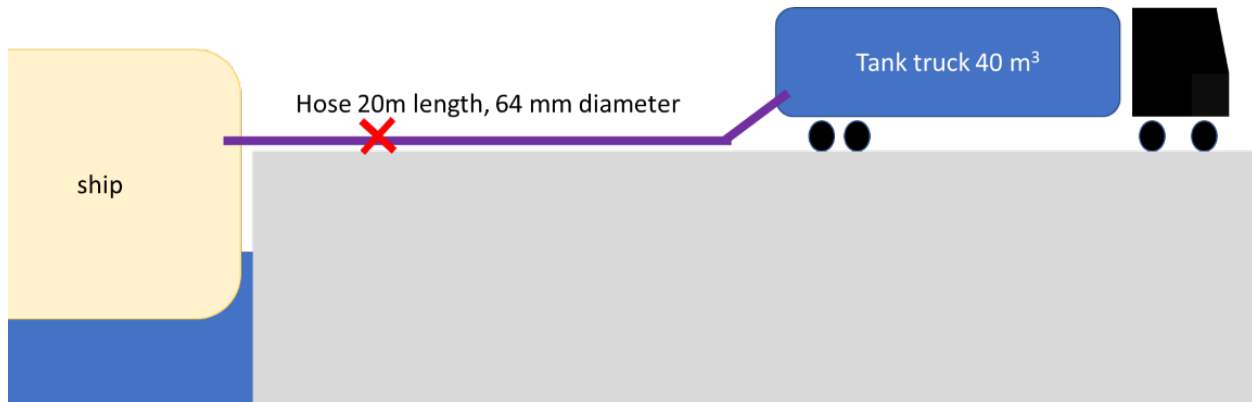


Figure 3.8: Schematic representation of methanol bunkering, with the dimensions and properties that are used in the example calculation in this section

The spilled methanol will form a pool. As methanol is both flammable and toxic the presence of this pool may form a hazard for people present in that area.

The hazardous consequences that could result from this, are:

- Toxic methanol cloud.
- Flammable methanol cloud (delayed ignition).
- Pool fire (direct ignition).

These consequences will be addressed in the following sections.

### 3.6.2 Method

The outdoor spill of a hazardous substance is a typical external safety issue. For this type of questions several software packages are available: EFFECTS [12], PHAST [10], Safeti-NL [11]. These software packages use analytical and empirical relations to calculate the effects and consequences of (accidental) releases of dangerous chemicals. In this document the software EFFECTS (v11.5), which was originally developed by TNO, is used.

The calculation has several steps:

1. Liquid release from tank truck resulting in a methanol pool on the quay.
2. After pool formation, the following scenarios can occur;
  - a. Pool evaporation and followed by the formation and dispersion of a toxic cloud,
  - b. Pool evaporation and followed by the formation and dispersion of a flammable cloud (delayed ignition),
  - c. Pool fire (immediate ignition).

The main outcome of these calculations is concentration as a function of distance (2a and 2b) and heat flux as a function of distance (2c). For a toxic cloud the IDLH value of 6000 ppm (0.008 kg/m<sup>3</sup>) is used, for a flammable cloud the LEL value of 60 000 ppm (0.08 kg/m<sup>3</sup>) is used as the value of interest for the calculations. For the heat flux from the pool fire a value of 10 kW/m<sup>2</sup> is used. With this heat flux a lethality of 1% of the exposed 'general public' is expected [36].

### 3.6.3 Assumptions

The spill from the tank truck is on a solid ground. The methanol will form a (growing) pool. The hose diameter is fixed, the pressure inside the tank truck is varied.

The input parameters for step 1 are given in Table 3.17. The results from step 1, e.g. mass flow rate, are used as input for steps 2a, 2b, and 2c. The other input parameters for these steps are given in Table 3.18. Note that for the evaporation calculation night time conditions are taken (F2.0 atmospheric condition with 0 W/m<sup>2</sup> solar heat influx). These conditions are a conservative approach, leading to the largest effect distances.

Table 3.17: Input values for liquid release from tank truck

Property	Value	Unit
Tank volume	40	[m <sup>3</sup> ]
Tank shape	Horizontal cylinder	n.a.
Tank length	10	[m]
Filling %	90	[%]
Initial temperature	10	[°C]
Hose length	20	[m]
Hose diameter	64	[mm]
Height leak above bottom	0	[m]
Overpressure above liquid	0.03 – 1.0	[bar]
Ambient pressure	1.013	[bar]

Table 3.18: Input values for pool evaporation & pool fire

Property	Value	Unit
Mass flow rate from source	Depends on parameters in Table 3.17	[kg/s]
Temperature of pool	10	[°C]
Type of pool growth	Spreading	[-]
Stability class	F - stable	[-]
Windspeed @ 10m height	2	[m/s]
Temperature subsoil	10	[°C]
Solar heat flux radiation	0	[W/m <sup>2</sup> ]
Type of subsoil	Heavy concrete	n.a.
Subsurface roughness	Flat concrete	n.a.

### 3.6.4 Results

The outflow rate of methanol as a function of time is depicted in Figure 3.9. The outflow rate decreases over time and converges to a steady value for all initial pressures. The initial outflow rate increases with the initial pressure inside the tank. The range of overpressure to be used in practice is expected to range from 0.03 bar to 1.0 bar.

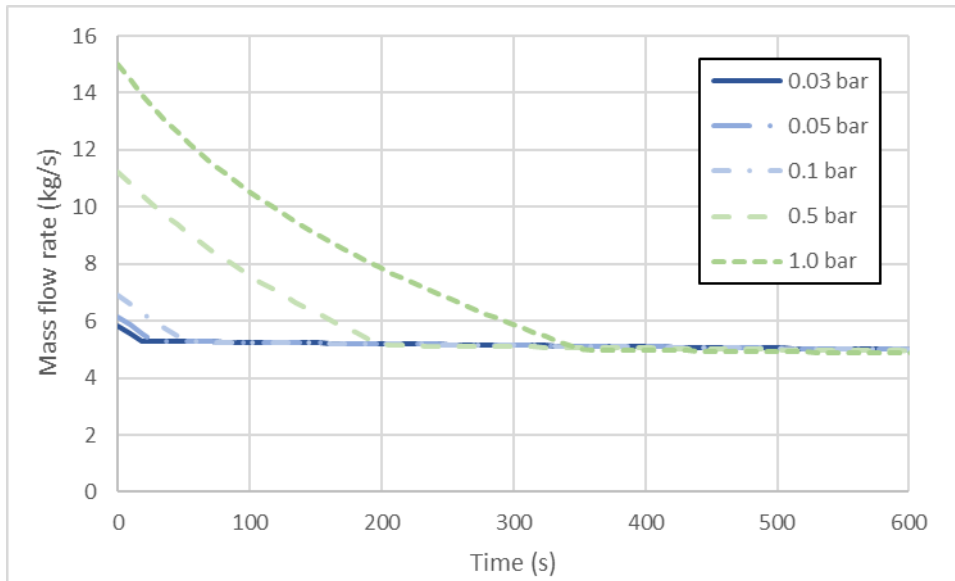


Figure 3.9: Outflow rate for various initial overpressures.

The methanol forms a pool on the quay. The size of the pool depends on the roughness of the surface of the quay and the equilibrium between inflow from the tank and evaporation due to heat influx. The equilibrium pool size for the various initial overpressures is shown in Figure 3.10. A higher overpressure inside the tank, with a higher mass flow rate results in a larger pool area.

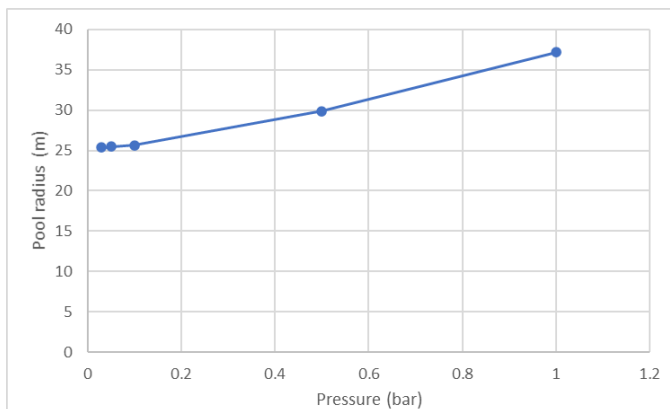


Figure 3.10: Pool radius as a function of overpressure.

The methanol evaporates from the pool and disperses to the surroundings. The maximum concentration as a function of downwind distance is shown in Figure 3.11. The maximum concentrations remain just below the toxic value of 0.008 kg/m<sup>3</sup> and clearly below the LEL of 0.08 kg/m<sup>3</sup> (not shown in Figure 3.11). This means that no toxic or flammable concentrations are expected to occur.



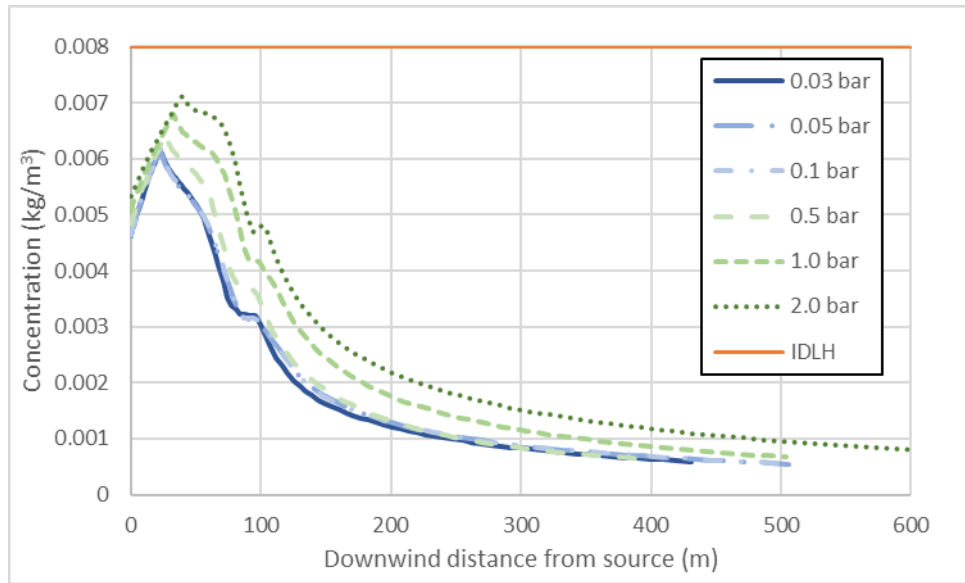


Figure 3.11: Maximum concentration vs downwind distance for various initial overpressures. Note that the concentrations of interest are 0.008 kg/m³ for IDLH and 0.08 kg/m³ for LEL.

However, because of its low flashpoint (11 °C) when an ignition source is present near the methanol pool, the vapour just above the pool will ignite and the resulting heat from the flame will increase evaporation rate sufficiently to maintain a pool fire. The heat flux as a function of distance for several initial pressures is shown in Figure 3.12. Inside the pool radius the heat flux has a constant value of 70 kW/m². Outside the pool the heat flux reduces with distance to the pool. At the pool edge the heat flux shows an unexpected jump. This is merely due to the transition between the used models, it has no physical meaning. Further away the decrease in heat flux is smoother.

The level of 10 kW/m² (the orange horizontal line in Figure 3.12) is reached at different distances for varying initial overpressure, the numerical values are given in Table 3.19. A lower overpressure gives a smaller mass flow rate and a smaller pool and results in smaller distance at which the heat flux decreases to 10 kW/m². These distances give an indication for the size of the zone around the bunkering activity where no ignition sources are allowed.

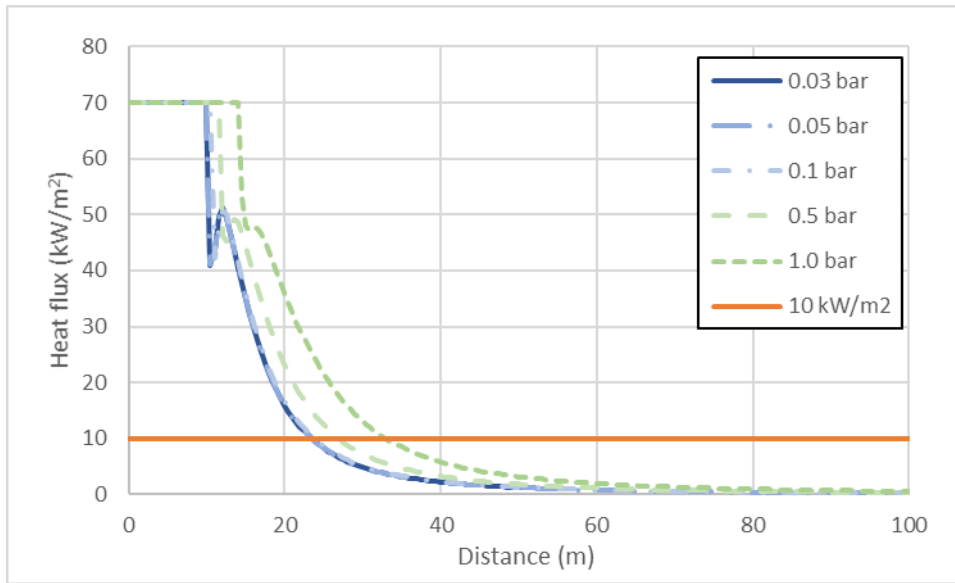


Figure 3.12: Heat flux vs distance for various initial overpressures. Horizontal orange line is 10 kW/m<sup>2</sup> value.

Table 3.19: Distance at which 10 kW/m<sup>2</sup> heat flux is reached for varying initial pressure.

Initial pressure (bar)	Distance 10 kW/m <sup>2</sup> contour (m)
0.03	23
0.05	23
0.1	24
0.5	27
1.0	33

### 3.6.5 Discussion & conclusions

The results of the dispersion calculations in the previous section (section 3.6.4) show that the concentration due to evaporation of a methanol pool does not lead to toxic or flammable concentrations in the vicinity of the pool. This seems to be in contrast to the results for concentration calculations for vapour release on deck (section 3.3) and the liquid spill in a confined space (section 3.5) for which concentrations above the toxic limit have been calculated.

The main difference between the liquid spill on quay and the liquid spill in the technical space is the amount of ventilation. Inside the technical space a limited amount of ventilation is available. On the quay even at low wind speeds sufficient mixing is present to lower the concentration.

During venting the methanol is directly entered into the atmosphere, whereas for a methanol pool the liquid has to evaporate to mix with air. The latter process is much slower than the former. This results in different risk profiles for venting methanol vapour to the atmosphere and evaporation from a methanol pool.

The main point of attention for a liquid spill on a quay is the risk of a pool fire. The contour for 10 kW/m<sup>2</sup> heat flux ranges from 23 to 33 m for this situation. This can be mitigated by defining a safety zone around the bunker activities where no ignition sources are allowed.

It is noted that current practice is that the road tanker and the shore part of the bunkering equipment (couplings, hose) are located within a (temporary) bunded area. This constrains the methanol pool in case of liquid leakage, which reduces fire and intoxication risks considerably.

## 3.7 Methanol liquid spill on water

This section provides the analysis of the possibilities with regards to the modelling of a spill of liquid methanol in water. It provides the train of thoughts, and explains why it is not deemed feasible to produce a sufficiently valid model based on analytical and (presently available) empirical relations.

### 3.7.1 Introduction

Methanol, expressed by the chemical formulation CH<sub>3</sub>OH is completely miscible in water in all concentrations. This is due to the strength of the attraction of the OH group to water. The O forms a hydrogen bond with one of the H atoms of water. However, the rate at which methanol mixes (dilutes) in water will affect the time in which a hazardous zone of flammable methanol-water mixture is present at the water surface. The methanol-water mixture is flammable for concentrations of methanol between 25% and 100% [29], [37]. So a significant dilution is needed to remove the possibility of a pool fire.

The case description of this scenario is:

Due to a leak of a tank, placed above the waterline to the shell (which is not allowed in the present Interim Guidelines from IMO [2], but this is studied to test the relevance of this requirement), liquid methanol is leaking/spilling onto the surface water. Depending on the origin of the leak (small crack due to a broken weld -can be fatigue or a production error- or a large hole due to a collision) methanol will trickle or flow out of the tank. The methanol will mix with the water body until uniformity is reached. In the section on Environmental fate and transport the Methanol Institute states that “*In an open ocean methanol spill, naturally occurring wave action, quick dissolution within the water column, and the near-infinite availability of water results in rapid dilution to nontoxic concentrations.*” [29]

However, when also considering the flammability (25 to 100% methanol concentration in water), the “rapid dilution” should be quantified in relation to the timescale to prevent a pool fire. The formulated hypothesis in this section is:

*Methanol will dilute rapidly when spilled into water. Due to the dynamic outflow in combination with waves in open water, there will not be a flammable pool on the water.*

This hypothesis requires testing. The goal of this section is to determine the feasibility of a simplified model to describe the effects of a methanol spill in open water.

### 3.7.2 Method

To meet the goal, to determine the feasibility of a simplified model to describe the effects of a methanol spill in open water, three steps are used:

1. A literature study into available models of chemical spills in open water.
2. The formulation of the outline of the model.
3. A critical reflection on the feasibility, using the input from the first two steps.

### 3.7.3 Literature

In scientific literature, only one source is found that presents results of a computer simulation of the concentration in the aftermath of a methanol spill in open water. Although often attributed to Machiele [38], the simulations are actually by the NEDO [39]. Unfortunately this source article was not obtained by TNO and is to the authors' knowledge not available online. Machiele cites:

*“Simulation of a large-scale (10,000 ton), open-sea, methanol spill revealed that the concentration near the spill site would be reduced to less than 0.36 percent within an hour of the spill. [39] A similar simulation of a 10,000 kl/hr spill on a coast (at a pier) revealed that even in the severe case where the wind was blowing toward the coast, the concentration was less than 1 percent at the spill site within 2 hours after the spill was stopped and 0.13 percent after 3 hours [39]” [38].*

To test this statement, assumptions are required with respect to wave conditions and shape of affected zone (hemisphere or a disc with thickness  $t$ ).

In [40] a comparison is made between several equilibrium models for a spill of a liquid fuel on concrete or vinyl (solid surfaces). For the comparison for transient models reference is made to [41]. A second comprehensive list of models is presented in [42]. Lastly a list of models is presented in [43]. From both [41], [42] and [43] the models that address a spill of the fuel on water are:

- [1974] The model by Raj and Kalelkar [44] does consider a spill on water, although only for still water. “Because of the mathematical difficulties, a complete solution could not be obtained for the spreading of fuel over water.” [41].
- [1980] SPILL model by Briscoe and Shaw [45], which models the spill of a cryogenic liquid, which vaporises quickly. However, the model can be used for all types of spilling liquids. The model is simple and conservative. It does not account for the water motion of the receiving volume, but only includes a multiplication of the pool volume with a factor  $1 - \rho/\rho_w$  to account for the water. This model is also incorporated in the LSM 90 and LPOOL model by Cavanaugh [46], which does not expand the modelling of the interaction with the water body.
- [1990] GASP by Webber [47], which accounts for a spill on water and land. However, the “model does not account for surface waves, or the effects of sloping or porous ground, nor multi-component liquid composition” [48].
- [2008] PHAST by Witlox, which uses the equations from Dodge et. al. [49] for a spill on water. It expands from the model by Briscoe and Shaw [45].
- [2009] Brambilla and Manca developed a model that is based on GASP, but does account for turbulent mixing on water.

The dissolution is only considered in PHAST and the model by Raj and Kalelkar [43]. However, due to the mathematical difficulties [41] in the latter, the dissolution is deemed best expressed using the equations from Dodge [49]. Dodge et. al. [49] have performed multiple experiments to build an empirical model to express the effect of waves in open water on the dissolution rate of a spilled chemical. The full expression of this model is presented in section 3.4.3 of [43]. The wave height is estimated from the wind velocity at 10 meters above the water surface.

A second type of models, that was not discussed in the section before, is for chemical spills in water. The problem is reformulated from 3D for open water to 2D for a river, enabling the formulation of a diffusion coefficient based on the roughness of the bottom of the river. **Examples are RDM2D [50] and [51], see an overview in the book by van Leeuwen [52].** Vertical (over the depth of the river) mixing is assumed to be rapid in relation to longitudinal mixing (in the downstream direction). The vertical mixing component is not included in the analysis and the assumption is made that the concentration is uniformly distributed over the depth. However, if a deep-water approximation is justified and the analysis is not for a river but for open water, the model is not valid anymore.

The conclusions that can be drawn from the river models are:

- The diffusion coefficient can be assumed proportional with the water velocity.
- The diffusion coefficient is influenced by the presence and the roughness of the sediment at the bottom of the waterbody.

### 3.7.4 Outline model liquid spill on water

The description of the phenomenon is separated into two phases. The description of phase 1 (convection) can be found in 3.7.4.1 and of phase 2 (diffusion) in 3.7.4.2.

- **Phase 1: rapid dilution, driven by highly dynamic outflow**  
This phase is characterised by convection (spreading due to velocity differences, caused by non-ideal flow patterns) and can be modelled as a jet. An example is the article by Li [53] considering the velocity decay of a jet in a narrow and wide environment (both confined).
- **Phase 2: slow dilution, driven by water movement and concentration differences**  
This phase is characterised by diffusion. It is often assumed that the diffusion is proportional with water velocity [52, 51]. This assumption is common in the modelling of chemical spills in rivers.

The terminology of diffusion and convection as is used in this report is:

**Diffusion** is spreading due to concentration gradient (molecular). It can be described using Fick's first law:

$$J = -E \frac{dc}{dx},$$

where  $c$  is mass concentration of the species of interest,  $E$  is the dispersion coefficient, and  $x$  is the position in the direction of the concentration gradient. The diffusion coefficient is approx. proportional with water velocity [52, 51].

**Convection** is spreading due to velocity differences (mechanical). Convection can be differentiated from diffusion in that it is caused by flow patterns and is a macroscopic phenomenon, whereas diffusion is caused by random molecular motions (i.e. Brownian motion) and is a microscopic phenomenon. Convection is often more significant than diffusion in convection-diffusion problems.

Accounting for convection would increase the mixing rate and therefore reduce the concentration at a faster rate. Not accounting for convection is therefore assumed to be conservative.

To combine the models of phase 1 (convection) and phase 2 (diffusion) the interface between both phases should be carefully designed. A suggestion could be to determine the size and concentration of zone 1 from the size of the dispersive volume from phase 1. In such a combined model, a significant error is introduced when fitting a cone-shaped distribution to a disc or (half-) hemisphere. However, no other analytical or empirical models are at hand. This is also why this combined model is not recommended for implementation, it merely illustrates the train of thoughts and indicates why a simplified model is not deemed feasible for this release case.

### 3.7.4.1 Phase 1: Rapid dilution

In phase 1 the methanol (100%) is flowing from the tank through a hole with a predefined diameter. The outflow can be modelled as a jet under the waterline, see Figure 3.13.

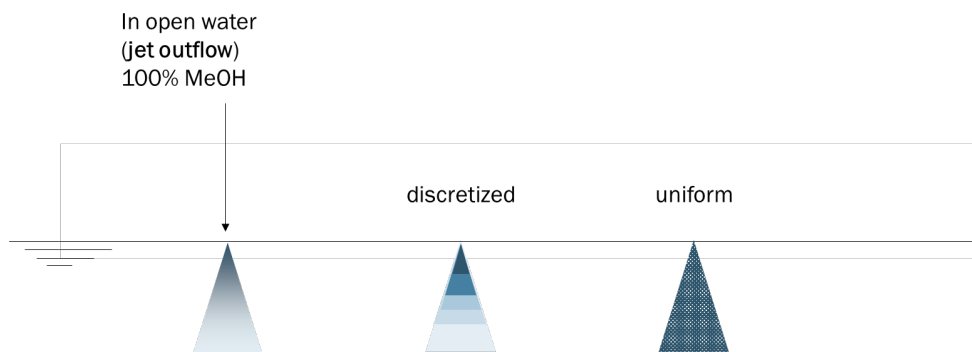


Figure 3.13: Three representations of the jet flow into the water, resulting from a methanol spill above the waterline. On the left the actual situation is presented: at the surface the concentration of methanol is close to the 100% of the spill, whereas the concentration (and velocity) decay with increasing distance from the source. The centre figure shows a discretisation of this jet. On the right a representation of an uniform distribution throughout the turbulent shown is presented – this is used in the most simplified model.

To determine the size of the turbulent zone, literature data on the velocity decay profile is used, such as the work by Li on the velocity decay of a horizontal jet in a confined space [53]. The outflow in a confined space would represent with an outflow next to the vessel.

The size of the turbulent zone could be approximated by a cone-shaped perimeter of the jet-affected zone, with a boundary at the velocity equal to the water velocity without considering the jet. Within this zone an uniform distribution of methanol is assumed (see the right side of Figure 3.13). The uniformity is assumed to simplify the model and to promote the interaction with phase 2.

When applying the article by Li [53] several errors are introduced:

- The article considers a horizontal jet instead of a vertical jet which could be subject to water surface effects. In the application of the work from Li in the GMM 2.0 project it is assumed that gravity has a negligible effect in relation to the water-methanol mixture.
- Water-in-water versus methanol-in-water, for which small buoyancy differences occur. However, as methanol is fully miscible in water, this effect is deemed negligible.

### 3.7.4.2 Phase 2: Slow dilution

In the second phase it is assumed that there is an initial zone (zone 1) with an uniform concentration of methanol. Driven by the concentration differences with zones around the initial zone 1, this methanol will dilute to adjacent zones until uniformity is attained in all zones. Figure 3.14 shows three differently shaped zones.

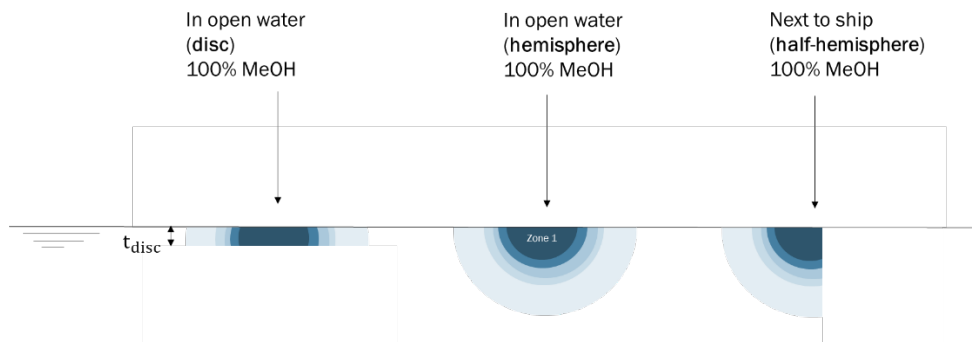


Figure 3.14: Three differently shaped zones that could be used in the diffusion model (phase 2).

For diffusion Fick's first law can be used. When applying a model based on the sketched zones in Figure 3.14 with one constant diffusion coefficient, some errors are introduced:

- The exponential velocity decay over the water depth is ignored. The assumption of an omnidirectional diffusion coefficient is un-conservative as it assumes more mixing in vertical direction than is justified.
- Directionality is not accounted for.

The difficulty in this diffusion model based on Fick's first law lies in the determination of the diffusion coefficient, which could even vary over time. No reliable estimate of this coefficient was found.

### 3.7.5 Reflection and discussion

As was indicated before, a simplified model for this scenario is not feasible. An alternative is CFD software or integrated models like EFFECTS. The presently available software EFFECTS does not account for mixing. It can only account for the outflow on a non-permeable surface (i.e. without motion within that surface/body). It is assumed that this exclusion of dilution provides for a conservative estimate of the concentration. However, when the concentration of the pool is reduced, the affected volume is increased. The flammable range of methanol is between 6.7% (LFL) and 36% (UFL) in air and between 25% and 100% in water, which means that a large range of diluted methanol could result in a flammable

mixture. Approaching the LFL the zone can be larger than near the UFL. It therefore does not mean that the analysis of the affected area is conservative when neglecting the dilution process in the water body.

Secondly, the results from NEDO [39] are for a spill that is several orders of magnitude beyond the expected liquid spill from a vessel. It is recommended to perform experiments on the concentrations that result from a spill of methanol in water, and to test the validity of the Dodge model [49] (well described in section 3.4.3 of [43]) for those spills, which is the most suitable model from literature to describe a liquid chemical spill in open water.

### 3.7.6 Conclusion

The goal of section 3.7 is to determine the feasibility of a simplified model to describe the effects of a methanol spill in open water. In short, a simplified model is not deemed feasible. This is because too many assumptions are combined, of which the combined effect is uncertain. To assess the extent of a flammable zone after the spill of liquid methanol in water, detailed CFD calculations and/or experiments of the dissolution behavior of methanol in water are recommended.

## 3.8 Recommendations

This section presents the recommendations for further research for each of the five release scenarios, being:

- a) Vapour release on deck.
- b) Vapour release below waterline.
- c) Liquid spill in confined space.
- d) Liquid spill at quay.
- e) Liquid spill on water.

ad a)

Study the duration and frequency of each venting event, to arrive at a time-dependent (as opposed to a time-independent) classification of hazardous zones. Including time as a parameter may create the opportunity to introduce temporary no-go zones following a scheduled or accidental venting event. This may alleviate crew access limitations. Study the effect of inert gas asphyxiation due to venting of gas on deck, using software such as EFFECTS.

ad b)

Study the scenario of venting below the waterline in more detail with experiments:

- a. Important variables to vary include diameter and depth, to help characterize, amongst other things, the rate of dissolution and the rise time of the bubbles.
- b. Experiments can also help determine the size regime of the bubbles and what can be done to reduce the size of the bubbles and promote dissolving of methanol. One way could be trying out various dispersion systems to see how finely bubbles can be created without compromising on backpressure effects.

ad c)

Detailed calculations are recommended to quantify both the probability of a leak and the potential consequences of a leak. For this dispersion modelling and/or experiments are required.



Recommendations for further research are:

- Expand the model from section 3.5 with a model that accounts for the expected pressure drop during a spill, as well as effects of the ventilation rate, with priority to the latter as pressure drop will only occur at large outflow areas exceeding the qualification as a leak.
- Study the scenario of a liquid release of methanol in a confined space in more detail with experiments and modelling:
  - a. Perform local CFD modelling to study the distribution of the methanol vapour throughout the technical space to relate the global concentrations to most likely maximum local concentrations. This relation could, ideally, be implemented in the presented first-principle model from section 3.5 by assuming a generic concentration distribution profile.
  - b. Identify whether the spray release is a likely scenario. This could be studied by means of experiments.

ad d)

Further emphasise the need for a safety zone around the bunkering operation. The issue of toxicity of vapours should to be further investigated and the results included in the determination of the zone.

ad e)

Both experiments and CFD modelling are recommended to quantify the hazard related to a methanol spill event on water. The model by Dodge is considered to be the most promising available model to assess the concentrations resulting from a chemical spill in water, but should first be validated with data obtained from experiments.

# 4 Fault and event tree examples

## 4.1 Introduction

This chapter describes the use of fault trees and event trees for quantifying the probability of occurrence of these incidents. Three examples are given to illustrate their possible use. Two of these came from workshops, held with several partners from the GMM II consortium. In the workshop they were requested to select a relevant scenario, after which the corresponding fault trees and event trees were set up.

Two cases were analysed:

- A hazardous area surrounding a cofferdam access hatch in an engine room.
- Methanol venting of the side.

The results of these workshops are presented in Section 4.4 and Section 4.5.

The third example, reported in section 4.3, comes from an exercise from within TNO.

Within the framework of the GMM II project it was decided to focus on setting up the fault and event trees and refrain from determining the corresponding probability of occurrence of the events and/or consequences.

## 4.2 Fault tree and event tree basics

A fault tree analysis is used to identify the causes of and determine the probability of occurrence of an undesired event, while an event tree is used to quantify the probability of occurrence of the consequences following the undesired event. This is illustrated in a bow-tie diagram linking causes to consequences, as shown in Figure 4.1.

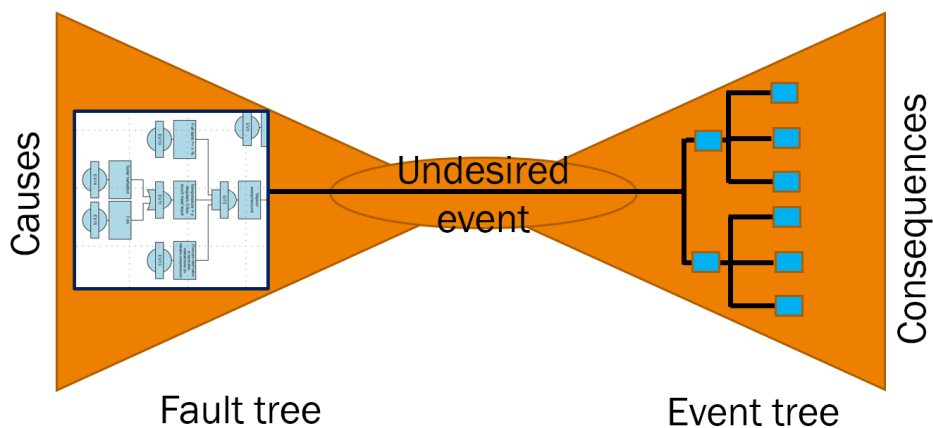


Figure 4.1: Schematic representation of a fault tree and an event tree in a bow-tie diagram.

A fault tree is a diagram that illustrates how different causal events lead to an undesired event. If two or more events need to occur simultaneously for a higher-level event to occur, this is illustrated by means of an “and” gate.

In this case the probability of the higher-level event to occur equals the multiplication of the probabilities of the events that need to occur simultaneously. If any of the events can cause the higher-level event to occur, this is illustrated by means of an “or” gate. In this case, the probability of the higher-level event to occur equals the sum of the probabilities of the preceding events. Figure 4.2 shows an example of an “and” and an “or” gate as used in a fault tree analysis.

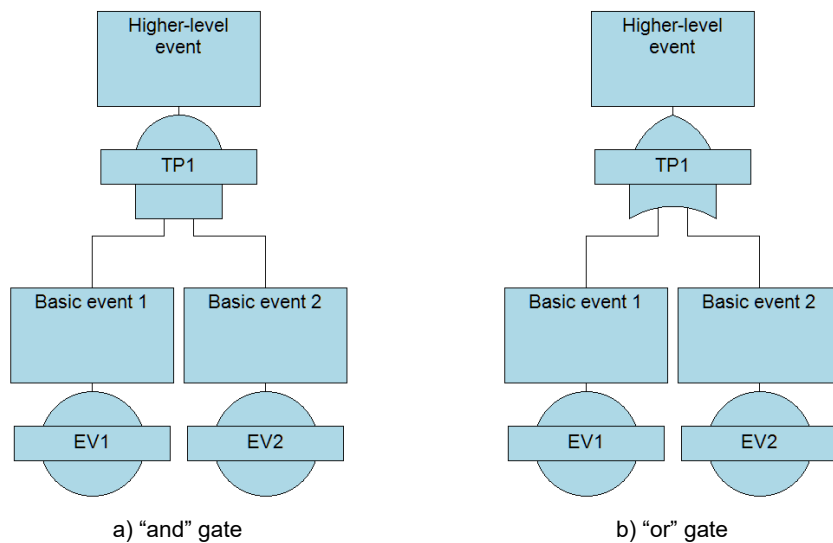


Figure 4.2: Example of an “and” gate and an “or” gate in a fault tree.

An event tree is a diagram that is used to identify possible consequences and their probability of occurrence following an undesired event. Starting from the undesired event, each subsequent column represent an action or situation following the undesired event, which can either be a success or a failure. This results in a series of branches, where each branch represents a consequence. The probability of this consequence occurring given the undesired event, can be calculated by tracing the branch from the undesired event to the consequence. Figure 4.3 shows an example of an event tree, where the success or failure of two actions result in four possible consequences. In case of multiple separate branches that lead to the same consequence, their probabilities of occurrence need to be added in order to obtain the overall likelihood of this consequence given the undesired event.

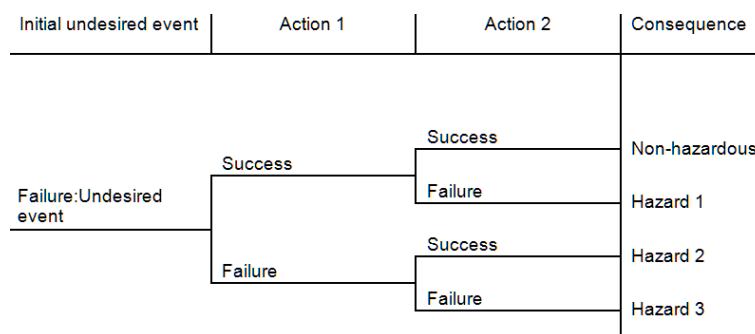


Figure 4.3: Example of an event tree.

The final probability of occurrence of the consequence is then given by multiplying the probability of occurrence of the undesired event, as derived from the fault tree, by the probability of occurrence of the consequence given this undesired event, as derived from the event tree.

In Section 4.3, a high pressure methanol fuel line running through the engine room is used as an example of a fault tree and event tree analysis.

## 4.3 Examples FT-ET analyses: Double walled fuel line in the engine room

In order to illustrate the use of fault and event trees to calculate the probability of consequences, the example of a double-walled fuel line in the engine room (ER) is used. Figure 4.4 shows a schematic overview of the system. The system bounds are given by on one side the connection of the high pressure common rail to the cylinders and on the other side the connection of the 10 bar double-walled fuel line to the rest of the fuel system in the fuel preparation room. The engine itself and any systems in the fuel preparation room are not part of the system analysed in the present example. The ship is sailing under normal operation conditions with the engines running. The fuel is supplied from the fuel preparation room (FPR) to the high pressure common rail pump (HPCR) through a double-walled pipe. The high pressure common rail pump is mounted directly on the engine and pressurises the methanol to 400 bar as required for fuel injection.

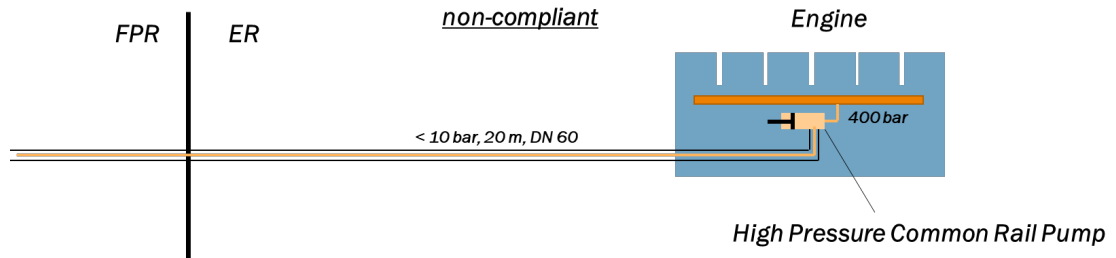


Figure 4.4: System description showing a double walled fuel-line supplying fuel from the fuel preparation room (FPR) to the high pressure common rail pump on the engine.

The undesired event in this case is a release of methanol through a leak in the system. Based on the system description in Figure 4.4, three potential causes for a release of methanol are identified:

1. Leak of the inner pipe.
2. Leak from the HPCR pump.
3. Leak from the common rail.

In order to identify the probability of occurrence of a leak of methanol, the probability of occurrence of each of these scenarios needs to be determined. In case of scenario 1, a leak of the inner pipe, statistics such as the statistics on Process Release Frequencies [7], can be directly used and a fault tree is not required.

*FT example*

However, in case of scenario 2, for the HPCR pump, different components can fail and a fault tree has been set up as an example in Figure 4.5. Table 4.1 provides a description of the corresponding gates and basic events. Three typical failures were identified that could lead to a release of methanol: an inlet gasket leak, an outlet gasket leak, and a de-airing leak. For the de-airing leak, a further subdivision is made in a gasket leak and a leak due to human error by not tightening the de-airing bolt sufficiently. The probability of occurrence of each of these basic events can be obtained from, failure statistics. As said, the overall failure probability is determined through multiplying probabilities in case of ‘and’ gates and summation in case of ‘or’ gates.

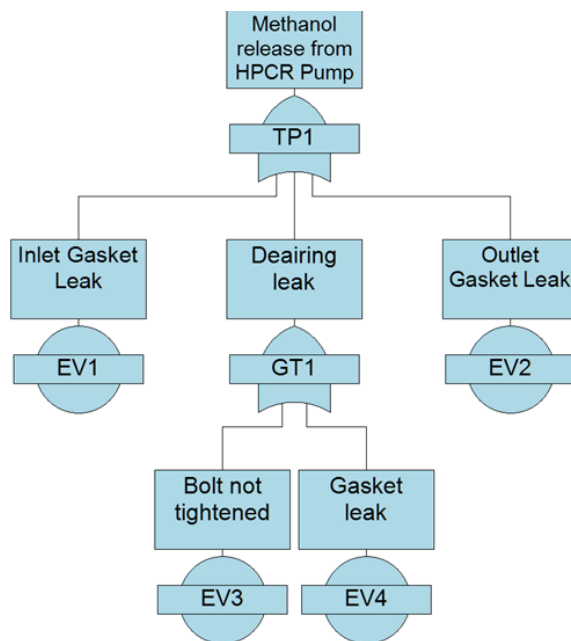


Figure 4.5: Fault tree for methanol release from a HPCR pump

Table 4.1: Gates and basic events for fault tree for methanol release from a HPCR pump

ID	Description
GT1 - Deairing leak	Leak past the deairing bolt for the HPCR pump
EV1 - Inlet gasket leak	Probability of a leak at the inlet gasket of the HPCR pump
EV2 - Outlet gasket leak	Probability of a leak at the outlet gasket of the HPCR pump
EV3 - Bolt not tightened	Probability of deairing bolt not being properly tightened
EV4 - Gasket leak	Probability of a leak at the gasket at the deairing bolt

The yearly probability for a de-airing bolt not being tightened properly can, for example, be based on human failure statistics. The probability of the gasket leaks can, for example, be taken from reference [7], table on ‘flanged joints’.

In order to complete the investigation into the probability of occurrence of a release of methanol, a similar fault tree should be set up for the common rail.

*ET example*

After the probability of occurrence of a release of methanol has been determined, an event tree is used to identify possible consequences and the corresponding probabilities of

occurrence. For this example, the scenario of a leak of the inner pipe has been developed into an event tree, as shown in Figure 4.6. Table 4.2 provides a description of the different events depicted in the columns of the event tree. Statistics and/or fault trees can then again be used to determine and/or calculate the probabilities of success or failure of detection, the emergency shutdown, outer pipe leak and leak rate exceeding critical rates. In this example, the probabilities of the outer pipe leakage can, for example, be taken from [7], table ‘steel process pipes’, the probability of detection can be taken from the characteristics of the sensor, the probability of an emergency shutdown can be determined by means of a fault tree analysis and the hazard given a certain leakage rate can be determined using, for example, the analysis methods described in Chapter 3.

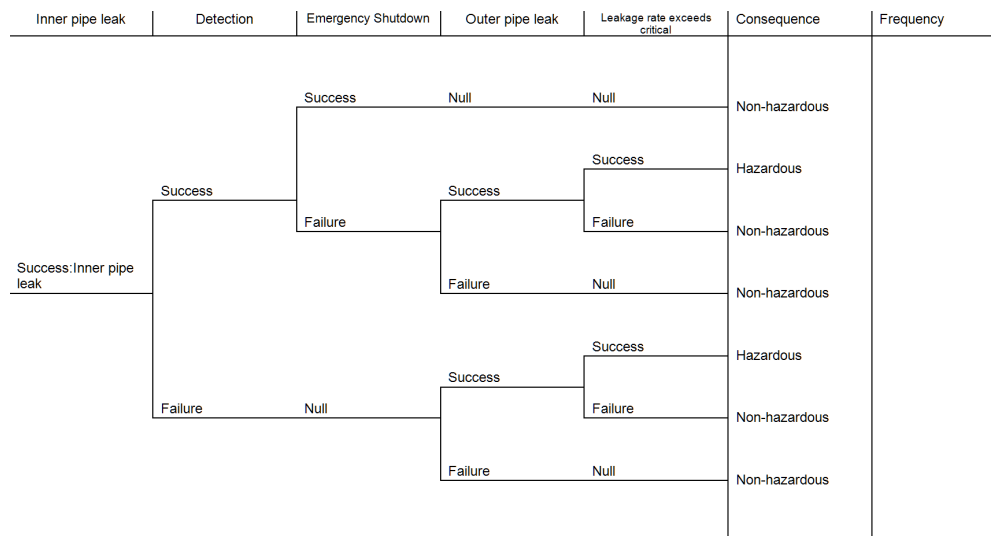


Figure 4.6: Event tree following the leakage of the inner pipe of a double-walled fuel line

Table 4.2: Events for event tree following the leakage of the inner pipe of a double-walled fuel line

Name	Description
<b>Detection</b>	Is the leak of the inner pipe successfully detected?
<b>Emergency shutdown</b>	In case of a successful detection, is the emergency shutdown procedure successful?
<b>Outer pipe leak</b>	In case of a failure of the emergency shutdown or in case of no detection of the leak, will methanol leak from the outer pipe?
<b>Leakage rate exceeds critical</b>	In case of a leak from the outer pipe, does the leakage rate result in a hazardous situation

In this section, by means of the example of a potential leak of methanol from the high-pressure fuel system, it is shown that by going through the bow-tie from the events that cause a potential leak to the possible consequences of such a leak, the probability of occurrence of various hazardous situations can be determined. Subsequently, a consequence analysis, as presented in Chapter 3, can be used to obtain the corresponding consequences and quantify the risk to people, property and planet.

## 4.4 Workshop case 1: Hazardous area surrounding a hatch in the engine room

The first system that was analysed during the workshops is the case of an access hatch in the engine room in order to access a fuel tank below the engine room, as shown Figure 4.7. In order to access a fuel tank for maintenance or inspection, an access hatch is placed on top of the fuel tank connecting the fuel tank to the cofferdam. Similarly, in order to access the cofferdam, an access hatch is placed between the engine room and cofferdam. Following IEC 60079-10-1 [9] and IEC 60092-502 [54], a conservative hazardous area classification would result in a hazardous area zone 2 of 1.5 m surrounding the access hatch in the engine room, as illustrated in Figure 4.7. This is, however, undesirable from an operational point of view and, hence this case was selected for further analysis.

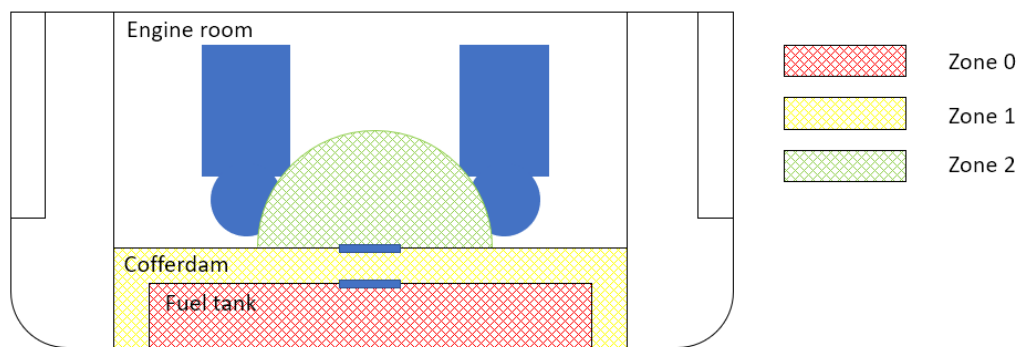


Figure 4.7: System description illustrating access hatch in the engine room to access fuel tank below the engine room

A leak from the cofferdam to the engine room was selected as the undesired event in the centre of the bow-tie. During the workshop, an initial fault tree was set up for a methanol leak from the tank to the engine room, as shown in Figure 4.8. Table 4.3 provides a description of the corresponding gates and basic events. In order for methanol to leak from the fuel tank to the engine room, two events need to occur: (i) a methanol leak from the fuel tank to the cofferdam and (ii) a methanol leak from the cofferdam to the engine room. Only scenario (i) was detailed further and a distinction is made between a liquid and vapour leakage of methanol. Given the limited time available, only the case of vapour leakage was evaluated in more detail. A leakage through the tank hatch, a crack in the tank, and a leakage of one of the pipes connected to the tank were identified as potential vapour leakage events. Similar to the example in Section 4.3, these were subsequently further detailed to identify possible events that could lead to these leakages.

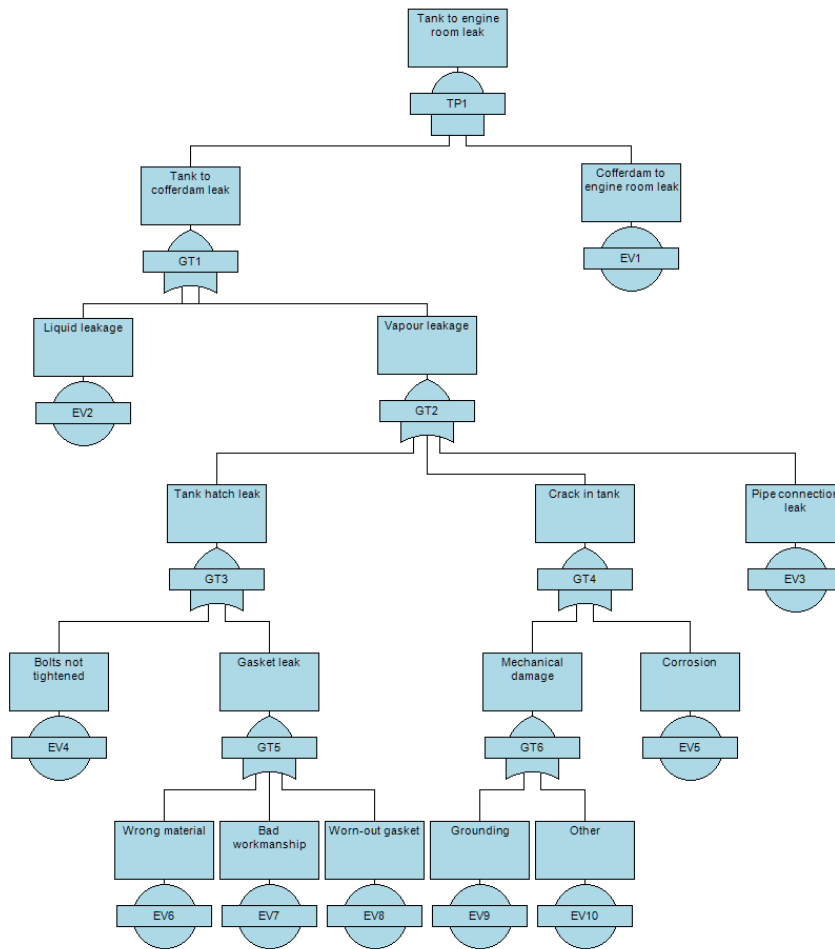


Figure 4.8: Initial fault tree for methanol leakage from the fuel tank to the engine room



Table 4.3: Gates and basic events for fault tree for methanol leakage from the fuel tank to the engine room

ID	Description
GT1 – Tank to cofferdam leak	Leak from the fuel tank to the cofferdam
GT2 – Vapour leakage	A vapour leakage from the fuel tank
GT3 – Tank hatch leak	A leak from the tank hatch between the fuel tank and the cofferdam
GT4 – Crack in tank	A crack in the fuel tank through which methanol vapour can leak
GT5 – Gasket leak	A leak of the gasket at the fuel tank hatch
GT6 – Mechanical damage	Mechanical damage causing a crack in the fuel tank
EV1 – Cofferdam to engine room leak	Leak from the cofferdam to the engine room. This basic event needs to detailed further in the future.
EV2 – Liquid leakage	A leakage of liquid methanol from the fuel tank to the cofferdam. This basic event needs to detailed further in the future.
EV3 – Pipe connection leak	Methanol vapour leakage at the pipe connections to the fuel tank. This basic event needs to detailed further in the future.
EV4 – Bolts not tightened	Bolts of tank hatch not properly tightened.
EV5 – Corrosion	Crack in the fuel tank because of corrosion
EV6 – Wrong material	Use of incorrect gasket material
EV7 – Bad workmanship	Leakage of gasket because of human error
EV8 – Worn-out gasket	Leakage because of a worn-out gasket
EV9 – Grounding	Mechanical damage of the fuel tank because of grounding
EV10 – Other	Mechanical damage to the fuel tank through other means. This basic event needs to detailed further in the future.

Under the assumption that a methanol leak from the tank through the cofferdam has indeed occurred, as a second step, the event tree describing the events following a release of methanol in the engine room was created, as shown in Figure 4.9. A description of the different events that were identified is given in Table 4.4.

Table 4.4: Event descriptions leakage from cofferdam to ER

Name	Description
Detection	Is the leak of the cofferdam to the engine room successfully detected?
Increase ventilation rate	Following a successful detection, will the ventilation rate in the engine room be increased sufficiently?
Local accumulation	Will there be local accumulation of methanol?
Toxicity radius exceeds 1 m	Under the assumption that we deem a hazardous of 1 m surrounding the leak acceptable, will there be a toxic concentration outside this zone?
Lower flammability limit (LFL) exceeds 1 m	Under the assumption that we deem a hazardous of 1 m surrounding the leak acceptable, will there be a concentration exceeding the LFL outside this zone?

Following the different branches, three possible consequences were identified: (i) a fire, (ii) a toxic cloud, (iii) a non-hazardous situation.

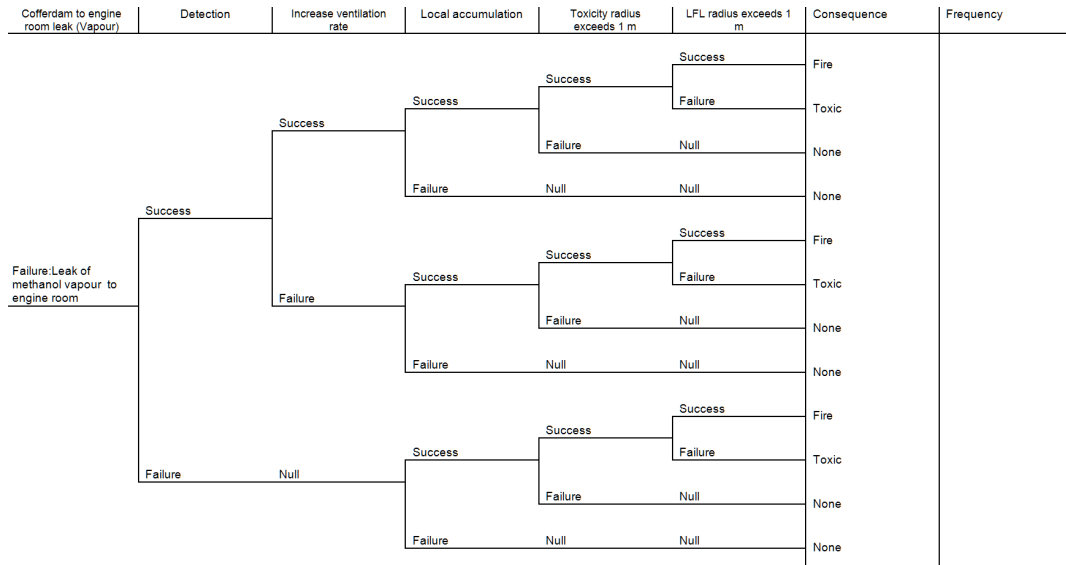


Figure 4.9: Event tree following a leak of methanol vapour in the engine room

Finally, as future step, in order to quantify the overall risk of a leak from the fuel tank, these fault and event trees need to be completed after which failure statistics, simulations and/or measurements should be used to quantify the probability of occurrence of the individual events.

## 4.5 Workshop case 2: Methanol venting over the side

The second system that was analysed during the workshops was the case of methanol venting over the side of the ship without applying the prescribed ([2]) vent stacks of 3 m. The corresponding system is illustrated in Figure 4.10.



Figure 4.10: Cross-section with schematic illustration of methanol venting over the side of the ship

A vapour release of methanol from the vent stack was defined as the undesired event. The initial fault tree is shown in Figure 4.11. A description of the gates and basic events in the fault tree is given in Table 4.5.

Table 4.5: Gates and basic events for fault tree for methanol leakage from the fuel tank to the engine room

ID	Description
GT1 – Heating of the tank	Heating of the methanol in the tank that results in a pressure build-up and subsequent vapour venting
EV1 – Filling of the tank	Overfilling the tank that results in a pressure build-up and subsequent vapour venting. This basic event needs to detailed further in the future.
EV2 – Tank compression	Compression of the tank, because of, for example, a collision. This could lead to a pressure build-up and subsequent vapour venting. This basic event needs to detailed further in the future.
EV3 – Thermal expansion of liquid	Thermal expansion of methanol, because of an increased temperature of the methanol.
EV4 – Heating of the vapour space	Pressure build-up in the vapour space above the methanol because of an increased temperature.

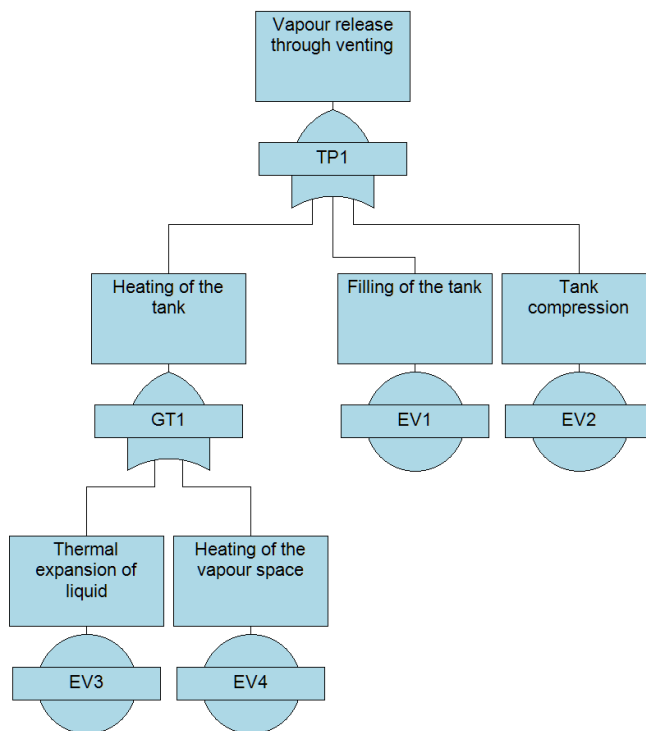


Figure 4.11: Initial fault tree for vapour release of methanol through venting

The corresponding event tree following a release of methanol from the vent opening is shown in Figure 4.12. As initial “events” a number of aspects related to the situation in which the venting occurs were identified:

- Is there a ship alongside or is the ship alongside a quay, which influences the likelihood of people being affected by the vapour cloud.
- Are the dispersion conditions, such as ambient temperature and wind speed and direction, favourable or not?
- Depending on the temperature of the methanol/nitrogen mixture and ambient temperature, will the vapour condense on deck?

Once the aspects related to the situation in which the vapour is released have been determined, the corresponding consequences can be grouped depending on whether the mixture is toxic or not, whether the mixture is flammable or not and, if flammable, whether the mixture ignites or not.

Following the different branches, three possible consequences were identified: (i) a fire, (ii) a toxic/asphyxious cloud, (iii) a non-hazardous situation. Note that in case of vapour condensation on deck, the current event tree does not include potential hazardous events such as a potential pool fire. However, this will have to be taken into account in future work before the event tree can be finalised.

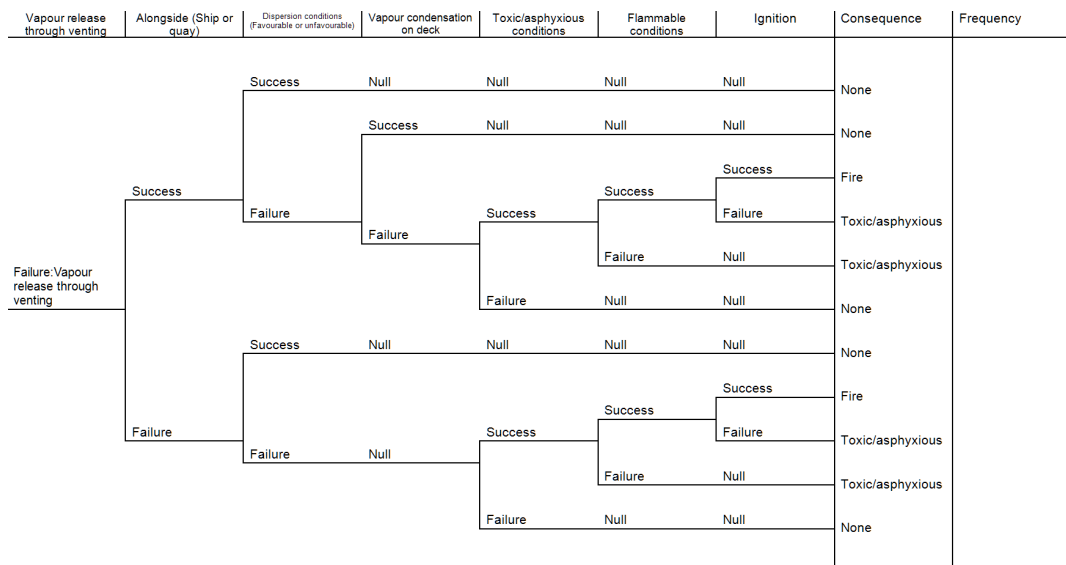


Figure 4.12: Event tree following a vapour release of methanol through venting

Finally, as a future step, in order to quantify the overall risk of venting methanol over the side of the ship, the fault and event tree need to be completed after which failure statistics, simulations and/or measurements should be used to quantify the probability of occurrence of the individual events.

## 4.6 Discussion and conclusion on the fault tree and event tree analyses

As illustrated by the examples, a bow-tie analysis by means of fault and event trees can be a useful method to identify basic events and the scenarios that could lead to an undesired event. Failure statistics, simulations and measurements should then be used to quantify the yearly or lifetime probability of occurrence of individual basic events, after which their relation in the fault tree can be used to calculate the probability of occurrence of the top-level undesired event. When the probability of occurrence of the top-level undesired event has been determined, an event tree can be used to identify and quantify the probability of occurrence of potential consequences, including the effect of any risk reducing measures.

When organising sessions on setting up and discussing fault trees and event trees for a specific system and specific scenarios, three roles are important:

- Process control.
- FT/ ET drafting.
- Content moderation.

For a successful session, it is recommended to appoint three different persons to play these roles during sessions. Furthermore, in order to guard the content of the session, preparation of the sessions and involvement of the correct experts is another important aspect. Drawings and diagrams describing the system under consideration should be available before the meeting in order to allow participants to prepare.

As pointed out in section 2.2, the process of a hazard identification (HAZID), in conjunction with determining hazard occurrence probabilities and consequences, is crucial for a proper risk assessment and identification of scenarios and hence an effective risk control. However, depending on the size of the system and the number of scenarios, the process of setting up fault trees and event trees for every scenario can be very time consuming and, hence, should only be performed for the most critical scenarios where further detailing and properly quantifying risk is crucial.

In order to speed up this process, a solution would be to develop generic HAZID lists for subsystems and components that are relatively stable and similar across ships as well as generic fault/event trees for functions that are similar across ships, such as tank venting or bunkering. These could then be used as templates to facilitate more effective risk workshops.

# 5 Knowledge and know-how gaps

## 5.1 Gaps identified

There are two reasons why an hazardous event with methanol may be worth further investigation:

1. The hazardous event has the potential of being unacceptable from a risk point of view but knowledge, know-how and tools currently available are insufficient to enable a proper analysis of this event. As a consequence the probability of occurrence of the event and/or the consequences following the event cannot be determined with sufficient confidence.
2. Prescriptive regulations, intended to cover an event or set of events, are too restrictive from a design point of view, while it is believed that alternative safety measures may be less restrictive while still providing sufficient safety, equivalent to the safety attained by complying with the prescriptive regulation.

Regarding insufficient knowledge and know-how, evaporation of methanol needs to be mentioned. Ongoing research on how methanol can be used in combustion engines shows that one of the issues is the low evaporation rate. This property is in fact an advantage when liquid is spilled in a technical room, because a toxic vapour cloud will not develop quickly. Hence it may prove easy to avoid toxic concentration through ventilation.

Regarding prescriptive regulations, two have been identified that are considered too restrictive from a design freedom point of view. The first one is about the location of venting exits, the second one is about the requirement to apply cofferdams. They are discussed in section 5.2 and 5.3 respectively.

## 5.2 Methanol vapour venting

The ‘interim guideline on application of methanol as fuel on board’ stipulates that fuel tank vent outlets should be situated normally not less than 3 m above the deck or gangway, if located within 4 m from such gangways (regulation 6.4.7 in MSC.1-Circ. 1621 [2]). In the vicinity of such openings a safety zone of 6 m radius must be observed where people are not allowed and no work can be done. In section 3.3 it is shown that this requirement is quite reasonable given the predicted extent of hazardous zones when methanol-nitrogen vapours are released from a venting stack. Unfortunately this prescriptive requirement restricts the ship designs to such an extent that ship designs become unpractical. As an alternative venting below the waterline (WL) has been proposed as a safe venting location (Figure 5.1).

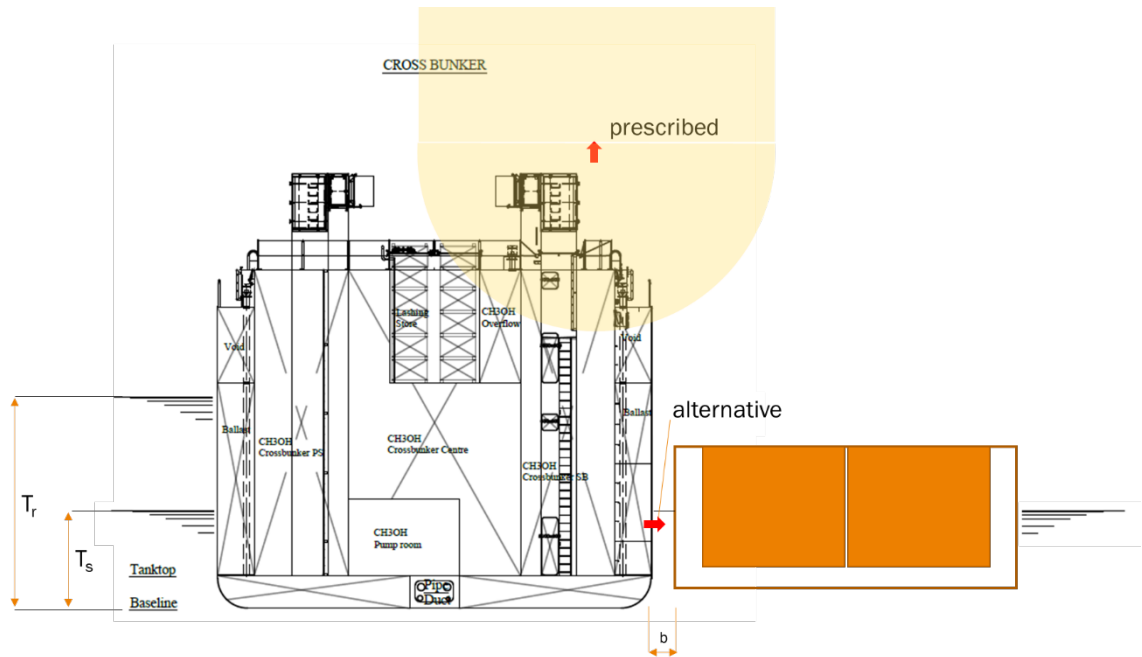


Figure 5.1: Vapour release of methanol through venting, deck (prescribed), below waterline (alternative)

The question is whether vapours breaking through the water surface can potentially reach the deck of say a bunker boat which happens to be alongside. If this is possible then again there are the hazards of fire and intoxication of people on board.

As described in section 3.4 no satisfactory calculation models are available to predict the behaviour of the methanol-nitrogen vapour cloud when it is released below the water line. Therefore under water venting tests are proposed. In order to avoid any scaling issues these test will be large scale, i.e. with a tank volume of about 200 m<sup>3</sup>.

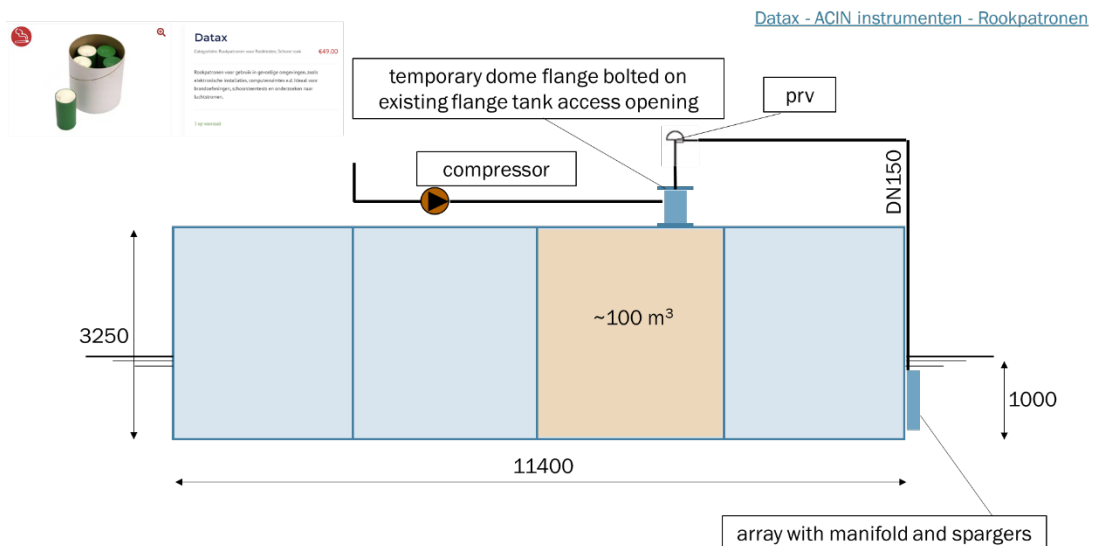


Figure 5.2: Test set up vapour release of methanol through venting below the WL

For this purpose a pontoon will be chartered. One of its ballast tanks will be used as a vapour tank. A cross section of the test lay out is shown in Figure 5.2. Realistic venting events will be emulated through pressurising the vapour tank and monitoring the development of vapour escape through the manifold with spargers, shown in the figure.

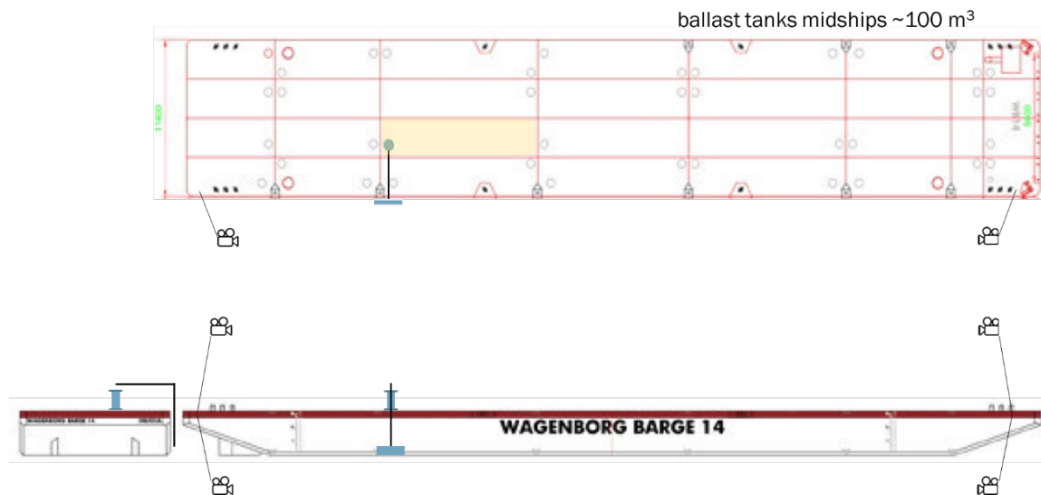


Figure 5.3: Test set up vapour release of methanol through venting below the WL, side view and top view.

There will be monitoring cameras below and above the waterline as indicated in Figure 5.3. Initial tests will be carried out with smoke in the vapour tank for visualisation purposes. At a later stage actual methanol-nitrogen vapours will be introduced in the vapour tank and consecutively vented. During these test vapour concentration sensors will be placed on deck and near the waterline. Test locations may be at Groningen Seaports, Delfzijl, Rotterdam harbour or Antwerp harbour. Further details are currently under investigation.

## 5.3 Cofferdams surrounding fuel tanks

The interim guideline on application of methanol as fuel on board stipulates that integral fuel tanks should be surrounded by protective cofferdams, except on those surfaces bound by shell plating below the lowest possible waterline, other fuel tanks containing methyl/ethyl alcohol, or fuel preparation space (regulation 5.3.2 in MSC.1-Circ. 1621 [2]). For the case of fuel above the WL this means that the space indicated in Figure 5.4 with blue cannot be used for fuel storage. The volumetric energy density of methanol is half the density of marine diesel oil so a designer needs more space for fuel tanks. In view of this the cofferdam requirement severely restricts the freedom of the ship designer to locate fuel tanks. Therefore it is worth investigating if other arrangements are possible which don't require cofferdams or cofferdams with reduced width, without compromising safety.



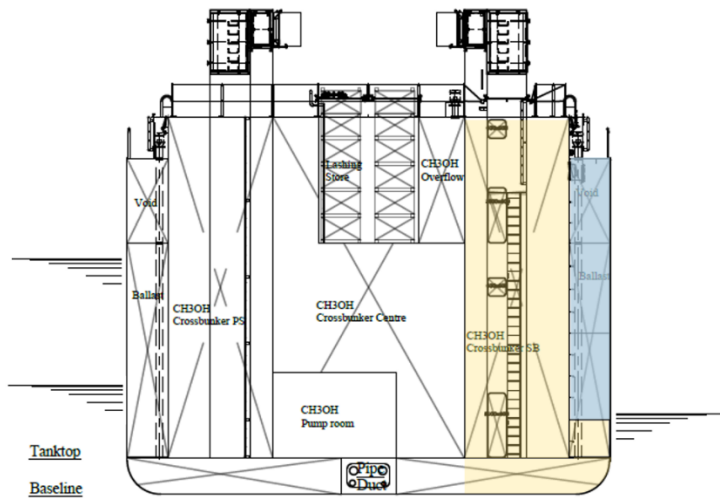


Figure 5.4: Fuel space, allowed (yellow) and prohibited (blue)

The reasoning behind the cofferdam requirement is that when a ship collision occurs in way of a fuel tank no fuel will be spilled above the WL. A fuel spill is considered dangerous for two reasons:

1. The fuel will not dissolve directly into the water and hence develop into a pool on the water surface which may catch fire and then become a threat to human life because of heat radiation.
2. The fuel will not dissolve directly into the water and hence develop into a pool on the water surface which will evaporate causing a toxic cloud above the waterline and then become a threat to human life because of intoxication.

There are two lines of defence against these scenarios:

- a) Protect the fuel tank from rupture following a collision by providing crashworthiness.
- b) Explicitly determine the consequences of heat radiation overexposure and intoxication and judge their severity.

How these can be investigated requires further detailing. Regarding crashworthiness it is noted that inland waterway shipping already uses this concept in case of tankers carrying dangerous good. The relevant regulation can be found in section 9.3.4 of the ADN [55].

Typical research questions are:

- What is the likelihood of a (double) breach?
- What is the environmental effect of a methanol spill?
- Is a cofferdam surrounding the fuel tank necessary? If yes, what are the minimum physical layout requirements of the cofferdam and steel plating?
- How to contain the risk of an explosive and flammable atmosphere at the location of the tank rupture?
- When spilling the methanol into the surrounding water, is there a methanol and air mixture at the surface of the water which is flammable, considering the leaking rate and pressure drop?
- How quickly does the methanol dissolve in the water?
- How quickly does the vapour dilute and spread?

## 5.4 Other issues

Apart from the issues mentioned in the previous sections, throughout the cause of the green maritime methanol project various other issues were tabled which are considered worthy of investigation.

They are listed here:

- a) Corrosion in fuel system due to methanol.
- b) Pressure increase in fuel system.
- c) Leaking methanol at flange couplings.
- d) Leaking methanol at the bunker hose.
- e) Engine room fire damaging the safety control system.
- f) Emptying the fuel tank with secondary pumps.

ad a)

Questions to be dealt with are:

- Which coatings are suitable in view of protection?
- How to apply coatings in confined spaces?
- Is coating required?

ad b)

Questions to answer are:

- What scenarios exist for this event to happen, are they fire load in adjacent compartment, blocking of vapour return during bunkering, ship collision?
- What are the probabilities of such events occurring, are there statistics available to extract probabilities (for collision there may be)?
- How to avoid these events (pressure relief valves, insulation of tank bulkheads)?

ad c) and ad d)

Questions to answer are:

- What are the probabilities (use statistics from UK HSE [8])?
- How large will effect distances become (use IEC code [9])?

ad e)

This scenario has not been identified before. Some argue that existing fire protection requirements for engine rooms already cover this scenario. Questions to answer are:

- What is the likelihood?
- How effective are fire prevention and extinguishing measures?

ad f)

This item is dealt with in general terms in the IGF code. However details are not given.

Questions to answer are:

- What if the regular pump does not work, can one apply a portable pump?
- Are there any additional hazards associated with this?

# 6 Conclusion and recommendations

## 6.1 Methanol safety characteristics spill behaviour

In Chapter 3 multiple models are created to study the methanol spill behaviour in different scenarios. It is concluded that there are, with the exception of the case of a methanol spill on water, tools available to calculate the development of toxic or flammable clouds following a methanol leak or loss of containment. Through making reasonable assumptions regarding the number of persons in the vicinity of the methanol fuel system in conjunction with the physical extent of toxic zones and zones of heat radiation exposure, it is possible to calculate how many person will be affected. Thus the consequences of hazardous events can be quantified.

For a gaseous methanol release on deck it is concluded that significant safety distances are required for both the flammability and toxicity hazard. In the most severe case the safety distances go up to 4.8 m for flammability and 16.1 for toxicity. In most ship designs these large safety zones cannot be accommodated. To arrive at a feasible solution, further research is required. It is suggested to include the time component in the hazardous zone classification, which would mean that the hazardous zone classification is only present for a limited amount of time. For the option of releasing the methanol vapour below the waterline it is identified that a severe knowledge gap exists. There are uncertainties to both the feasibility, nature and efficiency of the release below the waterline. Tests are proposed in Chapter 5 to deal with this knowledge gap.

The hazards related to methanol vapour in an enclosed space are significant and should be considered as such, both for larger and smaller spaces. It should be noted that the model described in this report only considers global concentrations. The local concentrations are expected to be higher and thereby more critical. This analysis is subject to extreme assumptions that could pose overly conservative results. It is recommended to critically revisit these assumptions.

Next to that, it is concluded that it is not likely that a methanol spill on a quay will lead to toxic or flammable concentrations in the vicinity of the pool. The difference with the conclusions concerning a release in a confined space is the higher level of ventilation on the quay. On a quay even at low wind speeds sufficient mixing is present to lower the concentration.

For a methanol spill on water, it is concluded that there is no simplified model that answers to the required complexity of the spilling scenario. Many uncertain assumptions should be combined. It is recommended to perform case-specific CFD calculations and/or experiments to study the behaviour and resulting maximum concentration over time.

## 6.2 Equivalent safety

The concept of a risk matrix to determine whether a system for unconventional fuels attains a safety level equivalent to that of conventional fuels is suitable. A shortcoming however is that no results are published or indeed available on the locus of conventional fossil fuels in the risk matrix. It is therefore recommended to do a risk analysis for conventional fuels as soon as possible.

It is noted that considering safety through first principles analysis, based on the concept of equivalent safety, will prove to be beneficial for the attained safety level and increased design freedom.

## 6.3 Fault trees and event trees

As illustrated by the fault tree and even tree examples, a bow-tie analysis by means of fault and event trees can be a useful method to identify basic events and the scenarios that could lead to an undesired event. Failure statistics, simulations and measurements can be used to quantify the yearly or lifetime probability of occurrence of individual basic events, after which their relation in the fault tree can be used to calculate the probability of occurrence of the top-level undesired event. When the probability of occurrence of the top-level undesired event has been determined, an event tree can be used to identify and quantify the probability of occurrence of potential consequences, including the effect of any risk reducing measures.

As pointed out in section 2.2, the process of a hazard identification (HAZID), in conjunction with determining hazard occurrence probabilities and consequences, is crucial for a proper risk assessment and identification of scenarios and hence an effective risk control. However, depending on the size of the system and the number of scenarios, the process of setting up fault trees and event trees for every scenario can be very time consuming and, hence, should only be performed for the most critical scenarios where further detailing and properly quantifying risk is crucial.

In order to speed up this process, a solution would be to develop generic HAZID lists for subsystems and components that are relatively stable and similar across ships as well as generic fault/event trees for functions that are similar across ships, such as tank venting or bunkering. These could then be used as templates to facilitate more effective risk workshops.

## 6.4 Knowledge and know-how gaps

Regarding knowledge gaps the following recommendations are made:

1. Acquire statistics on bulkhead fire exposure in terms of probability of occurrence and thermal load.
2. 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 vapour pressure build up.
3. Develop a research project aiming at exploring the concept of ship structural crashworthiness with regard to protecting fuel tanks against collision and grounding.

4. Investigate the severity of loss of containment of methanol following a ship collision, with special attention for LOC above the WL of liquid and vapour simultaneously.
5. Develop a validated calculation model for methanol vapour venting below the waterline, predicting methanol vapour concentrations on deck, to be compared with allowable toxicity levels.
6. Conduct an extensive quantitative risk analysis on a conventional fossil fuel system in order to determine the locus of such a system in the risk matrix, to be used as a reference for equivalent safety as stipulated by IMO.

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## 8 Signature

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## Appendix A Fraction of diffusive and jet-type outflow safety distances

The fraction the safety distance of a diffusive and a jet-type outflow for the 12 scenario's from the parameter study (section 3.3.5) is presented in Table A.1.

Table A.1: Fraction (diffusive/jet) of the safety distance of a diffusive and a jet-type outflow.

Parameter study results	Explosive atmosphere (IEC)	Toxicity
Zone type	Zone 1 or 2 <sup>10</sup>	IDLH
-15 degC, 5 kPa, 50 mm	2.14	2.04
35 degC, 5 kPa, 50 mm	2.03	1.94
-15 degC, 20 kPa, 50 mm	2.14	2.04
35 degC, 20 kPa, 50 mm	2.03	1.94
-15 degC, 5 kPa, 100 mm	2.08	1.99
35 degC, 5 kPa, 100 mm	1.98	1.89
-15 degC, 20 kPa, 100 mm	2.08	1.99
35 degC, 20 kPa, 100 mm	1.98	1.89
-15 degC, 5 kPa, 150 mm	2.05	1.96
35 degC, 5 kPa, 150 mm	1.95	1.86
-15 degC, 20 kPa, 150 mm	2.05	1.96
35 degC, 20 kPa, 150 mm	1.95	1.86
<i>Average</i>	<i>2.03</i>	<i>1.95</i>

<sup>10</sup> If a vapor return is present during bunkering, the classification is zone 2. Otherwise, the classification is zone 1.

## Appendix B Validity range IEC: Methanol vapour release on deck

In the IEC standard the characteristic outflow is given by:

$$Q_c = \frac{q_c}{\rho_{m,g} \cdot LFL}$$

in which  $Q_c$  is the characteristic outflow in m<sup>3</sup>/s,  $q_c$  is the mass release in kg/s and  $\rho_{m,g}$  is the density of methanol vapor in kg/m<sup>3</sup>. The mass release is expressed by:

$$q_c = C_d \cdot S \cdot p \cdot \sqrt{\frac{M}{Z \cdot R \cdot T} \cdot \frac{2 \cdot \gamma}{\gamma - 1} \cdot \left(1 - \left(\frac{p_a}{p}\right)^{\frac{\gamma-1}{\gamma}}\right) \cdot \left(\frac{p_a}{p}\right)^{\frac{1}{\gamma}}}$$

in which  $C_d$  is the discharge coefficient,  $S$  is the orifice area in m<sup>2</sup>,  $p$  is the tank pressure in Pa,  $M$  is the molar mass in kg/mol,  $Z$  is the compression factor (which is a function of the temperature and pressure in the tank, although within the considered ranges the variation is minimal),  $R$  is the gas constant in J/molK,  $T$  is the temperature in the tank in K,  $\gamma$  is the polytropic index for adiabatic expansion (assuming an ideal gas) and  $p_a$  is the atmospheric pressure in Pa.

The equation below highlights in blue all parameters that are fixed in the analysis. The temperature is highlighted in green, considering that this can differ per scenario. To conclude, the orifice area (a function of the valve diameter) is the most relevant parameter to consider in relation to the validity domain of the characteristic outflow.

$$q_c = C_d \cdot S \cdot p \cdot \sqrt{\frac{M}{Z \cdot R \cdot T} \cdot \frac{2 \cdot \gamma}{\gamma - 1} \cdot \left(1 - \left(\frac{p_a}{p}\right)^{\frac{\gamma-1}{\gamma}}\right) \cdot \left(\frac{p_a}{p}\right)^{\frac{1}{\gamma}}}$$

To fall within the validity bounds of 0.06 and 30 m<sup>3</sup>/s of the IEC curves, the following minimum and maximum valve diameters are in place:

At -15 (minus) degrees Celsius

PRV set pressure [kPa]	Minimum diameter [m]	Maximum diameter [m]
5	0.127	2.85
20	0.123	2.75

At 17 degrees Celsius (10vol% methanol in the vapour)

PRV set pressure [kPa]	Minimum diameter [m]	Maximum diameter [m]
5	0.055	1.21
20	0.053	1.17

At 35 degrees Celsius

PRV set pressure [kPa]	Minimum diameter [m]	Maximum diameter [m]
5	0.033	0.75
20	0.033	0.72

## Appendix C Example calculation: Methanol vapour release on deck

This example illustrates the considerations in the application of the IEC standard [9] to determine safety distances for a methanol vapour release (due to venting) on deck.

### 1. Identify sources of release

That is: the opening of the pressure relief valve at the occurrence of overpressure in the fuel tank.

### 2. Determine the release rate (Annex B) and grade of release (continuous/primary/secondary) for each source based on likely frequency and duration of release

For venting during bunkering this implies a **primary** grade: “Relief valves, vents and other openings which are expected to release flammable substance into the atmosphere during normal operation – is a primary grade of release.” (B.2.3)

However, if a vapour return is used during bunkering, the grade of release can be considered as **secondary** grade: “Relief valves, vents and other openings which are not expected to release flammable substance into the atmosphere during normal operation”. (B.2.4)

The release rate is calculated for a non-choked gas (subsonic release) as the pressure inside the fuel tank is not high enough to result in a choked flow. Parameters are:

- Pressure: 106325 Pa = atmospheric + 5 kPa<sup>11</sup> as valve threshold
- Discharge coefficient: 0.95 (typical for rounded orifices)
- Valve area: 0.008 m<sup>2</sup> (based on an assumed valve diameter of 100 mm) of which 10% is open during the venting event (table B.1 in the IEC).

The IEC standard states that for mixtures only the total mass of the flammable substance should be considered. In this case that is 10% (mass percentage when operating at 17 degrees Celsius) of 0.19 kg/s. For the above listed parameters the release rate is estimated at **0.019 kg/s**.

### 3. Assess ventilation or dilution conditions and effectiveness (Annex C)

“In open air situations the degree of dilution is generally considered as **medium** while the availability of ventilation in terms of wind presence may be considered as **good** unless there is restricted ventilation such as within pits, dykes or areas surrounded by high structures. “ (C.3.7.2)

The ventilation velocity is set to 0.15 m/s, which is what the IEC (see table C.1 in [9]) indicates for obstructed areas, up to 2 m above the ground for a gas or vapour that is heavier than air. Higher from the ground the ventilation velocity is assumed higher. The

<sup>11</sup> Initially a PRV setting of 5 kPa was suggested for MV Hunteborg. We now realise this value is far too low, 50 kPa would probably be a better choice. This issue will be re-addressed in GMM III.

selection of 0.15 m/s is therefore deemed conservative. The mixture of methanol vapour and air is explosive and somewhat heavier (relative density of 1.11) than air.

**4. Determine zone type based on grade of release and ventilation or dilution effectiveness**

Figure C.8.1 indicates the zone type classification based on a Primary grade of release, Medium dilution and Good ventilation. This combination results in a classification of the affected zone as **Zone 1**, which is an “area in which an explosive gas atmosphere is likely to occur occasionally in normal operation” (3.3.5).

A zone 1 classification is estimated to have an explosive atmosphere for more than 10 but less than 1000 hours per year [56].

However, if a vapour return is used during bunkering, the affected zone has a classification of **Zone 2**, which is an “area in which an explosive gas atmosphere is not likely to occur in normal operation, but, if it does occur, will exist for a short period only”.

A zone 2 classification is estimated to have an explosive atmosphere for less than 10 hours per year, but still sufficiently likely as to require controls over ignition sources [56].

**Table D.1 – Zones for grade of release and effectiveness of ventilation**

Grade of release	Effectiveness of Ventilation						
	High Dilution			Medium Dilution			Low Dilution
	Availability of ventilation						
	Good	Fair	Poor	Good	Fair	Poor	Good, fair or poor
<b>Continuous</b>	Non-hazardous (Zone 0 NE) <sup>a</sup>	Zone 2 (Zone 0 NE) <sup>a</sup>	Zone 1 (Zone 0 NE) <sup>a</sup>	Zone 0	Zone 0 + Zone 2 <sup>c</sup>	Zone 0 + Zone 1	Zone 0
<b>Primary</b>	Non-hazardous (Zone 1 NE) <sup>a</sup>	Zone 2 (Zone 1 NE) <sup>a</sup>	Zone 2 (Zone 1 NE) <sup>a</sup>	<b>Zone 1</b>	Zone 1 + Zone 2	Zone 1 + Zone 2	Zone 1 or zone 0 <sup>c</sup>
<b>Secondary<sup>b</sup></b>	Non-hazardous (Zone 2 NE) <sup>a</sup>	Non-hazardous (Zone 2 NE) <sup>a</sup>	Zone 2	<b>Zone 2</b>	Zone 2	Zone 2	Zone 1 and even Zone 0 <sup>d</sup>

<sup>a</sup> Zone 0 NE, 1 NE or 2 NE indicates a theoretical zone which would be of negligible extent under normal conditions.  
<sup>b</sup> The Zone 2 area created by a secondary grade of release may exceed that attributable to a primary or continuous grade of release; in this case, the greater distance should be taken.  
<sup>c</sup> Zone 1 is not needed here. I.e. small Zone 0 is in the area where the release is not controlled by the ventilation and larger Zone2 for when ventilation fails.  
<sup>d</sup> Will be Zone 0 if the ventilation is so weak and the release is such that in practice an explosive gas atmosphere exists virtually continuously (i.e. approaching a 'no ventilation' condition).  
 '+' signifies 'surrounded by'.  
 Availability of ventilation in naturally ventilated enclosed spaces is commonly not considered as good.

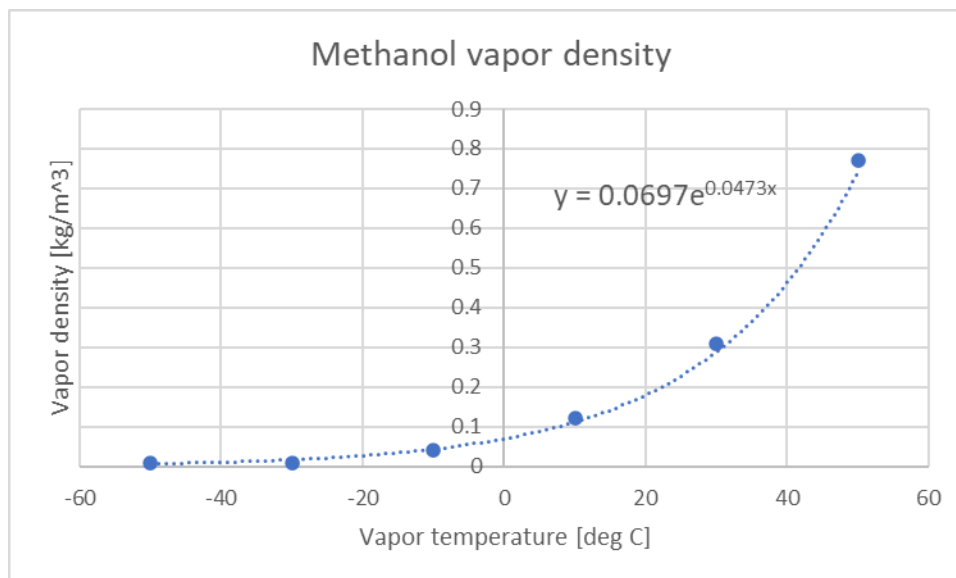
Figure C.1: Table D.1 from the IEC [9], indicating the zone 1 classification for a primary release and a zone 2 classification for a secondary release

**5. Determine extent of zone**

All above listed considerations yields a hazardous area with a radius of **1.9 m** for the considered example.

## Appendix D Methanol: vapour density as a function of temperature

As a function of temperature, data from engineeringtoolbox.com [57].





## Appendix E Methanol liquid spill in a confined space: results of the global concentration development over time

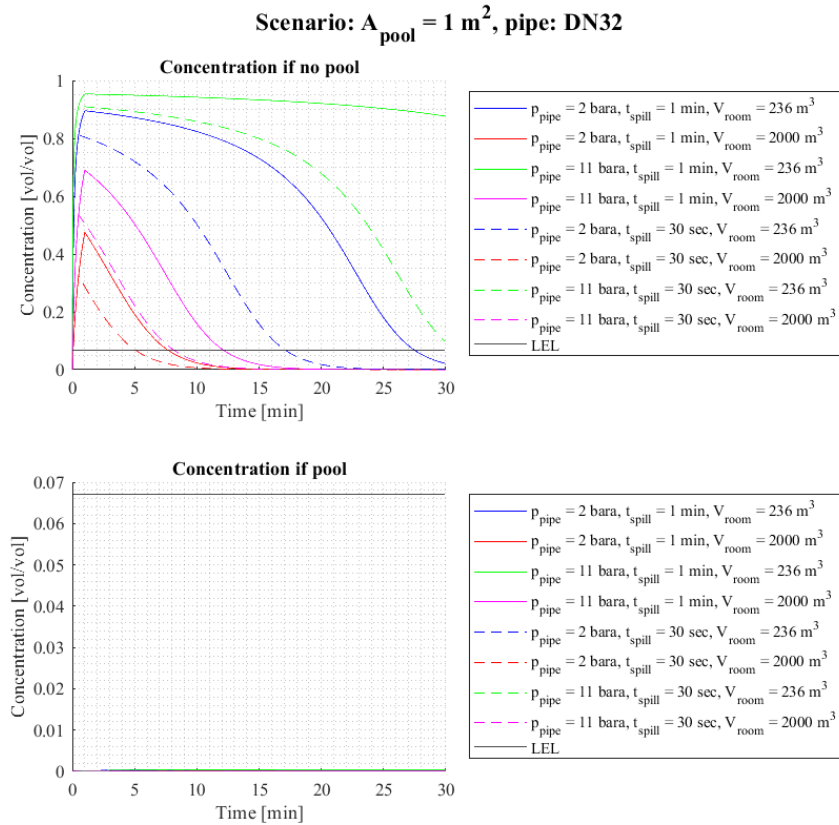


Figure E.1: Global (uniformly distributed) concentration in the air in [vol/vol] for both model assumptions for a pool of  $1 \text{ m}^2$  and a hole size conform 100% of the area of a DN32 pipe

**Scenario:  $A_{pool} = 5 \text{ m}^2$ , pipe: DN32**

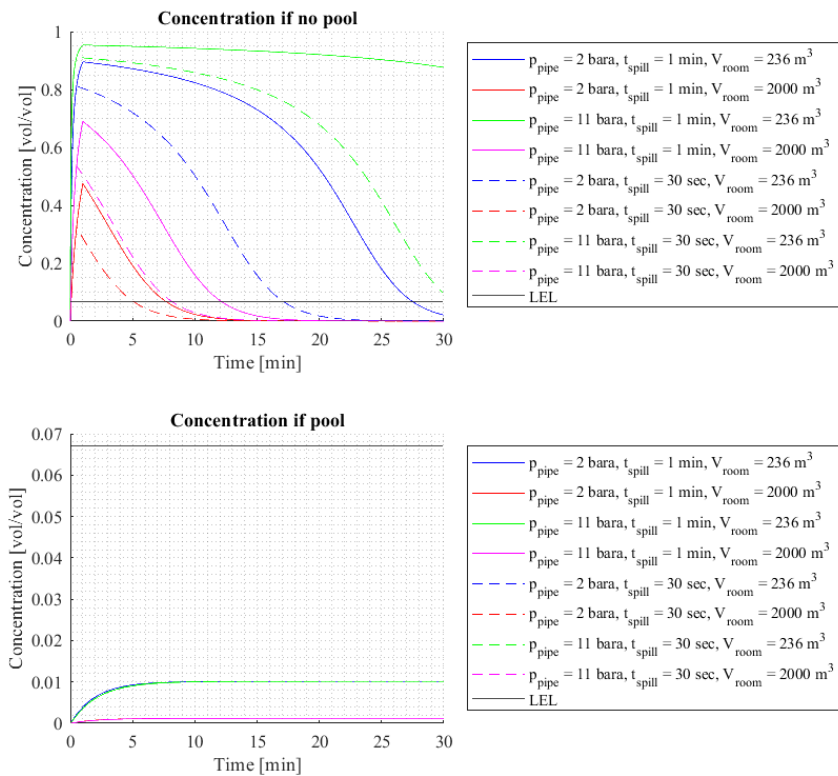


Figure E.2: Global (uniformly distributed) concentration in the air in [vol/vol] for both model assumptions for a pool of  $5 \text{ m}^2$  and a hole size conform 100% of the area of a DN32 pipe

Scenario:  $A_{pool} = 1 \text{ m}^2$ , pipe: DN32

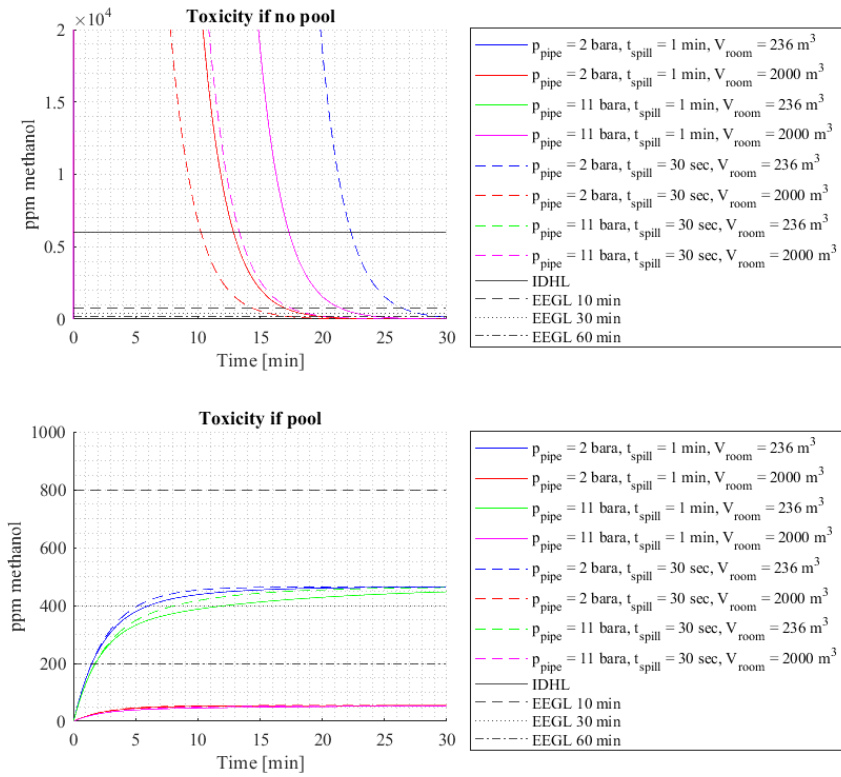


Figure E.3: Global (uniformly distributed) concentration in the air in [ppm] for both model assumptions for a pool of  $1 \text{ m}^2$  and a hole size conform 100% of the area of a DN32 pipe

Scenario:  $A_{pool} = 5 \text{ m}^2$ , pipe: DN32

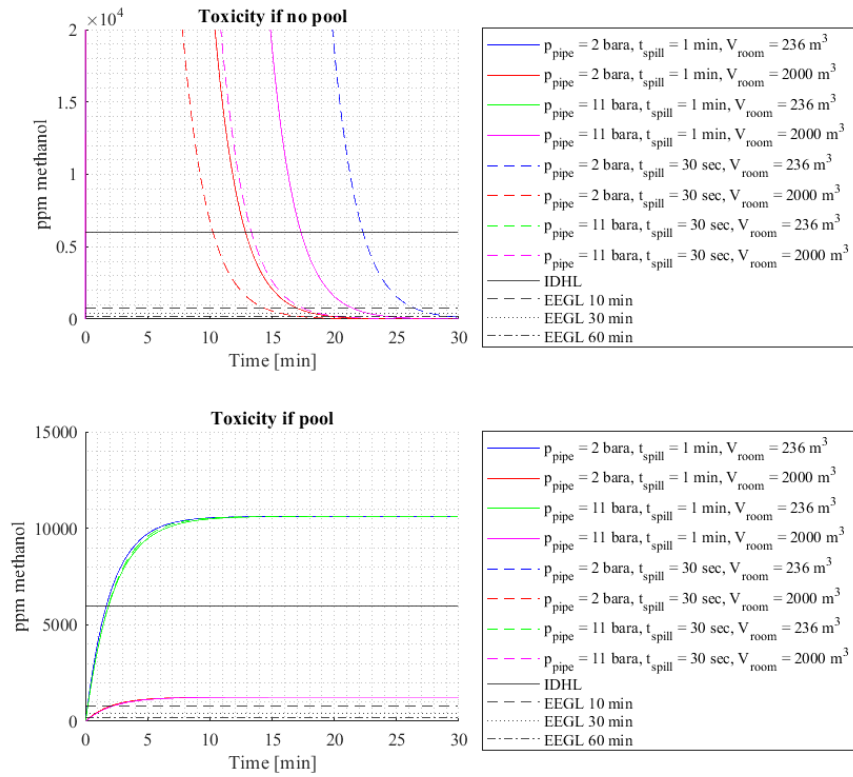


Figure E.4: Global (uniformly distributed) concentration in the air in [ppm] for both model assumptions for a pool of  $5 \text{ m}^2$  and a hole size conform 100% of the area of a DN32 pipe