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Toxicity aspects of dimethylether in comparison with automotive fuels currently in use

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1. Introduction

DME is a possible alternative fuel for diesel engines. In its characteristics DME is much alike LPG, although there are differences. In this document the toxicity aspects of dimethyl ether in comparison to other automotive fuels are presented. The main point of attention is the presence of a certain amount of methanol in DME, which may be in industrial grades range from 100 ppm up to 2%. In order to make clear the toxicity aspects of methanol in DME two concentrations are considered namely 10% and 20% as a conservative approach.
The automotive fuels that are compared with DME are: gasoline (the most relevant component is here benzene), LPG and CNG (Compressed Natural Gas).

The comparison has been done mainly on basis of the acute toxicity. The aspects of chronic exposure are described qualitatively. Acute toxicity plays a role only in case of accidental releases of material. The impact of accidental releases have been calculated for the transhipment from a tank truck to a storage tank at a filling station.

Besides the toxicity data also relevant physical properties like boiling point, vapour pressure explosion limits etc. are listed. These properties play a role in the effects upon a release and the possibility of exposure to people.

The paragraphs given below contain:
1. A qualitative description of the toxicology of the considered automotive fuels;
2. An overview of the toxicology of the automotive fuels;
3. A comparison of the toxicology of all fuels;
4. An overview of calculation results into the possible affected area upon an accidental release;
5. The conclusion of the comparison.

2. Toxicity aspects

2.1 Qualitative description of the toxicology aspects of the fuels

Below a comprehensive overview is given of the qualitative toxicity aspects of the fuels considered.

DME
DME is an irritating substance for the eyes and respiratory organs. Due to the quick evaporation of the material, freezing phenomena can occur upon a release [4].
DME is not acute toxic.

In [9] mentioning is made of concentrations of 80,000 to 120,000 ppm as the lowest at which a narcotic effect is caused by DME. This value is slightly better than those that apply to propane and butane (50,000 to 100,000 ppm).

Methanol
According to the MSDS (Material Safety Data Sheet), methanol is "mutagen" and is a "reproductive effector" [8], the material is irritating for the eyes and respiratory organs and scours the skin [4]. Methanol is not acute toxic.

Benzene
According to the MSDS is benzene: tumorigen, mutagen and a reproductive effector. Benzene is irritating for the eyes and breathing organs [4]. The liquid scours the skin and has an influence on the blood producing organs.
If a person becomes sensible for benzene due to (over)exposure any further exposure should be avoided. The use of alcoholics amplifies the toxic activity of the material. The toxicity of benzene is related to chronic exposure.

Gasoline
According to the MSDS gasoline is a tumorigen material. The liquid scours the skin. Gasoline has an effect on the nerve system. In case of aspiration pneumonia can be caused. Gasoline is not acute toxic.

Natural gas
Natural gas (mainly methane) is an asphyxiant and is not considered as a toxic material.

2.2 Toxic and physical properties of DME

In table 2.2 an overview is given of the toxic and physical properties of (pure) DME.

Table 2.2 Overview of toxic and physical properties of DME.

Property		Value	Ref.
Physical properties			
Molecular formula	[-]	CH_3OCH_3	
Molecular weight	[kg/kmol]	46	[4]
Density (20 °C)	[kg/m³]	700	[4]
Vapour pressure (20 °C)	[bar]	5.3	[4]
Boiling point	[K]	248.5	[4]
Explosion limits	[% by vol.]	2.7 - 18.6	[4]
Auto ignition temperature	[K]	508	[4]
Toxic properties (inhalation)			
LC_{50} (mouse)	[mg/m³, 15 minutes]	940,800	[1,3]
LC_{50} (mouse)	[mg/m³, 30 minutes]	729,600	[1,3]
IDLH	[mg/m³]	-	
MAC (8 hours) [1])	[mg/m³]	950	[4]
MAC (15 min)	[mg/m³]	1500	[4]

[1]) Maximum Allowable Concentration, value used in the Netherlands for workers (comparable with the TLV value).

2.3 Toxic and physical properties of methanol

In table 2.3 an overview is given of the toxic and physical properties of methanol.

Table 2.3 Overview of toxic and physical properties of methanol.

Property		Value	Ref.
Physical properties			
Molecular formula	[-]	CH_3OH	[4]
Molecular weight	[kg/kmol]	32	[4]
Density (20 °C)	[kg/m³]	800	[4]
Vapour pressure (20 °C)	[bar]	0.127	[4]
Boiling point	[K]	338	[4]
Explosion limits	[% by vol.]	5.5 - 36.5	[4]
Auto ignition temperature	[K]	728	[4]
Toxic properties (inhalation)			
LC_{50} (rat)	[mg/m³, 4 hours]	85,120	[1]
LC_{lo} (mouse)	[mg/m³, 2 hours]	50,000	[1]
IDLH	[mg/m³]	7980	[2]
MAC (8 hours)	[mg/m³]	260	[4]
STEL (15 min)	[mg/m³]	444	[2]

2.4 Toxic and physical properties of benzene

In table 2.4 an overview is given of the toxic and physical properties of benzene.

Table 2.4 Overview of toxic and physical properties of benzene.

Property		Value	Ref.
Physical properties			
Molecular formula	[-]	C_6H_6	[4]
Molecular weight	[kg/kmol]	78.1	[4]
Density (20 °C)	[kg/m^3]	900	[4]
Vapour pressure (20 °C)	[bar]	0.100	[4]
Boiling point	[K]	353	[4]
Explosion limits	[% by vol.]	1.2 - 8.0	[4]
Auto ignition temperature	[K]	828	[4]
Toxic properties (inhalation)			
LC_{50} (rat)	[mg/m^3, 7 hours]	32,500	[1]
IDLH	[mg/m^3]	1625	[2]
MAC (8 hours)	[mg/m^3]	3.25	[4]
TLV	[mg/m^3]	0.325	[2]
STEL (15 min)	[mg/m^3]	3.25	[2]

2.5 Toxic and physical properties of gasoline

In table 2.5 an overview is given of the toxic and physical properties of gasoline.

Table 2.5 Overview of toxic and physical properties of gasoline.

Property		Value	Ref.
Physical properties			
Molecular formula	[-]	C_4 - C_{12}	[4]
Molecular weight	[kg/kmol]	≅ 115	[4]
Density (20 °C)	[kg/m^3]	700 - 800	[4]
Vapour pressure (20 °C)	[bar]	0.05 - 0.40	[4]
Boiling point	[K]	311 - 478	[4]
Explosion limits	[% by vol.]	0.6 - 8.0	[4]
Auto ignition temperature	[K]	> 493	[4]
Toxic properties (inhalation)			
LC_{50} (mouse)	[mg/m^3, 5 minutes]	300,000	[1]
LC_{50} (rat)	[mg/m^3, 5 minutes]	300,000	[1]
IDLH	[mg/m^3]	-	[1]
MAC (8 hours)	[mg/m^3]	240	[4]
MAC (15 min)	[mg/m^3]	480	[4]
TLV	[mg/m^3]	1440	[1]
STEL (15 min)	[mg/m^3]	2400	[1]

2.6 Toxic and physical properties of natural gas

In table 2.6. an overview is given of the toxic and physical properties of natural gas.

Table 2.6 Overview of toxic and physical properties of natural gas (methane).

Property		Value	Ref.
Physical properties			
Molecular formula	[-]	CH_4	[4]
Molecular weight	[kg/kmol]	16	[4]
Density (20°C)	[kg/m^3]	-	
Vapour pressure (20°C)	[bar]	46.7	[4]
Boiling point	[K]	112	[4]
Explosion limits	[% by vol.]	5 - 15.8	[4]
Auto ignition temperature	[K]	943	[4]
Toxic properties (inhalation)			
LC_{50} (mouse)	[mg/m^3]	-	
LC_{50} (rat)	[mg/m^3]	-	
IDLH	[mg/m^3]	-	
MAC (8 hours)	[mg/m^3]	-	
MAC (15 min)	[mg/m^3]	-	
TLV	[mg/m^3]	-	
STEL (15 min)	[mg/m^3]	-	

2.7 Comparison of the physical and toxic properties of DME, LPG, methanol, benzene, gasoline and natural gas

For the comparison of the toxic properties of the automotive fuels the procedure as described in the Green book [5] has been applied. This implies that threshold values are converted to an exposure time of 30 minutes and toxicity data for animals are converted to humans. This conversion method is an accepted method in The Netherlands, although the method has its uncertainty for which no further quantification can be given.

The toxicity data as converted are based on equivalent exposure duration. Two threshold values are calculated (if possible):
1. the threshold value for 50% lethality (LC_{50}) and
2. the threshold value for 1% lethality (LC_{01}).

Both thresholds are valid for an exposure duration of 30 minutes. The LC_{01} value is commonly used as a threshold value for lethality in quantitative risk analysis.

The toxic dose is expressed as: $C^2 . t$ (C in mg/m^3 and t in minutes)

The results are presented in table 2.7.

Table 2.7 Comparison of the calculated toxic properties of DME, methanol, gasoline, benzene, LPG and natural gas.

Type of fuel	LC_{50} (human) [mg/m^3]	LC_{01} (human) [mg/m^3]
LPG (as propane)	non toxic	non toxic
CNG (natural gas)	non toxic	non toxic
DME	25.8 10^4	8.05 10^4
Methanol	6.0 10^4	1.88 10^4
Gasoline	1.19 10^4	0.38 10^4
Benzene	0.95 10^4	0.31 10^4

The overview shows that the toxicity (based on LC_{01} value) increases in the order: DME, methanol, gasoline and benzene. For LPG and CNG no data were available to calculate a LC_{01} value and are in general considered not to be toxic.

3. Comparison of the effect and consequences of DME in relation to the other automotive fuels

In this chapter the results of the effect calculations are presented. The starting point for the calculations is an accidental release of a fuel during transhipment from a tank truck (contents 40 to 50 m^3) to a storage tank at a filling station for cars as a result of a hose failure (diameter 3”). The release is considered to be continuous.

3.1 Calculation procedure

For the calculation of the effects of a release of the fuels the models as presented in the Yellow Book [6] have been used. The following models and assumptions have been applied.

Outflow model
For the release of DME and LPG the two phase flow release model has been applied. The starting point for the release of gasoline is a liquid pool with a maximum area of 1500 m^2 [7]. A hose failure during the transhipment of natural gas results in a release of a gas only.

Evaporation models
The evaporation rate of gasoline is calculated with the evaporation model for non boiling liquid from a liquid pool. For DME and LPG no specific evaporation model has been used as these substances instantaneous evaporate on release. A remark has to be made with regard to the content of methanol in DME. Upon a release the DME will evaporate rather immediately including a certain fraction of methanol. How large this fraction is not known. It is conceivable that a certain amount will remain in the liquid phase or will be condensed because of the evaporating DME. The liquid form of methanol will enter the soil and could in theory be transported to ground water. Practical tests have to be done to provide more information on this point.

Dispersion models
For the determination of distances and areas where a certain threshold value exist, calculations have been carried out for the dimensions of a:
- flammable cloud
- toxic cloud in which persons may be exposed during a certain period of time.

For the dispersion of DME and LPG use has been made of the dispersion model for gases denser than air. For the dispersion of gasoline, natural gas and benzene the neutral gas dispersion model has been used.
The dispersion is calculated for very stable weather and a wind velocity of 1.5 m/s. This represents a conservative approach and results in the largest effect distance.

Toxicity threshold values
The effect distances for toxicity effects have been calculated for the IDLH value (Immediate Danger for Life and Health) and the LC_{01} concentration. The LC_{01} value (see table 2.7) gives the percentage of people which will be lethally effected in case of exposure during a certain period of time (here 30 minutes is taken as a maximum).
The toxicity criteria for acute toxicity have been used because of the relatively short period of the release and subsequent exposure duration to a evaporated fuel.

Flammability
The flammability effects have been calculated for the occurrence of a flash fire/explosion. The dimensions of the flammable gas cloud, defined by the lower and upper explosion limit, are presented.

3.2 Results

3.2.1 DME

For the calculation of the effects and consequences given a release of DME in general the physical properties of propane is used as normally is done for almost idetical substances. The calculations have been carried out for DME with a content of 10% methanol and DME with 20% methanol.

The calculation has resulted in for
- DME with 10% methanol: $2.5.10^{-3}$ kg/s methanol and 12.8 kg/s DME;
- DME with 20% methanol: $5.7.10^{-3}$ kg/s methanol and 12.8 kg/s DME.

The results of the effect distances for DME pure and with a certain content of methanol are presented in the tables 3.1.1 and 3.1.2

Table 3.1.1 Effect distances for DME pure.

Release rate [kg/s]	Flammable cloud area and maximum threshold distance for toxicity		
	Cloud dimensions [m^2]	IDLH [m]	LC_{01} [m]
12.8	37 x 10	-	19

Table 3.1.2 Effect distances for DME with 10 and 20% methanol respectively. Distances are based on the released amount of methanol.

Release rate [kg/s]	Flammable cloud area and maximum threshold distance for toxicity		
	Cloud dimensions [m²]	IDLH [m]	LC_{01} [m]
2.5 10^{-3} (10% methanol)	<LEL	< threshold	< threshold
5.7 10^{-3} (20% methanol)	1 x 1	< threshold	< threshold

From the tables it can be seen that the contribution of methanol hardly influences the effect distances in comparison to DME pure.

3.2.2 LPG

Table 3.2 Effect distances for LPG.

Release rate [kg/s]	Flammable cloud area and maximum threshold distance for toxicity		
	Cloud dimensions [m²]	IDLH [m]	LC_{01} [m]
12.8	50 x 17	495	-

3.2.3 Gasoline

Gasoline contains about 5% (w/w) benzene. The effect distances are calculated for pure gasoline as well as for benzene evaporated from the gasoline.
A content of 5% benzene results in an evaporation rate of 0.10 kg/s benzene. The average evaporation rate for gasoline is 5.7 kg/s with an assumed pool area of 1500 m^2.

The average release rate has been based on a release between 0 and 100 seconds for the flammable cloud and between 0 and 1,400 seconds for the toxic cloud. The difference is caused by the assumption that a flammable cloud will be ignited rather soon after release (conservative approach).

Table 3.2.1 Effect distances for gasoline pure.

Release rate [kg/s]	Flammable cloud area and maximum threshold distance for toxicity		
	Cloud dimensions [m^2]	**IDLH** [m]	**LC_{01}** [m]
13.9 (flammable) 5.9 (toxic)	60 x 44	-	185

Table 3.2.2 Effect distances for benzene from gasoline.

Release rate [kg/s]	Flammable cloud area and maximum threshold distance for toxicity		
	Cloud dimensions [m^2]	**IDLH** [m]	**LC_{01}** [m]
0.1	0.7 x 43	< threshold	< threshold

From table 3.3.2 it can be seen that the contribution of benzene can be neglected compared with the effects of gasoline pure.

3.2.4 Natural gas

Natural gas is stored in cylinders with a capacity of 0.08 m^3 at a pressure of 200 bar.
The diameter of the loading line is estimated on 7 mm. As a result of the presence of couplings, restrictions etc. the effective release diameter, according to reference [8], is about 4 mm.
A failure of the loading line results in a turbulent free jet of natural gas.

Table 3.3 Effect distances for CNG (natural gas).

Release rate [kg/s]	Flammable cloud area and maximum threshold distance for toxicity		
	Free jet length [m]	**IDLH** [m]	**LC_{01}** [m]
0.43	6	-	-

3.2.5 Summary

Table 3.4 Summary of the effect distances as calculated for all automotive fuels considered.

Scenario	Pool area [m^2]	Evaporation rate or source strength [kg/s]		Flammable gas cloud [m^2]	Maximum distance toxicity threshold [m]	
		Average for toxicity	Average for explosion	(l x w)	IDLH	LC_{01}
DME (pure)		12.8	-	37 x 10	-	19
DME (10% MeOH)	-	12.8	-	37 x 10	-	19
DME (20% MeOH)	-	12.8	-	37 x 10	-	19
LPG	-	12.8	12.8	50 x 17	495	-
Gasoline (pure)	1500	5.9	13.9	60 x 44	-	185
Benzene (from gasoline)	1500	0.1	0.1	0.7 x 43	< threshold	< LC_{01}
CNG natural gas	-	0.43	0.43	6 [m]	-	-

The calculations results show that:

- Up to 20% in methanol in DME does not give an additional effect in the calculated distances for flammability and toxicity.
- The sizes of the flammable cloud increase in the following: CNG, DME, LPG, gasoline.
- The toxicity of the fuels can be ranked in the order: CNG, DME, gasoline and LPG (the last one mainly on basis of the IDLH value).

4. Conclusions

From the results of the effect calculations it is concluded that the use of DME as an alternative automotive fuel does not result in an increase of the risk of a fuel station.
Furthermore it is concluded that the methanol content (up to 20%) of DME has no influence on the effect and consequence distances.

5. Literature

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