A. Methanol is a safe, stable, energy dense, hydrogen rich, liquid transport fuel

Summary

Methanol is a stable, flammable liquid that is hydrogen and energy dense. It has unique physical and chemical properties that make it particularly suitable as an advanced automotive fuel for current modern ICE engines.

When suitably formulated – for example as Zero-m's ZM95[1], it is safe to store, distribute and fuel vehicles without special precautions other than those normally associated with conventional vehicle fuels.

Impact on the environment from accidental release is less than petrol and diesel. In addition, it is without doubt the easiest of the three renewable energy fuels - methanol-electricity-hydrogen - to store and distribute.

Establishing a methanol distribution system to supply the commercial transport sector over the coming years will speed the arrival of the Hydrogen Economy.

A.1. Methanol - a stable, energy dense liquid - safe to store and distribute

Methanol[2] is a stable liquid under ambient conditions and therefore does not require any special containment systems to be stored safely.

Methanol's density (specific gravity) is similar to ethanol and lies between that of petrol and diesel. Its energy density is approximately half that of petrol and diesel and it therefore requires twice the tank size to store an equivalent amount of energy.

Methanol's energy density is twice that of LNG and it is 10 times more energy dense than liquid hydrogen. See Figures A-1, A-2 and A-3 for comparisons of the detailed characteristics of methanol with petrol, diesel, and a range of other alternative fuels.

A.1.1. Methanol - storage and energy density

Methanol, being a simple liquid at normal temperatures and pressures and having similar fluid properties to those of petrol and diesel, can be easily stored in normal tanks with only very minor modifications.

These physical properties mean that, unlike hydrogen or LNG, methanol (and ZM95) do not require any specialised pressurised or cryogenic containment, and no fuel is lost with prolonged storage due to evaporation or degradation. It also means that, unlike liquid hydrogen, LPG, CNG, DME or LNG, conventional petrol and diesel delivery and dispensing equipment may safely be utilised. Currently batteries have a much lower energy density than methanol and considerably greater weight. While battery technology continues to evolve, it seems unlikely that battery energy densities will approach the energy density of methanol in the foreseeable future.

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[1] Zero-m has developed a formulation for methanol fuel both to enhance its performance as a transport fuel and to make it safer to store & handle and to distribute for self-fuelling into vehicles.

[2] Material Safety Data Sheets (MSDS) are available for methanol and have been developed for ZM95 by Zero-m. Information and protocols such as the "Technical Information & Safe Handling Guide for Methanol" are also readily available. The "Technical Information & Safe Handling Guide for Methanol" is published by Methanex as part of their "Responsible Care®" programme and available from their web-site http://www.methanex.com/environment/responsiblecare.html

Properties of transport fuels		Pure Methanol	Zero-m Z95 Fuel	Zero-m EHR (1)	Anhydrous Ethanol	Natural Gas (8)	Hydrogen
Basic Properties							
Density at 15 C	g/l	0.796	0.817	N/A	0.780	0.42(2)	0.07(2)
Boiling Point	C	64.6	66	N/A	77.8	-161	-253
Freezing Point	C	-97.7	< -105	N/A	-114	-182	-259
Flash point	C	11	12	N/A	13	N/A	N/A
Vapour Presure at 20 C	kPa	37	35	N/A	26	N/A	N/A
Heat of vaporisation	mj/kg	1.101	1.172	0.433	0.842	0.51	0.44
Molecular Weight		32.0	31.2	26.4	46.1	17.3	2.0
Carbon Content	%m	37.5%	35.1%	35.1%	52.2%	75.4%	0%
Hydrogen Content	%m	12.6%	12.5%	12.5%	13.1%	24.6%	100%
Oxygen Content	%m	49.9%	52.4%	52.4%	34.7%	0.0%	0%
Hydrogen:Carbon ratio	atomic	4.0	3.8	3.8	3.0	3.9	N/A
Hydrogen content: per litre	g/l	100.3	102.1	N/A	102.2	103.3	71.0

Figure A-1 Properties Transport Fuels: Methanol & other Alternative Fuels

Properties of transport fuels		Pure Methanol	Zero-m Z95 Fuel	Zero-m EHR (1)	Diesel (7)			Gasoline (Petrol) (7)		
					Typical	Lower	Upper	Typical	Lower	Upper
Basic Properties										
Density at 15 C	g/l	0.796	0.817	N/A	0.83	0.80	0.84	0.74	0.70	0.76
Boiling Point	C	64.6	66	N/A	330(3)	200(3)	400(3)	138(3)	30(3)	210(3)
Freezing Point	C	-97.7	< -105	N/A	2	-5	5	-48	-60	-40
Flash point	C	11	12	N/A	> 42			< 0		
Vapour Presure at 20 C	kPa	37	35	N/A	low	low	low	66	45	80
Heat of vaporisation	mj/kg	1.101	1.172	0.433	0.24	0.21	0.25	0.33	0.31	0.35
Molecular Weight		32.0	31.2	26.4	128-320	180 (avge)	220 (avge)	58-170	100 (avge)	105 (avge)
Carbon Content	%m	37.5%	35.1%	35.1%	86%	84%	87%	85%	84%	87%
Hydrogen Content	%m	12.6%	12.5%	12.5%	14%	13%	16%	15%	13%	16%
Oxygen Content	%m	49.9%	52.4%	52.4%	0%	0%	0%	0%	0%	0%
Hydrogen:Carbon ratio	atomic	4.0	3.8	3.8	1.9	2.2	1.7	2.1	2.4	2.0
Hydrogen content: per litre	g/l	100.3	102.1	N/A	116.0	104.0	135.0	110.4	91.0	121.6

Figure A-2 Properties Transport Fuels: Methanol and petrol and Diesel

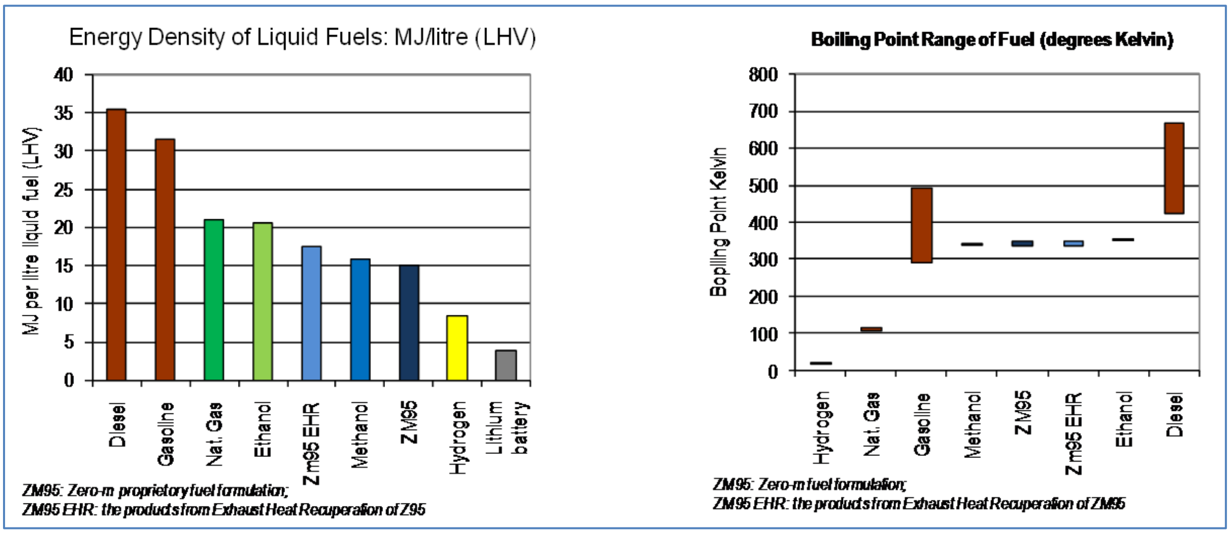

Figure A-3 Energy density - liquid fuels / batteries; fuel boiling point ranges

A.1.2. Methanol – materials compatibility

Plastics

Some plastics are incompatible with methanol, as they are with other alcohols such as anhydrous ethanol and petrol blended with bio-ethanol. This can cause swelling, and, through this, failure of plastic fuel system components. Today it is well known which plastics and components are incompatible with alcohols and as a result the plastics throughout the whole of the petrol distribution system, including fuel delivery into vehicle and vehicle fuel-system components, are now compatible with alcohol fuels.

Corrosion

Pure methanol is a neutral compound and under normal circumstances does not lead to corrosion. However, there are certain metals that, when present in the moving parts of fuel pumps, can be damaged or can give rise to complex reactions, which can cause sludge formation. For storage tanks, pipes and passive components, avoiding certain metallurgy is sufficient to eliminate this effect. For components involved in the movement of the fuel – in particular in submerged on-board fuel pumps – careful selection of fit-for-purpose equipment avoids these problems.

A.1.3. Methanol - fire safety

Methanol's (and ZM95's) physical properties make it an intrinsically safer fuel than petrol and diesel. Several of its properties lie between those of petrol and diesel – including boiling point, flash point and vapour pressure. Methanol's key safety advantages are:

- Methanol vapour is not as easily ignited as petrol vapour and it has narrower explosion limits. The vapour does not pool in ground hollows in the same way that petrol vapour does.
- methanol burns with a much less intense and less radiant flame than petrol or diesel allowing fires to be approached much more closely and for longer by emergency services, ensuring easier rescue and considerably less property damage.
- Methanol fires are easily extinguished using water spray alone - the water immediately mixes with the fuel and quickly dilutes it to the point where it will no longer burn. Water cannot be used on petrol and diesel fires without foaming agents, as using pure water can spread the fire and cause explosions. Petrol and diesel require foam, powder or CO_2 extinguishers all of which also work well for methanol.

Methanol has one potentially hazardous combustion characteristic – when pure it burns with a very light blue flame that can be hard to see in bright daylight. This means that it can be hard to tell exactly where the limits of a fire are. Under the kind of fire circumstances likely when methanol is used as a transport fuel there are always likely to be other materials involved in the fire, such as tyres, paint, fabrics, plastics, oil, grease, any one of which will quickly impart colour and visibility to the flames.

Given the slow nature of a methanol fire and the coolness of the flame, the US authorities have been satisfied that overall there is less danger of injury or death and the likelihood of far less property damage in an automobile fire when methanol is the fuel rather than petrol.

This means that applying the safety precautions normally used for petrol are more than adequate to ensure safety in the use of methanol.

A.2. Methanol – a hydrogen dense liquid with unique properties as an automotive fuel

Methanol has many unique qualities as an automotive fuel as follows:-

- it is a hydrogen dense liquid that can be stored at normal pressures and temperatures

- being a single molecule product, it has constant quality
- it has a high latent heat of vaporisation
- it can be decomposed endothermically[3] to a hydrogen-rich gas by engine exhaust heat.

A.2.1. An excellent hydrogen carrier

Methanol and ZM95 are excellent hydrogen carriers containing more hydrogen, litre for litre, than is found in liquid hydrogen, largely because the density of liquid hydrogen is very low. Hydrogen can be readily generated at low temperatures and pressures from methanol, making it the ideal hydrogen carrier. This will ensure that its introduction as a transport fuel for today's ICE engined vehicles will put in place the foundation stones for the arrival of the hydrogen economy.

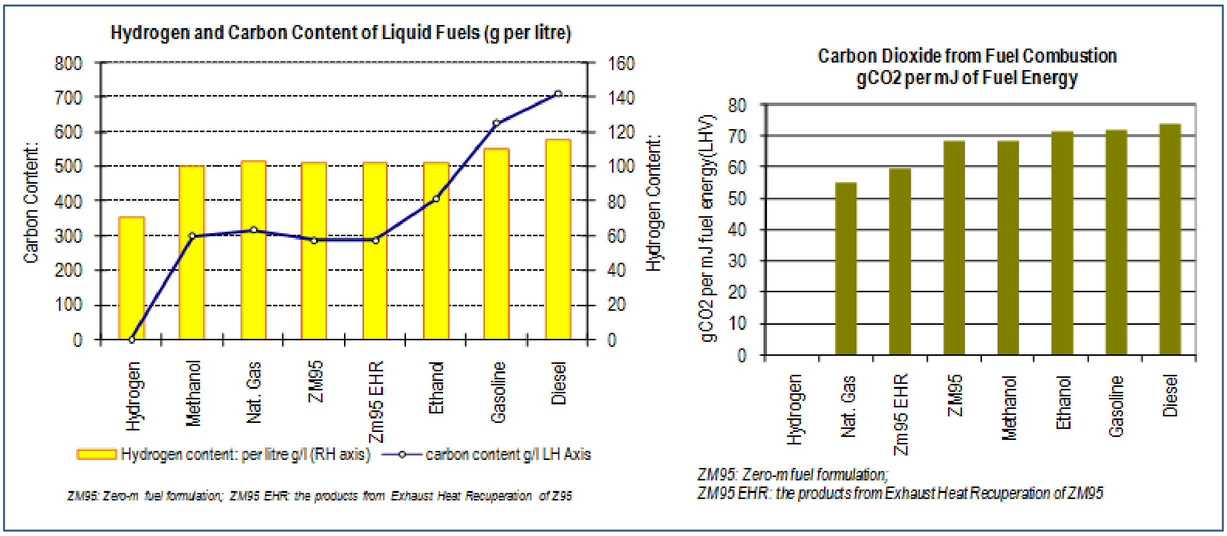

Figure A-4 Hydrogen and carbon content of fuels - gCO2 released per mJ of fuel energy

A.2.2. Consistent Quality

As methanol is a single chemical, the properties of the fuel are always the same. With petrol, diesel and LNG for example, quality can vary to the extent that the engine's electronic management systems must be capable of altering fuel injection and ignition timing to keep the engine running smoothly.

[3] Chemical reactions that are endothermic absorb heat as they proceed. Reforming of alcohols or of hydrocarbons are all endothermic reactions but methanol decomposition / reforming is particularly endothermic in relation to the quantity of heat released on combustion in air.

Properties of transport fuels		Pure Methanol	Zero-m Z95 Fuel	Zero-m EHR (1)	Anhydrous Ethanol	Natural Gas (8)	Hydrogen
Properties relating to Use as Fuel							
Research Octane	RON	105	> 107	105(4)	107	126	>130
Motor Octane Number	MON	92	> 94	92(4)	89	120	>120
Cetane Number		5	< 5	N/A	10	<0	N/A
Autoignition Temperature	C	450	> 450	N/A	441	>400	585
Stoichiometric Air/Fuel Ratio	mass	6.45	6.05	N/A	9.00	16.8	34.4
Air+Fuel (5) per MWh LHV	kg	1,345	1,357	1,173	1,345	1,309	1,034
Vol Air+Fuel (5) / MWh LHV	NM^3	1,031	1,046	1,083	1,031	1,058	1,140
Vol Products (5) / MWh LHV	NM^3	1,094	1,109	958	1,094	1,060	971
Calorific Value							
Gross Cal Value	mj/kg	22.7	21.3	24.2	29.7	55.2	142.0
Net Cal Value	mj/kg	20.0	18.7	21.7	26.7	50.0	120.5
Net Cal Value	mj/l	15.88	15.24	N/A	20.8	21.2	8.6
Net Cal Value	kWh/kg	5.54	5.20	6.0	7.41	13.21	33.47
Net Cal Value	kWh/l	4.41	4.14	N/A	5.78	5.64	2.38
Heat of vaporisation in relation to net calorific value	%	5.5%	6.3%	2.0%	3.2%	1.0%	0.4%
Greenhouse Gas							
CO2 from carbon in fuel	g/mJ	68.84	68.84	59.50	71.74	55.30	0.00

Notes
1 Fuel resulting from waste heat recuperation process using engine exhaust - **E**xhaust **H**eat **R**ecuperated
2 Liquid fuel density at boiling point
3 Diesel and petrol boil over a rage of temperate: Petrol typically 15-210; Diesel typically 150-400 C
4 Estimated
5 Air+fuel, products under stoichiometric conditions
6 Carbon Trust factors (gross only): Diesel: 45.5; Petrol 47.1
7 Values are for 100% hydrocarbons. With alcohol or biodiesel, values will differ
8 Natural Gas composition (typical): 93% Methane, 5% ethane, 2% other(higher H/C, CO2, etc)

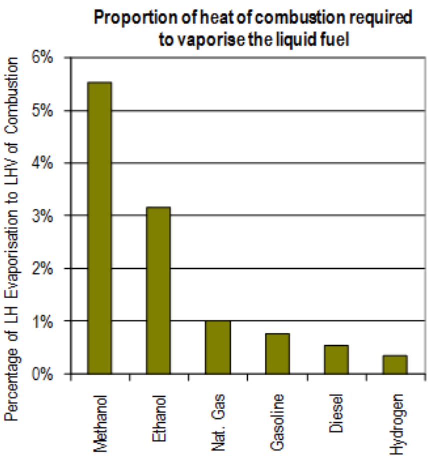

Figure A-5 Properties of fuels - methanol and alternative fuels and the heat required to vapourise them

With both petrol and diesel, while made to a specification with ranges for each property specified, the variation between batches of fuel can be quite significant. For example, properties such as density, boiling range, energy content per litre, and ignition related properties, such as octane and cetane, often vary. Variations also occur because of seasonal specification changes. The chemical make-up of each batch varies and the addition of different oxygenates and blend alternatives, such as biodiesel, from varying sources, adds further to the variation.

Although LNG is predominantly methane it also contains other hydrocarbons such that variations between different batches of LNG can be quite significant. Also the quality can change during storage as the lighter components, particularly methane, evaporate earlier than the heavier components such as ethane, propane or butane. This poses difficulties as systems have to be designed to cater for the worst quality that might result when using LNG after it has been stored for a period.

Methanol, by contrast, is a pure chemical with no quality variation possible between different batches, or between the first and last drop of fuel from the tank. This allows very specific optimisation of automotive engine systems.

Properties of transport fuels		Pure Methanol	Zero-m Z95 Fuel	Zero-m EHR (1)	Diesel (7) Typical	Diesel (7) Lower	Diesel (7) Upper	Gasoline (Petrol) (7) Typical	Gasoline (Petrol) (7) Lower	Gasoline (Petrol) (7) Upper
Properties relating to Use as Fuel										
Research Octane	RON	105	> 107	105(4)	N/A	N/A	N/A	96	92	98
Motor Octane Number	MON	92	> 94	92(4)	N/A	N/A	N/A	86	80	90
Cetane Number		5	< 5	N/A	50	40	55	12	8	14
Autoignition Temperature	C	450	> 450	N/A	250	280	230	392	228	501
Stoichiometric Air/Fuel Ratio	mass	6.45	6.05	N/A	14.7			14.7		
Air+Fuel (5) per MWh LHV	kg	1,345	1,357	1,173	1,319			1,322		
Vol Air+Fuel (5) / MWh LHV	NM^3	1,031	1,046	1,083	967			978		
Vol Products (5) / MWh LHV	NM^3	1,094	1,109	958	1,025			1,028		
Calorific Value										
Gross Cal Value	mj/kg	22.7	21.3	24.2	45.8(3)	44.5	46.5	46.4(3)	45.5	47.0
Net Cal Value	mj/kg	20.0	18.7	21.7	42.9	42.0	43.4	43.0	41.9	43.8
Net Cal Value	mj/l	15.88	15.24	N/A	35.57	33.60	36.63	31.70	29.3	33.3
Net Cal Value	kWh/kg	5.54	5.20	6.0	11.92	11.67	12.06	11.96	11.64	12.17
Net Cal Value	kWh/l	4.41	4.14	N/A	9.88	9.33	10.17	8.81	8.15	9.25
Heat of vaporisation in relation to net calorific value	%	5.5%	6.3%	2.0%	0.5%	0.5%	0.6%	0.8%	0.7%	0.8%
Greenhouse Gas										
CO2 from carbon in fuel	g/mJ	68.84	68.84	59.50	74.14	73.33	73.50	72.19	72.63	71.58

Notes
1 Fuel resulting from waste heat recuperation process using engine exhaust - Exhaust Heat Recuperated
2 Liquid fuel density at boiling point
3 Diesel and petrol boil over a rage of temperate: Petrol typically 15-210; Diesel typically 150-400 C
4 Estimated
5 Air+fuel, products under stoichiometric conditions
6 Carbon Trust factors (gross only): Diesel: 45.5; Petrol 47.1
7 Values are for 100% hydrocarbons. With alcohol or biodiesel, values will differ
8 Natural Gas composition (typical): 93% Methane, 5% ethane, 2% other(higher H/C, CO2, etc)

Figure A-6 Properties of fuels (for use)- methanol and petrol & diesel

A.2.3. Methanol's special properties and their uses and value in internal combustion engines

Latent heat of Vaporisation

Methanol's relatively high latent heat of vaporisation improves engine efficiency by the cooling the charge air to the engine.

By absorbing energy from the induction air as it vaporises, methanol increases the cylinder charge density. This increases the amount of both fuel and air that can enter on each stroke and also reduces the compression energy needed. The outcomes are an increase in power and also a reduction in the combustion zone temperature, which in turn leads to reduced formation of harmful NOx.

Endothermic decomposition

A further property of methanol that has significant fuel efficiency implications is that methanol can be decomposed into hydrogen and oxides of carbon in such a way that these more energetic gases can be used directly as the fuel.

The decomposition reaction of methanol to hydrogen and CO_2 is endothermic, absorbing the equivalent of nearly 20% of the energy released when methanol is normally combusted. The additional energy effectively goes into the gaseous products reducing the quantity of fuel required to deliver a given amount of energy to the engine. As this decomposition energy can be taken from the waste heat from the engine's exhaust, it is effectively obtained without the need for further fuel combustion.

Zero-m has developed a system to use the vehicle's methanol fuel to recuperate waste heat from the vehicle exhaust which turns the methanol into a gaseous fuel that can then be being supplied to the engine.

It is only possible to carry out this energy saving exhaust heat recuperation with methanol because its unique chemistry allows the reaction to occur at the low temperatures found in vehicle exhausts.

Any fuel containing conventional hydrocarbons, such as petrol, diesel, LNG, blends of gasoline and ethanol or even methanol blends such as M15 and M85 cannot take advantage of the reaction to recover waste engine heat because the hydrocarbons will not decompose at low enough temperatures.

Fuel formulation for safe and effective use as a fuel – Zero-m (ZM95™)

Historically, there have been certain concerns surrounding the potential use of methanol as a fuel.

These are mainly that methanol can be corrosive to engine components under certain automotive application/conditions, that methanol lacks the lubricity of diesel and so could damage fuel pump bearings, unless dosed with a suitable additive in the same way petrol needs to be, and that it can be toxic by accidental ingestion (or abuse) or by excessive inhalation of its vapours.

While it is important to be aware of these concerns, there is nothing that does not apply also to other fuels already in common use, and therefore nothing that cannot be properly and safely managed by careful fuel formulation and prudent procedures during handling and use of the same nature as those needed for the safe handling and use of petrol and diesel.

Against this background, Zero-m have formulated a fuel (ZM95™) so that it is suitable:-

- as an ICE fuel,
- as a fuel for incorporation into an exhaust heat recuperation system as described above
- as a source of hydrogen for fuel cells

ZM95™ formulation fully mitigates all the technical issues of concern and makes the fuel suitable for distribution to, and use in, today's vehicles.

Toxicity

Methanol is already widely used safely in a variety of commercial and consumer products. For example it is found in car windscreen washer fluid, carburettor and other cleaning fluids, solvents and, with bitterants to prevent their abuse, as a denaturant in a wide range of alcohol products.

It has also been accepted for fuel use blended at 3% in petrol by the EU, and at M15 and M85 blends with petrol in the US in the 1980s and 90s and in China today where its use as a transport fuel is growing rapidly.

Obviously care must be taken to avoid vapour inhalation, ingestion and skin contact with all fuels, and, like petrol, diesel and LPG, methanol can have negative health consequences if handled carelessly.

Methanol has not been shown to be carcinogenic or harmful to human reproduction and in this respect is considered more benign than petrol or diesel, both of which are known to contain carcinogenic compounds. Ingestion of petrol and diesel is very undesirable due to the presence of the carcinogens and also because, particularly with petrol, ingestion can trigger pneumonia.

Unlike petrol, diesel and LPG, methanol is a pure chemical that occurs naturally in the environment and is also present in low concentrations naturally within the human body. According to the FDA, "as much as 500 milligrams per day of methanol is safe in an adult's diet as, in the body, methanol is metabolized in the liver, converted first to formaldehyde, then to formate". The formate is slowly metabolised to carbon dioxide and water or excreted from the body.

There is a considerable body of reference work on methanol toxicity in which some data suggests that methanol's level of ingestion toxicity is of a similar order of magnitude to that of ethanol, petrol or diesel. LD50[4] values of 6.2 to 13g/kg have been reported for rats compared to 10.3 for ethanol, 18.85 for gasoline and 12 to 17.5 for diesel. Other work suggests however, that, on occasion, ingestion of as little as 10ml has been known to cause death. In the main it seems that researchers agree on somewhat higher numbers; that, if left untreated for many hours or even days, ingestion of between 50 and 150mls can cause death.

The major negative impact of methanol ingestion comes from the toxicity of its metabolite - formate. If not treated in timely fashion, the formate can cause blindness and or death. Treatment within a few hours, either with ADH inhibitors, or by providing a more preferred metabolite such as ethanol, which interrupts the formation of formaldehyde and formate, halts the toxic effects.

Inhalation of methanol is also obviously to be avoided in principle. Unlike petrol, however, methanol has a high latent heat of vaporisation, which means that it only evaporates slowly. This means that vapours only build up slowly and in areas with bad ventilation. The literature suggests that only inhalation for extended times of airborne concentrations that would only come about by bad practice are likely to lead to symptoms. A current source of inhalation toxicity cases is the amateur manufacture of biodiesel where methanol is used as a reagent. Treatment is again totally effective if timely. Safe working air concentrations are already specified within the existing HSE code.

In times past, there was danger of accidental ingestion of petrol or diesel through siphoning by mouth. All codes of practice for handling petrol and diesel in the oil and auto industries now prohibit this practice much reducing this source of potential risk today. The codes of practice also require skin contact to be avoided by the wearing of gloves when contact with fuel is likely.

These now well established codes of practice mean that, where the normal precautions taken when dealing with petrol and diesel fuels are being taken, accidental ingestion, inhalation or skin contact with toxic quantities of methanol in circumstances where treatment cannot be obtained within a reasonable time, is very unlikely.

Addition of bitterant

Nevertheless, to prevent accidental ingestion of methanol, ZM95 is formulated with a bitterant to make accidental ingestion of a significant quantity almost impossible. Because methanol has a similar effect on the body to ethanol[5], the fuel might be illegally mixed with water or with other fluids to give a drink that could be consumed for recreational abuse. The level of bitterant added to the Zero-m fuel formulation is aimed to be sufficient to ensure that even at relatively high dilutions it is still extremely unpalatable.

A.3. Environmental impact of release

Methanol is naturally present and widely distributed in the environment. In the atmosphere, it has a half life of 17.8 days and reacts with photochemically produced hydroxyl radicals. In the soil there are several bacteria capable of using methanol as a carbon source and it is rapidly bio-degraded. Methanol is also readily biodegraded in water and is not as toxic to fish as to land mammals. Its short half life and the fact that it already naturally present mean that the harmful effects of accidental spills are much less than for those of petrol or diesel.

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[4] LD50: the level of ingestion at which 50% of the individuals ingesting the substance would not survive

[5] It should be noted that "Meths", which is occasionally consumed illegally, is comprised predominantly of tax free ethanol with a methanol content of approximately 5%. The methanol is added to the "Meths" by Government regulation to de-nature and toxify the tax free ethanol content so as to discourage recreational or ethanol-addicted consumption of tax free ethanol intended for non-potable uses and consequent loss of ethanol tax revenue.

A.4. US EPA: Chemical Summary

CHEMICAL SUMMARY FOR METHANOL

prepared by

OFFICE OF POLLUTION PREVENTION AND TOXICS, U.S. ENVIRONMENTAL PROTECTION AGENCY

August 1994

This summary is based on information retrieved from a systematic search limited to secondary. These sources include online databases, unpublished EPA information, government publications, review documents, and standard reference materials. No attempt has been made to verify information contained in these databases and secondary sources.

CHEMICAL IDENTITY AND PHYSICAL/CHEMICAL PROPERTIES

The chemical identity and physical/chemical properties of methanol are summarized in Table 1.

TABLE 1. CHEMICAL IDENTITY AND CHEMICAL/PHYSICAL PROPERTIES OF METHANOL

Characteristic/Property	Data	Reference
CAS No.	67-56-1	
Common Synonyms	methyl alcohol, wood alcohol, wood spirit	(Budavari et al. 1989)
Molecular Formula	CH_4O	
Chemical Structure	H | H - C - OH | H	
Physical State	colourless liquid	Verschueren 1983
Molecular Weight	32.04	Budavari et al. 1989
Melting Point	-97.8°C	Budavari et al. 1989
Boiling Point	64.7°C at 760 mm Hg	Budavari et al. 1989
Water Solubility	miscible	Budavari et al. 1989
Density	d20/4, 0.7915 g/mL	Budavari et al. 1989
Vapor Density (air = 1)	1.11	Budavari et al. 1989
KOC	9	CHEMFATE 1994
Log KOW	-0.77	HSDB 1994

Vapor Pressure	126 mm Hg at 25øC	CHEMFATE 1994
Reactivity	Flammable; may explode when exposed to flame	HSDB 1994
Flash Point	12°C	Budavari et al. 1989
Henry's Law Constant	4.55 x 10-6 atm m3/mol	CHEMFATE 1994
Fish Bioconcentration Factor	<1 (estimated)	HSDB 1994
Odor Threshold	highly variable, ranges over several orders of magnitude(10 ppm to 20,000 ppm in air)	HSDB 1994
Conversion Factors	1 ppm = 1.33 mg/m3; 1 mg/m3 = 0.76 ppm	Verschueren 1983

ENVIRONMENTAL FATE

A. **Environmental Release**: Methanol ranked third in the U.S. among all chemicals for total releases into the environment in 1992. Of the total released, 195 million pounds were into the atmosphere, 16.4 million pounds were into surface water, 27 million pounds into underground injection sites, and 3.3 million pounds were onto land (TRI92 1994). Methanol detected in the air from Point Barrow, Alaska averaged 0.77 ppb (CHEMFATE 1994). Ambient concentrations from Stockholm, Sweden ranged from 3.83 to 26.7ppb while concentrations from two remote locations in Arizona were 7.9 and 2.6 ppb (HSDB 1994). In one survey, methanol was detected in drinking waters from 6 of 10 U.S. cities (HSDB 1994) but levels were not included. The chemical has also been detected in rainwater collected from Santa Rita, Arizona (HSDB 1994).

B. **Transport:** The miscibility of methanol in water and a low KOC (9) indicate that the chemical will be highly mobile in soil (HSDB 1994). Volatilization half-lives from a model river and an environmental pond were estimated at 4.8 days and 51.7 days, respectively (HSDB 1994). Methanol can be removed from the atmosphere in rain water (HSDB 1994).

C. **Transformation/Persistence**

1. **Air -** Once in the atmosphere, methanol exists in the vapour phase with a half life of 17.8 days (HSDB 1994). The chemical reacts with photochemically produced hydroxyl radicals to produce formaldehyde (HSDB 1994). Methanol can also react with nitrogen dioxide in polluted air to form methyl nitrite (HSDB 1994).

2. **Soil -** Biodegradation is the major route of removal of methanol from soils. Several species of Methylobacterium and Methylomonas isolated from soils are capable of utilizing methanol as a sole carbon source (CHEMFATE 1994).

3. **Water** – Most methanol is removed from water by biodegradation. The degradation products of methane and carbon dioxide were detected from aqueous cultures of mixed bacteria isolated from sewage sludge (CHEMFATE 1994). Aerobic, Gram-negative bacteria (65 strains) isolated from seawater, sand, mud, and weeds of marine origin utilized methanol as a sole carbon source (CHEMFATE 1994). Aquatic hydrolysis, oxidation, and photolysis are not significant fate processes for methanol (HSDB 1994).

4. **Biota** - Bioaccumulation of methanol in aquatic organisms is not expected to be significant based on an estimated Bio-concentration factor of 0.2 (HSDB 1994).

HUMAN HEALTH EFFECTS

A. Pharmacokinetics

1. **Absorption -** Methanol is readily absorbed after oral, inhalation, or dermal exposure. Oral doses in humans of 71 to 84 mg/kg resulted in blood levels of 4.7 to 7.6 mg/100 mL of blood within 3 hours (Rowe and McCollister 1981). Inhalation of 500 to 1000 ppm methanol for 3 to 4 hours gave urine concentrations of 1 to 3 mg methanol/100 mL of urine at the end of exposure (Rowe and McCollister 1981). Based on urinary methanol levels, the rate of absorption of the chemical appears to be proportional to the concentration of vapour inhaled (HSDB 1994). The rate of dermal absorption increased for 35 minutes then decreased over the next 25 minutes (no other details given) (HSDB 1994).

2. **Distribution** - Methanol distributes rapidly in dogs exposed to 4000 to 15,000 ppm for 12 hours to 5 days; the highest concentrations of the chemical were found in blood, eye fluid, bile, and urine (HSDB 1994).

3. **Metabolism** - Methanol is oxidized in the human liver by the enzyme alcohol dehydrogenase (Rowe and McCollister 1981). Metabolic products include formaldehyde and formic acid (HSDB 1994). The rate of metabolism for methanol (25 mg/kg/hr) is much slower than for ethanol (175 mg/kg/hr) and is independent of concentrations in the blood (HSDB 1994). Formic acid is responsible for the toxic effects of methanol (ACGIH 1991).

4. **Excretion** - Methanol is excreted either as the parent compound in the urine or expired air, or as the formic acid metabolite in urine (Rowe and McCollister 1981; HSDB 1994). The amount of formic acid excreted varies greatly with species from 1% in rabbits to 20% in dogs; humans are intermediate (HSDB 1994). In humans, the half-life of methanol elimination in expired air after oral or dermal exposure is 1.5 hours (HSDB 1994).

B. Acute Toxicity

Acute methanol intoxication is manifested initially by signs of narcosis. This is followed by a latent period in which formic acid accumulates in the body causing metabolic acidosis. Severe abdominal, leg, and back pain occur and visual degeneration can lead to blindness.

1. **Humans** - Ingestion of 80 to 150 mL of methanol is usually fatal to humans (HSDB 1994). One worker died from exposure to vapor ranging from 4000 to 13,000 ppm over 12 hours (ACGIH 1991). The concentration of 4000 ppm is roughly equivalent to a total of 1140 mg/kg over the 12 hour period (see end note 2). Poisoning by non-lethal doses can be described in three stages: (1) narcotic stage similar to ethanol; (2) latent period of 10-15 hours; (3) visual disturbances and central nervous system lesions (Rowe and McCollister 1981). Visual disturbances can lead to blindness due to edema of the retina and atrophy of the optic nerve head (HSDB 1994). Third-stage CNS lesions include headache, dizziness, abdominal, back, and leg pain, delirium that can lead to coma, and nausea (HSDB 1994). Formic acid production causes severe metabolic acidosis (Rowe and McCollister 1981).

2. **Animals** - Oral LD50 values for methanol in animals are 0.4 g/kg in the mouse, 6.2 to 13 g/kg in the rat, 14.4 g/kg in the rabbit, and 2 to 7 g/kg in the monkey (Rowe and McCollister 1981). The LD50 for dermal application to rabbits is 20 mL/kg (approximately 16 g/kg) (Rowe and McCollister 1981). Dose-response data for inhalation vary with species, dose, and duration (8800 ppm for 8 hours to 152,800 ppm for 94 minutes). Symptoms of intoxication include incoordination, salivation, lethargy, narcosis, and death (Rowe and McCollister 1981).

C. Subchronic/Chronic Toxicity

Chronic exposure to methanol, either orally or by inhalation, causes headache, insomnia, gastrointestinal problems, and blindness in humans and hepatic and brain alterations in animals. EPA has derived an oral RfD (reference dose) (see end note 3) for methanol of 0.5 mg/kg/day, based on the absence of liver and brain effects in animals exposed by mouth to 500 mg/kg/day.

1. **Humans** - "Chronic" exposure to methanol vapors (no time or dose given) caused conjunctivitis, headache, giddiness, insomnia, gastric disturbances, and bilateral blindness (ACGIH 1991). Marked vision loss occurred in one worker exposed to 1200 to 8000 ppm vapor for 4 years (ACGIH 1991).

2. **Animals** - No effects were seen in rats given 1% (approximately 140 mg/kg/day) methanol in drinking water for 6 months (Rowe and McCollister 1981). Hepatic abnormalities (proteinic degeneration, altered RNA metabolism) occurred in rhesus monkeys given 3 to 6 g/kg for 3 to 20 weeks and in rats given 10, 100, or 500 mg/kg/day for one month (Rowe and McCollister 1981). Rabbits chronically fed methanol (no dose or time given) had increasing blood levels, brain and eye edema, and myelin thinning (HSDB 1994). Male and female rats were lavaged with 100, 500, or 2500 mg/kg/day for 90 days (U.S. EPA 1994). Increased levels of SGPT and SAP as well as decreased brain weights were seen in both sexes at the highest dose; a no-observed-adverse effect level (NOAEL) for the study was 500 mg/kg/day. Based on these data, the U.S. EPA (1994) calculated a chronic RfD (see end note 4) for methanol of 0.5 mg/kg/day. No toxic effects were seen in dogs exposed by inhalation to either 10,000 ppm for 3 minutes, 3x/day, for 100 days or to 450 or 500 ppm, 8 hours/day for 379 days (Rowe and McCollister 1981). Ultra-structural changes were observed in the photoreceptor cells of rabbits exposed to 46.6 ppm for 6 months (Rowe and McCollister 1981). Rowe and McCollister (1981) concluded that the effects of combined oral and inhalation exposure appear to be additive. Rats exposed by inhalation to 16.8 ppm, 4 hours/day, for 6 months and administered 0.7 mg/kg/day orally had changes in blood morphology, oxidation-reduction processes, and liver function (Rowe and McCollister 1981).

D. Carcinogenicity

No information was found on the carcinogenicity of methanol in the secondary sources searched.

1. **Humans -** No information was found in the secondary sources searched concerning the carcinogenicity of methanol to humans.

2. **Animals -** No information was found in the secondary sources searched concerning the carcinogenicity of methanol to animals. The NTP has assigned a project leader for methanol and the design of the study is in progress (NTP 1994).

E. Genotoxicity:

Methanol was negative for cell transformation in Syrian hamster embryo cells (clonal assay and viral enhanced), sister chromatid exchange in vitro, and for aneuploidy and chromosome aberrations in Neurospora crassa (GENETOX 1992). The micronucleus test and the assay for chromosome aberrations in mammalian polychromatic erythrocytes were inconclusive (GENETOX 1992).

F. Developmental/Reproductive Toxicity

No information was found on the developmental toxicity of methanol in humans. Methanol can cause adverse effects in the developing offspring in rats at doses that cause overt maternal intoxication.

1. **Humans -** No information was found in the secondary sources searched regarding the developmental or reproductive toxicity of methanol to humans. However, one of the breakdown products of the artificial sweetener asparatame is methanol. Increased blood methanol levels did not lead to increased formic acid levels in women receiving up to 200 mg/kg asparatame (no other details reported) and no evidence of foetal risk was detected (HSDB 1994).

2. **Animals -** Rats were exposed by inhalation, 7 hours/day, to 5000 or 10,000 ppm methanol on gestation days 1-19 or to 20,000 ppm on days 7-15. Maternal intoxication (unsteadiness) occurred at the highest dose and coincided with extra or rudimentary ribs and urinary or cardiovascular defects in the foetuses (ACGIH 1991). Male rats had significantly lowered testosterone levels after inhalation exposure to 200 ppm methanol for 6 weeks; at 10,000ppm a change in luteinizing hormone was also observed (HSDB 1994).

G. Neurotoxicity

Methanol causes central nervous system depression in humans and animals as well as degenerative changes in the brain and visual system.

1. **Humans -** Methanol causes narcosis similar to ethanol intoxication and non lethal doses can lead to blindness. Autopsy of individuals after lethal doses revealed edema and hyperaemia of the brain and degeneration of the ganglion cells of the retina (Rowe and McCollister 1981).

2. **Animals -** Acute methanol intoxication in animals causes CNS depression as observed by narcosis, in coordination, lethargy, drowsiness, and prostration (Rowe and McCollister 1981).

ENVIRONMENTAL EFFECTS

A. Toxicity to Aquatic Organisms

Methanol has low acute toxicity to aquatic organisms; lethal concentrations are much greater than 100 mg/L. Ninety-six hour LC50 values for fish are 28,100 mg/L for Pimephales promelas (fathead minnow), 20,100 mg/L for Oncorhynchus mykiss (rainbow trout), and >28,000 mg/L for Alburnus alburnus (bleak) (AQUIRE 1994). Forty-eight hour LC50 values for Cyprinus carpio (common carp) and Carassius auratus (goldfish) are 28,000 mg/L and 1,700 mg/L, respectively (AQUIRE 1994). Growth inhibition occurred for 4 strains of Anabaena (bluegreen algae) over a range of EC50's of 2.57-3.13% for 10-14 days (AQUIRE 1994). The LC50 for Artemia salina (brine shrimp) is >10,000 mg/L in 24 hours and that for Culex restuans (mosquito) is 20,000 mg/L in 18 hours (AQUIRE 1994).

B. Toxicity to Terrestrial Organisms

No information was found in the secondary sources searched regarding the toxicity of methanol to terrestrial organisms. However, based on the range of oral LD50's, 0.4 to 14.2 g/kg, for monkeys, rats, mice, and rabbits (Rowe and McCollister 1981), it is unlikely that methanol would be toxic to terrestrial animals at environmental levels.

C. Abiotic Effects

Methanol reacts with nitrogen dioxide in polluted atmospheres to produce methyl nitrite (HSDB 1994). According to the definition provided in the Federal Register (1992), methanol is a volatile organic compound (VOC) substance. As a VOC, methanol can contribute to the formation of photochemical smog in the presence of other VOCs.

END NOTES

1. Standard Industrial Classification code is the statistical classification standard for all Federal economic statistics. The code provides a convenient way to reference economic data on industries of interest to the researcher. SIC codes presented here are not intended to be an exhaustive listing; rather, the codes listed should provide an indication of where a chemical may be most likely to be found in commerce.
2. Calculated using the factor 1.33 (Verschueren 1983) to convert 4000 ppm to 5320 mg/m3 which is multiplied by 0.214 (the 12-hour breathing rate, 15 m3 [from the occupational standard 8-hour breathing rate, 10 m3] divided by the assumed adult body weight, 70 kg) to obtain the dose in mg/kg (U.S. EPA 1988).
3. The RfD is an estimate (with uncertainty spanning perhaps an order of magnitude) of the daily exposure level for the human population, including sensitive subpopulations, that is likely to be without an appreciable risk of deleterious effects during the time period of concern.
4. The RfD is an estimate (with uncertainty spanning perhaps an order of magnitude) of the daily exposure level for the human population, including sensitive subpopulations, that is likely to be without an appreciable risk of deleterious effects during the time period of concern.
5. The ACGIH/NIOSH exposure limits are time-weighted average (TWA) concentrations for an 8-hour workday (ACGIH) and up to a 10-hour workday (NIOSH) for a 40-hour workweek.
6. This is a recommended 15-minute exposure limit value that should not be exceeded at any time.
7. The OSHA exposure limit is a time-weighted-average (TWA) concentration that must not be exceeded during any 8-hour workshift during a 40-hour workweek.

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Submitted by US EPA to ICCA/OECD Chemical Challenge: October 2004.

CHEMICAL NAME Methanol: STRUCTURAL FORMULA CH3OH

SUMMARY CONCLUSIONS OF THE SIAR

Human Health

Toxicokinetics, Metabolism, and Distribution:

Methanol is readily absorbed by all routes of entry, inhalation, oral ingestion and dermal contact and distributes rapidly throughout the organism. Net absorption of inhaled methanol was estimated to be 60 to 85 percent in humans. Metabolism in humans (and also in rodents and monkeys) contributes up to 98 percent of the clearance, whereas renal and pulmonary excretion contributes only about 2 – 3 percent. More than 90 percent of the dose is exhaled as CO_2. In humans, the half-life was approximately 2.5 – 3 hours at doses lower than 100 mg/kg, corresponding to a first-order elimination constant of 0.23 – 0.28/h. At higher doses, the half life is longer. The mammalian metabolism of methanol mainly occurs in the liver and leads to carbon dioxide via formate. A catalase reaction is the rate-limiting step in rats and mice, its saturation giving rise to a disproportionate increase in blood methanol. However, in humans the conversion of formate is rate-limiting. Formate itself is poorly excreted into the urine even when it accumulates in the blood; metabolism is required for excretion to occur.

In rats, monkeys and humans exposed to concentrations of 0.26 – 2.6 mg/L (administered for 6 to 8 hours), blood methanol remains close to 50 mg/L with no signs of accumulation and the formation of formate is still insignificant compared to the endogenous formate pool. Up to an air concentration of 0.065 mg/L (50 ml/m3), no increase of blood methanol is expected. Up to 0.26 mg/L (single or repeated exposure), the methanol blood level is likely to increase 2 to 4-fold above the endogenous methanol concentration in humans, but still remains significantly below 10 mg/L. Baseline levels of formate are about 3 to 19 mg/L (0.07 – 0.4 mM) in humans. Toxic blood formate concentrations are reported to be between 220 and >450 mg/L (5 – >10 mM formate). Inhalation of about 1.20 mg methanol/L (2h) contributed only insignificantly to the internal formate pool of monkeys (in the µM-range), whereas formate accumulation has been observed in primates at methanol doses greater than500 mg/kg.

Acute Toxicity:

Formate is considered to be the ultimate toxicant in acute intoxication in humans. Acidosis and ophthalmologic changes are typical primary effects that do not occur in rodents or rabbits. In these animals, which are able to remove formate more efficiently, consequences of CNS depression are usually the cause of defects and finally death.

The minimal lethal acute methanol dose to humans is considered to be 300 to 1000 mg/kg. A blood level of 500 mg/L in acutely poisoned patients generally is regarded as requiring haemodialysis. This blood concentration can transiently be achieved in an adult person (70 kg) by ingestion of 0.4 ml methanol/kg (approximately 0.32 mg/kg). Generally, in humans, transient central nervous system (CNS) effects appear above blood methanol levels of 200 mg/L; serious ocular symptoms appear above 500 mg/L, and fatalities have occurred in untreated patients with initial methanol blood levels in the range of 1500-2000 mg/L.

However, such high blood methanol levels able to cause death are hardly achievable through inhalation exposure: e.g. at 2.6 or 6.5 mg/L, levels would barely exceed 100 and 200 mg/L, respectively, after an 8- hour working shift. Exposure to 0.26 mg methanol/L for 4 hours was without significant physiologic effects in test persons.

In rats, LC50 values of 128.8 mg/L (after 4 hours) and 87.5 mg/L (after 6 hours) were calculated. In monkeys, lethal concentrations of 52 mg/L after 1-4 hours and 13 mg/L after 18 hours have been calculated. A dermal LD50 of 17000 mg/kg was calculated for rabbits and in monkeys; four daily dermal doses of 400 mg/kg eventually resulted in death. Oral LD50s range from 5600 to 14400 mg/kg in rats, mice, rabbits, and dogs. Monkeys that received oral doses of 3000 to 8000 mg/kg died within two days.

Irritation/Sensitisation: Methanol exhibited no skin irritation in one study but moderate irritation in a study that could not be verified. Available studies show that it is a mild to moderate eye irritant (with some reversibility of effects). High concentration of methanol vapours may be irritating to mucous membranes. A guinea pig maximization bioassay gave no evidence of contact sensitisation.

Repeated-Dose Toxicity:

In a chronic exposure study in monkeys, some histological findings were observed in the cerebral area after prolonged exposure to doses of up to 1.3 mg/L, although the effects were generally of a mild nature. Several additional effects, including dose-related liver effects, were observed in this study. Effects in other organs and systems were also observed. The neurological effects were assumed to be due to methanol because several such effects were observed, neurological effects were also seen in the sub-chronic monkey study, and neurobehavioral effects were observed in a reproductive/developmental study in monkeys. A LOAEL of 0.013 mg/L was chosen for this study.

Although the statistical significance of the effects cannot be verified from the study report, the number of effects and systems affected indicate a relationship with methanol.

In a sub-chronic study in monkeys, 3.9 mg/L (3000 ml/m3) was chosen as the LOAEL (sub-acute) where neurotoxic lesions appeared to progress in monkeys. This exposure concentration correlated with methanol blood levels 80 mg/L and formate levels 30 mg/L.

In other studies of chronic exposure in rats and mice, the effects are difficult to interpret from the available study and only NOELs could be established at the mid-dose of 0.13 mg/L.

In a 28-day study, there was no evidence of adverse effects in rats exposed to methanol up to 6.5 mg/L (6 hours per day for 28 days), except local nasal irritation and increased relative spleen weights, which were observed only at the middle dose. The estimated blood level of methanol is expected to be about 250 mg/L under this condition.

Mutagenicity:

The majority of the numerous in vitro and in vivo assays are negative for mutagenic/clastogenic potential although a few of in vitro and in vivo assays were positive. Carcinogenicity: Methanol tested in two long-term inhalation studies gave no evidence of a carcinogenic potential in rats and mice exposed to air concentrations of up to 1.3 mg/L.

Reproduction: No epidemiological studies in humans have been located to demonstrate that there is a link between methanol exposure and an increased incidence of foetal malformations or developmental impairment.

In monkeys, inhalation exposure of parents prior to and during breeding as well as during pregnancy resulted in wasting syndrome and mild neurobehavioral effects in offspring as well as some vaginal bleeding and unproductive labour in mothers. These recordings resulted in the identification of 0.26 mg/L (the lowest dose tested), as a LOAEL. However, due to the normal variance in and the low number of animals, the observed findings are somewhat difficult to interpret.

Several inhalation studies in rats resulted in a variety of effects in offspring due to prenatal and/or postnatal dosing. In a 2-generation reproductive study, decreased brain weights resulted in a NOAEL of 0.13 mg/L. In another study, malformations and foetal weight changes resulted in a NOAEL of 6.5 mg/L (the lowest dose tested). A third study resulted in malformations, increased foetal resorptions, and decreased numbers of live foetuses, resulting in a NOAEL of 1.3 mg/L.

An inhalation study in mice resulted in developmental effects including increased exencephaly and cleft palate, fully resorbed foetuses, and decreased numbers of live pups; this study resulted in a NOAEL of 1.3 m /L. Oral studies in mice resulted in various malformations at 4000 mg/kg-bw and higher; no NOAELs could be established from these studies. Due to the normal variance in and the low number of animals, the observed findings are somewhat difficult to interpret.

Rodent data on reproductive and developmental toxicity are relevant for humans despite the known differences in methanol metabolism between rodents and humans. Rodents are adequate models for human exposure to methanol at levels where formate does not accumulate. However, blood methanol concentrations associated with serious teratogenic effects and reproductive toxicity are in the range associated with formate accumulation, which is likely to result in metabolic acidosis, and visual and clinical effects in humans. Other effects (e.g., subtle neurological effects observed in primates) are exhibited at lower inhalation doses and lower methanol blood levels.

Environment:

Methanol is a colourless, clear, highly flammable liquid with a mild alcoholic odour. Physical property values for methanol are: melting point –97.8 0C, boiling point 65 0C, density 0.79 g/m3, vapour pressure 129 hPa, and log

Kow –0.82. Methanol is miscible with water at all ratios at ambient temperature. It does not undergo hydrolysis. A value of 0.461 Pa m^3/mol for the Henry's Law constant indicates that volatilisation is not a significant removal process for in the aquatic compartment. Air is the main target compartment, based on a model calculation (Mackay Level III) with about 73 % of environmental methanol distributing to air and some 16 % to water. Methanol is degraded in the atmosphere by photochemical, hydroxyl-radical dependent reactions (estimated elimination half-life about 17-18 days) and is readily biodegradable (75 – 82 % and 95 % removal in standard ready tests after 5 and 20 days respectively). Bioaccumulation in fish is expected to be low.

There are a great number of aquatic tests on fish, daphnia, algae and bacteria that consistently demonstrate the low acute aquatic toxicity of methanol: lethal or effective concentrations are significantly above 1000 mg/L, with a majority above 10000 mg/L. The low toxicity of methanol for aquatic organisms is confirmed by QSAR calculations, resulting in acute toxicity values for fish, daphnids and algae well above 1000 mg/L. Methanol is not expected to result in short and long-term adverse effects on the environment under normal circumstances.

Exposure: The world-production volume of methanol is some 30 million tonnes annually in 2000, about 11 million tonnes used in countries participating in NAFTA (North American Free Trade Agreement) and about 3.3 million tonnes in Western Europe, of which 70% is being used for the manufacture of formaldehyde, MTBE and acetic acid.

Methanol occurs naturally in humans, animals and plants. Releases into the environment may occur from both natural and man-made sources. It is however released predominantly from production and use in industrial processes. The general population is exposed to methanol mainly through consumption of food and beverages and through use of consumer products, like paints, sealers and adhesives, containing it as a solvent. The most important route of potential exposure is considered inhalation and dermal exposure at the workplace.

A mean background body burden of 0.5 mg methanol/kg bw has been estimated based on baseline blood levels and elimination kinetics of methanol. Additional sources may still contribute to this burden at a similar or somewhat higher extent (e.g. from additional food sources such as the sweetener aspartame and its use as a fuel additive).