Danish Ministry of the Environment

Survey of methanol (Cas no. 67-56-1)

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Survey of methanol (Cas no. 67-56-1)Survey of methanol (Cas no. 67-56-1)

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Content

Preface

The Danish Environmental Protection Agency's List of Undesirable Substances (LOUS) is intended as a guide for enterprises. It indicates substances of specific concern due to the actual consumption in Denmark and for which the use should be reduced or eliminated completely. The first list was published in 1998 and updated versions have been published in 2000, 2004 and 2009. The latest version, LOUS 2009 (DEPA, 2011) includes 40 chemical substances and groups of substances which have either been classified as dangerous or identified as problematic due to other concerns. The criteria employed by the Danish EPA for inclusion of substances on the list include:

- Properties of concern according to the EU 'List of hazardous substances';
- Properties of concern identified using computer-based model calculations outlined in the Danish EPA's 'Advisory list for self-classification of dangerous substances' (the Self-classification list);
- PBT/vPvB substances as identified by the EU;
- Substances on the EU 'Priority list of substances for further evaluation of their role in endocrine disruption'.

Furthermore, a tonnage threshold has been used. Substances used in quantities exceeding 100 tonne per year in Denmark and fulfilling any of the abovementioned criteria have been included in LOUS 2009. For substances which are the subject of special focus in Denmark, the tonnage threshold can however be different.

Over the period 2012-2015 all 40 substances and substance groups on LOUS will be surveyed. The surveys include collection of available information on the use and occurrence of the substances, internationally and in Denmark, information on environmental and health effects, on alternatives to the substances, on existing regulation, on monitoring and exposure and information regarding ongoing activities under REACH among others.

The Danish EPA will on the basis of the surveys assess the need for any further regulation, substitution/phase out, classification and labeling, improved waste management, development of new knowledge or increased dissemination of information.

This survey concerns methanol. The reason for including this substance on LOUS 2009 is the fact that methanol is used in amounts exceeding 100 tonne per year in Denmark and is found on the EU 'List of hazardous substances'. Methanol is on the EU 'List of hazardous substances' since its classification according to CLP includes H370 (Causes damage to organs) (Corresponding to R39 (Danger of very serious irreversible effects in the old directive).

The preparation of this report has been supervised by a steering committee consisting of:

- Peter H. Schaarup, Danish Environmental Protection Agency
- Helle Winther, Danish Environmental Protection Agency
- Christina Ihlemann, Danish Environmental Protection Agency
- Anne-Louise Rønlev, Danish Environmental Protection Agency, Århus
- Poul Erik Andersen, The Danish Product Register/Labor Inspectorate
- Ulla Hansen Telcs, Confederation of Danish Industry
- Bjørn Knudsgaard, Danish Environmental Protection Agency, Virksomheder (Companies)

The project has been carried out in the period June – December 2012.

Summary and Conclusion

The purpose of this project has been to conduct a systematic mapping of the LOUS substance methanol. The mapping is performed in order to clarify a potential need for further regulatory actions regarding the use of the substance. Below main elements from the different areas of the mapping are presented, followed by a short summary of the identified potential ‘hotspots’ – i.e. areas which *may be* subject to further regulatory actions.

Regulatory framework

Methanol is regulated within approx. 30 Danish Statutory Orders and a number of EU Regulations. The most important rules concern:

- Methanol is not allowed for use in deicing fluids, engine coolants or in solutions for preventing freezing of carburetors.
- It is not allowed to sell products containing methanol in a concentration ≥ 10% to the general public – with certain exceptions (hospitals, dentists, etc.).
- There are rules regarding safe transport and storage of methanol as well as for avoiding spills.
- The EU sets limits for content of methanol in different alcoholic beverages.
- There is a Danish dispensation scheme, that allows for certain recreational organizations to use methanol as a fuel (for speedway motorcycles, etc.).

Manufacture and uses

Methanol is the simplest alcohol and can be made from a variety of sources, including natural gas, biomass, agricultural and timber waste, solid municipal waste, etc. The methanol industry spans the entire globe and has a collected production capacity of approx. 76 mio. tonne per year. The current world wide consumption is around 50 mio. tonne. However, some uncertainties are linked to the number. Denmark does not produce methanol, but consumes approx. 80,000 tonne of methanol each year. The main use categories of methanol in Denmark are:

- Production of glue
- Production of biodiesel
- As hydrate inhibitor in the oil and gas industry
- As solvent or reagent (primarily in pesticide production)

World-wide methanol is used in a variety of applications – from antifreeze fluids to paint, plastics, dyes, cements, gasoline, etc. The consumption of methanol is not expected to increase significantly in Denmark or Europe, however, a massive increase in production and consumption of methanol is expected to happen in China (increase of approx. 220% from 2010 – 2017). The Chinese growth is particularly in new areas like fuel (as blending or as DME) and MTO (methanol to olefins). Recently, an organization has been established in Denmark (the Danish Methanol Union) with the goal of promoting production and use of methanol in Denmark – partly based on agricultural waste and partly on recycling carbon dioxide in power plant smoke.

Waste management

Waste containing methanol must be handled as ‘dangerous waste’ and thus disposed of through an authorized waste facility, which typically burns the methanol-contaminated waste. The burning of methanol results in the formation of CO_2 and water. Contact to four representatives within the four main use categories revealed, that the majority of methanol is used in chemical processes, where it is converted to other chemical compounds, thus no waste containing methanol remains. If methanol containing waste is produced it is either re-used in the production process, used as ‘food’ for microorganisms in the waste water treatment or disposed of through an authorized waste facility. The exception is the oil and gas industry, which has permission to release (rather large) amounts of waste water containing methanol to the sea.

Environmental effects and fate

Main elements related to the environmental impacts/effects of methanol cover:

- Methanol is readily degraded in the environment by photo-oxidation.
- Methanol is readily biodegradable under both aerobic and anaerobic conditions in a wide variety of environmental media.
- Generally 80% of methanol in sewage systems is biodegraded within 5 days.
- Methanol is a normal growth substrate for many soil micro-organisms, which are capable of completely degrading methanol to carbon dioxide and water.
- Methanol is of low toxicity to aquatic and terrestrial organisms and does not bioaccumulate.
- Effects due to environmental exposure to methanol are unlikely to be observed, unless it is released to the environment in large quantities, such as a spill.

Human health effects

Main elements related to health impacts/effects of methanol cover:

- Methanol is more toxic to humans than animals, which can be problematic since the classification system is based on studies on animals.
- The most pronounced effect of methanol is damage to the eyes.
- Methanol is readily absorbed through dermal contact, ingestion or inhalation.
- Methanol is rather quickly excreted from the body.
- According to IPCS (1997) no studies have been reported on methanol in the peer-reviewed literature on reproductive and developmental effects. Likewise with chromosomal and mutagenic effects and carcinogenic effects.
- Folate-deficient individuals might be at greater risk from inhalation of low concentrations of methanol, compared to normal individuals. Folate-deficient individuals cover pregnant women, the elderly, individuals with poor-quality diets, alcoholics and individuals on certain medications or with certain diseases (IPCS, 1997).

Monitoring data and exposure

Methanol occurs naturally in humans, animals and plants. It is a natural constituent in blood, urine, saliva and expired air. The average intake of methanol from natural sources varies, but limited data suggests an average intake of considerably less than 0.17 mg/kg bw/day, which is well below the US EPA TDI value of 0.5 mg/kg. A Finnish study has performed a number of risk evaluations related to different exposure scenarios of non-natural exposure to methanol. They found that for several exposure scenarios (manufacturing of products with methanol (incl. production of windscreen washing fluids); use of methanol in waste water treatment; use of methanol as solvent in the extraction process and use of methanol based fuels in speedway, drag racing, etc.) there was a need for using protective equipment.

Information on alternatives

As methanol is primarily used in different chemical processes due to its distinctive chemical properties, it is difficult to discuss the use of alternatives. The only reported (partly successful) use of an alternative is the use of ethanol as solvent instead of methanol in certain applications (within the rubber and plastic industry and in the process of immune blotting).

Overall conclusion

Related to the area of environmental concerns, potential hotspots – i.e. areas that might need to be regulated further – comprise:

- *The importance of avoiding spills.* IPCS concludes that effects from environmental exposure to methanol are unlikely to be observed, unless it is released to the environment in large quantities. They suggest that care should be taken to avoid spills, especially to surface waters. There is a Danish Statutory Order that regulates issues regarding spill. This Statutory Order is linked to a minimum Directive; however, it is unclear whether this means that all Member States regulate this area sufficiently.

Related to the area of health concerns, potential hotspots – i.e. areas that might need to be regulated further – comprise:

- *A need for evaluating the new proposed classification of methanol.* Italy has proposed a new classification of methanol as being toxic to reproduction. The background information for this suggested altered classification should be evaluated and commented, bearing in mind that methanol is much less toxic for animals than for humans and that classification is often based on animal studies. It should also be taken into consideration that folate-deficient individuals might be at greater risk from inhalation of low concentrations of methanol, compared to normal individuals. Folate-deficient individuals cover pregnant women, the elderly, individuals with poor-quality diets, alcoholics and individuals on certain medications or with certain diseases. The fact that the minimum dose causing permanent visual defects is unknown should also be taken into consideration. Also important to bear in mind is the fact that IPCS concludes that a conventional risk assessment of methanol is not feasible and that an alternative approach should be an evaluation based on blood levels of the most toxic metabolite (formate).
- *Evaluate whether EU legislation regarding prevention of ingestion of methanol-contaminated alcoholic beverages is sufficient.* A number of countries (Finland, Poland, the Czech Republic) has experienced problems with people dying from ingestion of methanol contaminated alcoholic beverages. Latest (September 2012) 20 people died in the Czech Republic and concerns were raised regarding whether the EU legislation is sufficient in this area. While this does not seem to be a problem in Denmark it may be worth while investigating further whether the EU legislation is sufficient in this area.
- *Make sure that protective equipment is used where necessary.* A Finnish study exemplified the need for making sure that sufficient protective equipment is used, especially in the following scenarios: manufacturing of products with methanol (incl. production of windscreen washing fluids); use of methanol in waste water treatment; use of methanol as solvent in the extraction process and use of methanol based fuels in speedway, drag racing, etc.). It could be relevant to inform relevant groups of the need for protective equipment.
- *Investigate further whether there is a problem related to exposure to methanol from food sweetened with aspartame.* A rough calculation has shown that if aspartame was used to replace all sucrose in the diet, it would correspond to an average daily ingestion of 0.85 mg methanol/kg, which is *above* the US EPA TDI value of 0.5 mg/kg (IPCS, 1997). It could be investigated further whether there in reality is a problem related to (the expanding) use of aspartame in foodstuff.

Sammenfatning og konklusioner

Formålet med dette projekt har været at udarbejde en systematisk kortlægning af LOUS-stoffet methanol. Kortlægningen er gennemført med henblik på at afklare, om der er behov for yderligere regulatoriske tiltag relateret til brugen af stoffet. Nedenfor er hovedpointerne fra de forskellige områder i kortlægningen præsenteret, fulgt af en kort sammenfatning af de identificerede potentielle 'hotspots' – dvs. områder som *måske* har behov for yderligere regulatoriske tiltag.

De regulatoriske rammer

Methanol er reguleret gennem ca. 30 danske bekendtgørelser og en række EU-Forordninger. De vigtigste regler omhandler:

- Methanol er ikke tilladt til brug i afisningsvæsker, kølervæsker eller i opløsninger, der bruges til at forhindre, at karburatorer fryser til.
- Det er ikke tilladt at sælge produkter indeholdende methanol i koncentrationer ≥ 10% til almindelige forbrugere – med enkelte undtagelser (hospitaler, tandlæger, mv.).
- Der findes regler vedrørende sikker transport og opbevaring af methanol såvel som for at undgå spild.
- EU sætter grænser for indholdet af methanol i forskellige alkoholiske drikke.
- Der findes et dansk dispensationssystem, der tillader visse fritidsorganisationer at bruge methanol som brændstof (til speedway motorcykler, mv.)

Produktion og brug

Methanol er den mest simple alkohol og kan fremstilles ud fra en lang række råvarer, inklusiv naturgas, biomasse, landbrugsaffald, træaffald, (fast) kommunalt affald, mv. Methanolindustrien spænder over hele kloden og har en samlet produktionskapacitet på ca. 76 mio. ton per år. Det nuværende forbrug verden over ligger på omkring 50 mio. ton. Der er imidlertid nogen usikkerhed forbundet med dette tal. Danmark producerer ikke methanol, men forbruger ca. 80.000 ton methanol om året. De primære brugskategorier i Danmark er:

- Produktion af lim
- Produktion af biodiesel
- Som hydratinhibitor i olie- og gasindustrien
- Som opløsningsmiddel eller reagent (primært i pesticid produktion)

Methanol anvendes verden over i en lang række funktioner/produkter – fra antifrostvæsker til maling, plastik, farvestoffer, cement, brændstoffer, mv. Forbruget af methanol forventes ikke at stige signifikant i Danmark eller Europa, men en massiv stigning i produktion og forbrug af methanol forventes at finde sted i Kina (en stigning på ca. 220 % fra 2010 – 2017). Den kinesiske vækst finder sted primært i nye områder som brændsel (som blandingsprodukt eller DME) og MTO (methanol til olefins). En dansk organisation (Dansk Methanolforening) er for nylig blevet etableret med det formål at fremme produktion og brug af methanol i Danmark – til dels baseret på landbrugsaffald og til dels på genanvendelse af kuldioxid fra røgen fra kraftværker.

Affaldshåndtering

Affald indeholdende methanol skal håndteres som 'farligt affald' og derfor bortskaffes via et autoriseret affaldsanlæg, som typisk brænder det methanol-forurenede affald. Afbrændingen af methanol resulterer i dannelsen af CO_2 og vand. Kontakt til fire repræsentanter indenfor de fire primære brugskategorier afslørede, at hovedparten af methanolen bruges i kemiske processer, hvor det omdannes til andre kemiske forbindelser, hvilket betyder, at der som sådan ikke er affald indeholdende methanol tilbage. Hvis der produceres affald indeholdende methanol, bliver det enten genanvendt i produktionsprocessen, brugt som 'føde' for mikroorganismer i spildevandsanlæg eller bortskaffet via et autoriseret affaldsanlæg. Undtagelsen er olie- og gasindustrien, som har tilladelse til at udlede (ganske store) mængder af spildevand indeholdende methanol til havet.

Miljøeffekter og skæbne
Hovedpointerne relateret til miljøeffekter af methanol omfatter:
- Methanol er let nedbrydeligt i miljøet ved photo-oxidation.
- Methanol er let bionedbrydeligt under såvel aerobiske og anaerobiske forhold i en lang række forskellige miljøer.
- Generelt nedbrydes 80 % af methanolen i kloaksystemer indenfor 5 dage.
- Methanol er et typisk vækstsubstrat for mange mikroorganismer i jorden. Disse er i stand til fuldstændig at nedbryde methanol til kuldioxid og vand.
- Methanol udviser lav toksicitet overfor akvatiske og terrestiske organismer og bioakkumuleres ikke.
- Effekter forårsaget af miljømæssig eksponering af methanol forventes ikke sandsynlige, medmindre methanolen er frigivet i store mængder i miljøet, f.eks. i form af en spildulykke.

Sundhedseffekter
Hovedpointerne relateret til sundhedseffekter af methanol omfatter:
- Methanol er mere toksisk overfor menneske end dyr, hvilket kan være problematisk, da klassficeringssystemet er baseret på studier med dyr.
- Den mest udtalte virkning af methanol er skader på øjnene.
- Methanol optages nemt gennem hudkontakt, indtagelse eller inhalering.
- Methanol udskilles ganske hurtigt fra kroppen.
- Ifølge IPCS (1997) er der ikke rapporteret methanol-studier (der har været igennem et peer-review), som har vist effekter relateret til reproduktion og udvikling. Ligeledes med kromosom- og mutagene effekter og kræftfremkaldende effekter.
- Individer, der mangler folat, kan være udsat for en større risiko ved inhalering af lave mængder af methanol, sammenlignet med normale individer. Individer, der mangler folat, omfatter gravide kvinder, gamle mennesker, individer med dårlig kvalitetskost, alkoholikere og individer, der anvender bestemte medicinpræparater eller har specielle sygdomme (IPCS, 1997).

Monitoreringsdata og eksponering
Methanol forekommer naturligt i mennesker, dyr og planter. Det er en naturlig bestanddel i blod, urin, spyt og udåndingsluft. Det gennemsnitlige indtag af methanol fra naturlige kilder varierer, men begrænsede data tyder på et gennemsnitligt indtag betydeligt under 0,17 mg/kg lgv./dag, hvilket er klart under US EPA's TDI værdi på 0,5 mg/kg. Et finsk studie har gennemført en række risikoevalueringer over forskellige eksponeringsscenarier – alle omhandlende eksponering af methanol fra ikke-naturlige kilder. De fandt, at i adskillige eksponeringsscenarier (fremstilling af produkter med methanol (inkl. produktion af sprinklervæske); brug af methanol i spildevands-renseanlæg; brug af methanol som opløsningsmiddel i ekstraktionsprocesser og brug af methanolbaserede brændstoffer i speedway, dragracing, mv.) var der et behov for brug af beskyttelsesudstyr.

Information om alternativer
Siden methanol primært anvendes i forskellige kemiske processer grundet dets specifikke kemiske egenskaber, er det svært at diskutere anvendelse af alternativer. Det eneste (delvist succesfuldt) rapporterede tilfælde af brug af alternativ er brugen af ethanol som opløsningsmiddel i stedet for

methanol i specielle tilfælde (indenfor gummi- og plastindustrien og i en proces vedrørende immun-blotting).

Overordnede konklusioner

I relation til miljømæssige problemstillinger er der fundet følgende potentielle hotspots – dvs. områder, som måske har behov for yderligere regulatoriske tiltag:

- *Vigtigheden af at undgå spild*. IPCS konkluderer, at effekter relateret til miljømæssig eksponering af methanol er usandsynlige, medmindre methanolen frigives til miljøet i store mængder. De foreslår, at man sørger for at undgå spild, især til overfladevand. Der findes en dansk bekendtgørelse, som regulerer området vedrørende spild. Denne bekendtgørelse er relateret til et minimumsdirektiv. Det er imidlertid uklart, hvorvidt dette betyder, at alle medlemslande regulerer dette område tilstrækkeligt.

I relation til sundhedsmæssige problemstillinger er der fundet følgende potentielle hotspots – dvs. områder, som måske har behov for yderligere regulatoriske tiltag:

- *Behov for evaluering af det nye forslag til klassificering af methanol.* Italien har foreslået en ny klassificering af methanol som værende 'giftig i relation til reproduktion'. Baggrundsdokumentationen for dette forslag bør evalueres og kommenteres med det in mente, at methanol er mindre giftig for dyr end for mennesker, og at klassificering ofte er baseret på dyrestudier. Det bør ligeledes tages med i betragtning, at mennesker med folat-mangel kan være udsat for større risiko fra inhalering af lave mængder methanol sammenlignet med normale mennesker. Individer, der mangler folat, omfatter gravide kvinder, gamle mennesker, individer med dårlig kvalitetskost, alkoholikere og individer, der anvender bestemte medicinpræparater eller har specielle sygdomme. Det faktum, at minimumsdosen, der forårsager permanente visuelle defekter, er ukendt, bør også tages med i betragtning. Også vigtigt at have in mente er det faktum, at IPCS konkluderer, at en konventionel risikovurdering af methanol ikke er mulig, og at en alternativ tilgang bør være en evaluering baseret på blodniveauer af den mest toksiske metabolit (formiat).
- *Evaluering af hvorvidt EU-lovgivning vedrørende forhindring af indtagelse af methanol-forurenede alkoholiske drikke er tilstrækkelig.* En række lande (Finland, Polen, Tjekkiet) har oplevet problemer med personer, som dør efter indtagelse af methanol-forurenede alkoholiske drikke. Senest (september 2012) døde 20 mennesker i Tjekkiet, og bekymringer om, hvorvidt EU-lovgivningen er tilstrækkelig på dette område, blev rejst. Selvom dette ikke lader til at være et stort problem i Danmark, kan det give mening at undersøge nærmere, hvorvidt EU-lovgivningen på dette område er tilstrækkelig.
- *Sikre at beskyttelsesudstyr anvendes, hvor det er nødvendigt.* Et finsk studie eksemplificerede behovet for at sikre, at tilstrækkeligt beskyttelsesudstyr anvendes, især i følgende scenarier: fremstilling af produkter med methanol (inkl. produktion af sprinklervæske); brug af methanol i spildevands-renseanlæg; brug af methanol som opløsningsmiddel i ekstraktionsprocesser og brug af methanolbaserede brændstoffer i speedway, dragracing, mv. Det kunne være relevant at informere relevante grupper om behovet for brug af beskyttelsesudstyr.
- *Undersøge hvorvidt der er et problem relateret til eksponering af methanol fra fødevarer sødet med aspartam.* En grov beregning har vist, at hvis aspartam blev anvendt som erstatning for sukker i al mad i en persons diæt, så ville det svare til et dagligt indtag af 0,85 mg methanol/kg, hvilket er *over* US EPA's TDI værdi på 0,5 mg/kg (IPCS, 1997). Det bør undersøges nøjere, hvorvidt der vitterlig er et problem relateret til (det stigende) forbrug af aspartam i fødevarer.

1. Introduction to methanol

Methanol, also known as methyl alcohol, wood alcohol, wood naphtha or wood spirits, is a chemical with the formula CH_3OH (often abbreviated MeOH). Methanol belongs to the chemical group of VOCs (Volatile Organic Compounds). Methanol acquired the name "wood alcohol" because it was once produced as a byproduct of the destructive distillation of wood.

Methanol contains less carbon and more hydrogen than any other liquid. It is a stable biodegradable chemical, which is produced and shipped around the globe every day (in large quantities) for a number of industrial and commercial applications. Methanol can be made from virtually anything that is or has been a plant. This includes common fossil fuels (natural gas and coal) and renewable resources like biomass, landfill gas and even power plant emissions and CO_2 from the atmosphere. Methanol has been one of the world's most widely used industrial chemicals since the 1800s (The Methanol Institute, 2012).

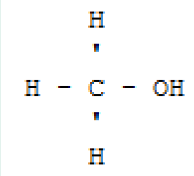
The largest industrial use of methanol in Denmark is as a raw material in the production of formaldehyde contained in urea-formaldehyde glue. Moreover, methanol is used in the production of biodiesel and feedstock for synthesis and purification in the chemical and pharmaceutical industries. Methanol is also used as solvent in many chemical products for industrial use and as fuel in engines with extreme tuning, for example model airplanes and speedway motorcycles. Worldwide, methanol is on the top 5-list of chemicals that are exchanged between the continents. Methanol is considered by many to be a "clean" energy source and is as such used for example in fuel cells. It is expected that the use as a fuel in the transport sector will increase.

Methanol occurs naturally in the environment and quickly breaks down in both aerobic and anaerobic conditions. Methanol is also quickly absorbed in the body, through inhalation, ingestion or dermal contact. Methanol ingested in large quantities is metabolized to formic acid or formate salts, which are poisonous to the central nervous system, and may cause blindness, coma, and death. Because of these toxic properties, methanol is frequently used as a denaturant additive for ethanol manufactured.

1.1 Physical and chemical properties

Methanol is the simplest alcohol and is a light, volatile, colorless, flammable liquid with a distinctive odor very similar to, but slightly sweeter than, ethanol (drinking alcohol). At room temperature, it is a polar liquid.

TABLE 1
PHYSICAL AND CHEMICAL PROPERTIES OF METHANOL (IPCS, 1997).

Physical and chemical properties of methanol	
Chemical formula	CH3OH
Chemical structure	
Relative molecular mass	32.04
CAS chemical name	Methanol
CAS no.	67-56-1
Synonyms	Methyl alcohol, carbinol, wood alcohol, wood spirits, wood naphtha, Columbian spirits, Manhattan spirits, colonial spirit, hydroxymethane, methylol, methylhydroxide, monohydroxymethane, pyroxylic spirit.
Appearance	Clear, colorless liquid
Odor	Slight alcoholic when pure
Boiling point	64.7 ^{o}C
Specific gravity	0.7915 (20/4 ^{o}C) 0.7866 (25 ^{o}C)
Freezing point	-97.68 ^{o}C
Flash point	15.6 ^{o}C (open cup) 12.2 ^{o}C (closed cup)
Vapor pressure	160 mmHg (at 30 ^{o}C) 92 mmHg (at 20 ^{o}C)
Henry's Law Constant (25 ^{o}C)	1.35 x 10^{-4}atm.m^3/mole
Log P (octanol/water)	-0.82; -0.77; -0.68
Partition constant	-0.66; -0.64
Ignition temperature	470 ^{o}C
Explosive limits in air (% by volume)	Lower 5.5 Upper 44
Methanol volatilization half-life (model river)	5.3 days
Methanol atmospheric half-life	8.4; 8 and 7.3 days
Bioconcentration factors	0.2 <10 (Golden ide) 1 (Carp) 28,400 (green alga)

1.2 Classification

Methanol is classified as the following according to the harmonized classification (Annex VI of Regulation (EC) No. 1272/2008 (CLP Regulation):

- Flam. Liq. 2 (H225) / Highly flammable (R11)
- Acute Tox. 3 (H301, H311, H331) / Toxic if swallowed, in contact with skin and by inhalation (R23/24/25)
- STOT SE 1 (H370) / Toxic: danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed (R39/23/24/25)

However, on the homepage of ECHA[1] it can be seen, that Italy has recently proposed the following new classification of methanol:

- Proposed classification according to Directive 67/548/EEC (DSD): Toxicity to reproduction – development
- Proposed classification according to Reg (EC) No 1272/2008 (CLP): Reproductive toxicity

[1] http://echa.europa.eu/registry-of-submitted-harmonised-classification-and-labelling-intentions/-/substance/753/search/+/term

2. Regulatory framework

2.1 Existing legislation

In the following sections ‘legislative documents’ comprise the following types:

- Statutory Orders (which implements the EU Directives within Danish law)
- National Statutory Orders (which are purely Danish laws)
- Regulations (which are EU ‘regulative documents’ which apply directly in the different Member States)

The section regarding ‘Existing legislation in DK’ examines all the Statutory Orders that deal with methanol – both Statutory Orders and National Statutory Orders. Since it is a very comprehensive task to distinguish whether a Statutory Order is related to a Directive or not, only the most important Statutory Orders have been investigated further, in order to clarify whether they belong to an EU Directive (a harmonized or minimum Directive) or is purely a Danish law (see later).

In the section regarding ‘Existing legislation in the EU’ only Regulations – that deals with methanol – are presented. These can be seen as ‘pure EU legislation’ since the wordings apply directly in the different Member States.

However, this division means that the majority of the Statutory Orders presented in section 2.1.1 can also be seen as EU legislation, since some of these Statutory Orders are derived from EU Directives.

2.1.1 Existing legislation in DK

A search on www.retsinformation.dk – a site presenting all Danish legislation – resulted in 214 hits on methanol. A ‘hit’ means that the word ‘methanol’ is included somewhere in the legislation text. Of the 214 hits 30 were found in Statutory Orders. The remaining hits were primarily guidance documents, etc. – of which the majority are historic. Below keywords on how methanol is regulated in these 30 Statutory Orders are presented. All 30 Statutory Orders are still active/valid and requirements in them are mandatory.

TABLE 2
HOW METHANOL IS REGULATED IN 30 DANISH STATUTORY ORDERS (KEYWORDS ONLY). ALL STATUTORY ORDERS ARE VALID PER 12TH SEPTEMBER 2012

Statutory Order	How methanol is regulated
Statutory Order No. 1403 of 15/12/2009 on ’biofuel sustainability etc.”.	- Different standard values on methanol are presented, which should be used when calculating green house gas emissions related to the use of biofuels.
Statutory Order No. 9307 of 08/03/2011 on ”flight permits and certification requirements etc.”	- Auto petrol used in air craft’s must not contain methanol (unless a specific approval is issued).
Statutory Order No. 10538 of 20/12/2007 on ”flight permit	- Auto petrol used in air craft’s must not contain methanol (unless a specific approval is issued).

and airworthiness requirements in general etc.”	
Statutory Order No. 11200 of 31/05/1985 on ”technical requirements for road transport of toxic substances”.	- Special requirements for solutions of hydrogencyanide in methanol.
Statutory Order No. 908 of 27/09/2005 on ” Measures to prevent exposure to carcinogenic substances and materials”	- Certain rules apply for work with, production and handling of certain substances – including methanol (in concentration above 0.1%). - No further specific rules apply to methanol. NB: another Statutory Order describes amendments to this Order. However no changes are related to methanol.
Statutory Order No. 75 of 30/01/1992 on ”limits on discharges of certain dangerous substances into rivers, lakes and the sea”.	- Only requirements for substances produced by use of methanol or based on methanol. - No direct requirements towards methanol.
Statutory Order No. 579 of 01/06/2011 on ”food contact materials”	- Methanol is part of the list of substances, that can be used during production of regenerated cellulose films, however only as ’esters of methanol’ etc.
Statutory Order No. 874 of 01/08/2011 on ”additives etc. for food”.	- Methanol can be used as extraction substance in certain (undefined) cases. However, only a maximum residue content of 10 mg methanol/kg is allowed in the extracted foodstuff/ingredient. - When preparing aroma substances a maximum residue content of methanol of 1.5 mg/kg is allowed.
Statutory Order No. 770 of 27/06/2012 on ”order amending the order on pesticides”.	- Only requirements towards methanol compounds (like for instance (benzyloxy)methanol) – no requirements towards methanol alone.
Statutory Order No. 707 of 19/06/2012 on ” Danish Medicine Standards”	- A test method involving methanol has been changed.
Statutory Order No. 702 of 24/06/2011 on ”Pesticides”	- The solution factor of the pesticide in methanol must be presented.
Statutory Order No. 188 of 22/02/2012 on ”order amending the order on pesticides”.	- Only requirements towards compounds of methanol (like for instance ethylendioxy-dimethanol).
Statutory Order No. 857 of 05/09/2009 on ”restricting the use of certain dangerous chemical substances and products for specific purposes”.	- Methanol must not be used in engine coolants, in solutions used for preventing the freezing of carburetors or in deicing fluids (as for instance washing fluid). The restriction does not apply to water-methanol solutions used in aircrafts.
Statutory Order No. 422 of 04/05/2006 on ”cosmetic products”.	- Acetophenon, reaction product with among others, methanol, must not be used. - Methanol can be used (as denaturant for ethanol and isopropylalcohol), however in a maximum allowed

	concentration (in the final product) of 5 % calculated as percentage of ethyl- and isopropylalkohol. NB: two other Statutory Orders amend this Statutory Order – however no change related to methanol is presented.
Statutory Order No. 507 of 17/05/2011 on "Occupational exposure limit values for substances and materials".	- Limit value of 200 ppm or 260 mg/m^3 is presented for methanol. - Methanol is listed as a substance that has an EU-limit value and can be absorbed through the skin. NB: another Statutory Order amends this Statutory Order – however no change related to methanol is presented.
Statutory Order No. 1075 of 24/11/2011 on "classification, packaging, labeling, sale and storage of substances and mixtures".	- Mixtures, that contain methanol in a concentration of 3 % or above, must be labeled as 'Warning: May cause damage to organs' ('Harmful') and be fitted with child-resistant closures. - It is not allowed to sell products labeled 'toxic' to people under the age of 18. With certain exceptions they are not allowed to be sold to the general public either and they are submitted to the rules regarding requisition to use toxic substances. A product must be labeled as 'Danger: Causes damage to organs' ('Toxic') if it contains ≥10 % methanol. - Very toxic and toxic substances and mixtures are allowed to be sold to hospitals, laboratories, doctors, dentists, etc.
Statutory Order No. 557 of 31/05/2011 on "drugs"	- Only requirements towards compounds of methanol (like for instance [2-[2,6-dimethoxy-4-(2-methyloctan-2-yl)phenyl]-7,7-dimethyl-4-bicyclo[3.1.1]hept-3-enyl]methanol).
Statutory Order No. 366 of 15/04/2011 on "the quality of petrol, diesel and gas oil for use in motor vehicles etc."	- Limit values on methanol in gasoline presented (value: max. 3 % v/v).
Statutory Order No. 11020 of 31/05/1987 on "technical requirements for the carriage of flammable liquids"	- Presumably the requirement concerns special packaging rules for methanol.
Statutory Order No. 11150 of 31/05/1985 on "technical requirements for road transport of corrosive substances"	- Requirements related to formaldehyde solutions containing a maximum of 35 % methanol.
Statutory Order No. 1246 of 11/12/2009 on "releases from the Danish Maritime Authority – technical legislation on safety on ships".	- Transport of methanol as cargo must follow certain requirements – such as 'workplace assessments shall be based on evaluation of the substances dangerous properties, exposure conditions, limit values related to the working environment etc." - There are several more requirements concerning methanol.

Statutory Order No. 788 of 24/07/2008 on "food hygiene"	- Certain rules (cleaning procedures etc.) apply to transport of 'loadings'. Methanol is listed as a type of loading. If transport tanks are constructed by use of certain materials, three of the previous transported loadings must be one of those listed, etc.
Statutory Order No. 1666 of 14/12/2006 on "control of major-accident hazards involving dangerous substances".	- If methanol is used in amounts above 500 tonne (level 2) and 5,000 tonne (level 3) respectively, the Order applies. - The Order states rules for avoiding large accidents in companies.
Statutory Order No. 20 of 12/01/2006 on "control with the working environment in terms of risk related to larger accidents with dangerous substances".	- If methanol is used in amounts above 500 tonne (level 2) and 5,000 tonne (level 3) respectively, the Order applies. - The Order states rules for avoiding large accidents on companies.
Statutory Order No. 301 of 13/05/1993 on "determination of code-numbers"	- Certain code numbers are required for different types of products, depending on whether the product contains for instance fluids with a low boiling point etc. Also includes MAL codes etc. - Methanol is listed in a table, which is to be used for calculation of the MAL factor.
Statutory Order No. 13377 of 25/08/1988 on "common working methods of soil analysis".	- Methanol only mentioned as a component in a solution used in a soil analysis method.
Statutory Order No. 350 of 29/05/2002 on "the limitation of emissions of volatile organic compounds...".	- Methanol is not directly mentioned, but as it is a VOC it is covered by this Statutory Order. - The Statutory Order sets rules for the use and storage of VOC's. The larger quantities the stricter rules.
Statutory Order No. 17 of 04/01/2010 on "flammable liquids".	- Methanol is not directly mentioned, but it is a flammable liquid and thus covered by this Statutory Order. - The Statutory Order sets rules for the use and storage of flammable liquids. The larger quantities the stricter rules.
Executive Order No. 292 of 26/4/2001 on Work with Substances and materials	- Methanol is not directly mentioned, but as it is classified dangerous and on the list of occupational limit values it is covered by this Order. - The Order sets rules for any work with substances and materials, including their manufacture, use and handling.

NB: The regulatory requirements in the table are described with very few words/summarized. For full reference/description of the regulatory requirements, please see the Statutory Orders. Furthermore, only 'main requirements' regarding methanol are described – thus requirements towards for instance which test method to use when proving that auto petrol does not contain methanol are not described.

Within the context of the present mapping of methanol the most relevant/important rules regarding methanol are judged to be those mentioned in the table below. The criteria for selecting the most relevant rules are based on consideration towards consumers (i.e. the rule should be relevant for consumer products) and/or working environment. Regarding each of these most relevant rules, it has been attempted to clarify whether the Directive, of which the Statutory Order is related to, is a harmonized Directive (thus the rules apply equally across the EU) or a minimum Directive (thus Member States are able to set stricter rules than the minimum requirements stated in the Directive). If a Directive is a minimum Directive it should refer to Treaty Article 192 or 175 in the introduction. If it is a harmonized Directive it should refer to Treaty Article 114 (or if it is an old Directive Article 95).

TABEL 3
MOST RELEVANT STATUTORY ORDERS REGARDING METANOL AND TYPE OF LEGISLATION.

Statutory Order	How methanol is regulated	Type
Statutory Order No. 857 of 05/09/2009 on ”restricting the use of certain dangerous chemical substances and products for specific purposes”.	Methanol is not allowed for use in deicing fluids (washing fluids) – except for water-methanol mix solutions, which are allowed to be used in aircrafts. Methanol is furthermore not allowed for use in engine coolants or in solutions used for preventing the freezing of carburetors - except for water-methanol mix solutions, which are allowed to be used in aircrafts.	Purely **national**
Statutory Order No. 1075 of 24/11/2011 on ”classification, packaging, labeling, sale and storage of substances and mixtures”.	It is not allowed to sell products containing methanol in a concentration above 10% to the general public (with certain exceptions, as for instance hospitals, dentists, etc.).	Is linked to 10 different Directives. One of these (Directive 1999/45/EF) refers to Arcticle 95 and is thus a **harmonized Directive.**
Statutory Order No. 20 of 12/01/2006 on ”control with the working environment in terms of risk related to larger accidents with dangerous substances”	There are rules regarding safe transport of methanol and for avoiding spills (for companies using at least 500 tonne)	Is related to two Directives, of which one of them (Directive 2003/105/EF of December 16 2003) refers to article 175, which means that the Directive is a **minimum Directive.**
Statutory Order No. 350 of 29/05/2002 on “the limitation of emissions of volatile organic compounds…”.	The Statutory Order sets rules for the use and storage of VOC’s. The larger quantities the stricter rules.	Refers to EU Directive 1999/13/EF of March 11 1999, which does not seem to be either a harmonized or minimum Directive
Statutory Order No. 17 of 04/01/2010 on “flammable liquids”	The Statutory Order sets rules for the use and storage of flammable liquids. The larger quantities the stricter rules.	Purely **national**

2.1.2 Existing legislation in the EU

In this section primarily EU Regulations which deal with methanol are presented. Eur-lex is the main entrance to legislation in the EU. A search on this site has been performed with the criteria of the word 'methanol' being included in the title or the text of a legislative document. This resulted in 396 hits. Eur-lex offers the possibility of narrowing the search results by use of 'topics' such as 'Tax related questions', 'Energy', 'Joined foreign- and security politics' etc. The 396 hits have been narrowed down by use of the following topics – i.e. hits (legislation) within the following topics have been investigated.

- Agriculture (72 hits)
- Fishing (0 hits)
- Energy (9 hits)
- Industrial politics and the internal market (108)
- Environmental and consumer politics as well as health protection (38 hits).

If the title of the legislative document within the different topics seemed relevant (in terms of consumers exposure to methanol), the legislative document as well as a few hints on how methanol is regulated within the document, is presented in the table below. Regulations are directly applicable in Danish law, thus these are not converted into Danish Statutory Orders, and thus are not found in the list of legislation presented in section 2.1.1. Directives are included in the table in section 2.1.1 (since these are converted to Danish Statutory Orders) thus these are not mentioned here (again).

TABLE 4
REGULATORY DOCUMENTS WITHIN THE EU THAT DEAL WITH METHANOL (SOURCE: EUR-LEX).

Regulatory document	How methanol is regulated
33 pieces of legislation	- There are 33 pieces of legislation dealing with methanol in wines -but they all seem only to mention methanol as a dilutant used in testing methods.
A statement from the Economic and Social Committee on 'Research needs for a safe and sustainable energy". 2002/C 241/03.	- Examples of possible themes for future development include 'production techniques for alternative fuels (such as methanol...).
Regulation No. 231 of 9. March 2012 on specifications for food additives..	- Methanol is allowed as solvent in the production of certain colorants.
Regulation No. 10 of 14. January 2011 on "plastic materials and – objects destined for contact with food".	- Substances used for manufacturing of plastic materials must comply with requirements listed in table 1. Here it is stated that methanol must not be used as additive or polymerizing agent and that migration results of methanol cannot be corrected by use of a fat-consumption-reduction-factor.
Regulation No. 110 of 15. January 2008 on "definition, description, presentation, labeling and protection of geographic indications of spirits.."	- Wine, spirits and brandy must not exceed a maximum content of methanol of 200 g/hl alcohol (100%). Fruit spirits similar but with a limit value of 1000 g/hl alcohol (100%). Vodka similar but with a limit value of 10 g/hl alcohol (100%). Further different limit values for other types of spirits.
Regulation (EC) No 1907/2006	- According to REACH import into the EU or production

of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)		of methanol must be registered within the REACH system – either June 1 2013 (>100 tonne) or June 1 2018 (> 1 tonne) depending on the tonnage of the individual companies.
Regulation (EC) No 1272/2008 of 16 December 2008 on classification, labeling and packaging of substances and mixtures (CLP)	-	Describes the EU requirements for classification and labeling of methanol and chemical mixtures containing methanol.
	-	Annex II describes the special rule for methanol containing chemical mixtures concerning labeling and packaging (child-resistant fastening). See Table 2 for details.
	-	Annex VI describes the harmonized classification of methanol. See section 1.2 for details.

Within the context of the present mapping of methanol the most relevant/important rules regarding methanol seem to be:

- Limit values regarding content of methanol in alcoholic beverages
- Methanol is mentioned as a possible theme for future development of alternative fuels

2.1.3 Existing legislation globally

The only relevant global legislation regarding methanol is the Globally Harmonized System (GHS), which is a system for classification, labeling and packaging of chemicals. It was adopted by the UN in 2001 and it is the aim that all countries worldwide implement the system in order to ensure uniform methods for evaluation and communication of hazards. Today, GHS has been implemented widely mainly by large countries (e.g. China, the USA, Japan, Australia, Brazil) – however, most countries in Africa, South America, the Middle East and the East have not implemented the GHS.

In the EU, GHS was implemented in January 2009 – under the name CLP (Regulation (EC) No 1272/2008 of 16 December 2008 on classification, labeling and packaging of substances and mixtures (CLP)). The CLP classification of methanol can be seen in section 1.2.

The countries which have already implemented GHS or are in the process of implementing GHS can be seen in the figure below.

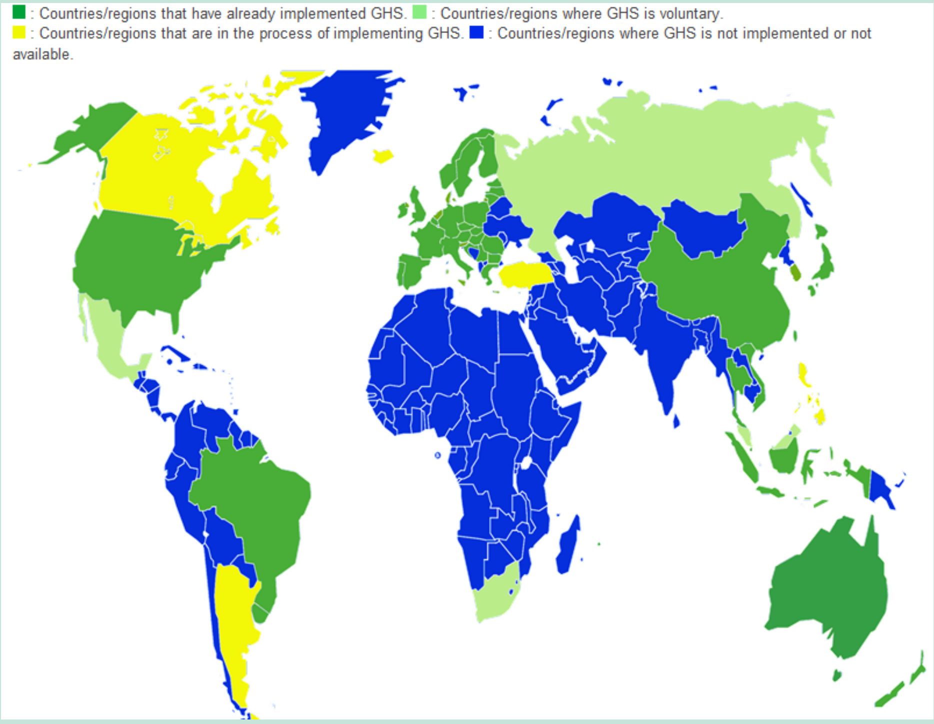


Figure 1

Countries that are in the process of implementing CLP or already have implemented CLP (www.ghs.dhigroup.com).

2.2 Other 'legislative' initiatives

In this section other legislative initiatives dealing with methanol are investigated. By other legislative initiatives is meant:

- Guidance documents
- Communications
- Suggestions to alter the law
- Substitution projects
- Information campaigns
- Ecolabels
- And other relevant documents/studies

2.2.1 Other 'legislative' initiatives in DK

2.2.1.1 Guidance documents, communications, suggestions to alter the law, etc.

Besides the 30 hits in Statutory Orders (listed above), 184 hits were found in 'other legislative documents' such as suggestions to changes in law, communications, guidance documents etc. Common for these 'other legislative documents' is that the requirements are not mandatory – thus they can be perceived as 'other legislative initiatives'. However, the majority of these documents are 'historic' – meaning they are no longer applicable. Only a few of the 184 documents are still valid/active. Below, it is shortly described how methanol is suggested regulated within each of these active documents.

TABLE 5
HOW METHANOL IS REGULATED IN 'OTHER LEGISLATIVE DOCUMENTS' (I.E. GUIDANCE DOCUMENTS, SUGGESTIONS TO ALTER THE LAW, ETC.). ALL DOCUMENTS ARE VALID PER 12TH SEPTEMBER 2012.

'Other regulatory document'	How methanol is regulated
CIR No. 14003 of 15/08/1986 on "communication on guidelines for police endorsement of toxic requisitions etc."	- The police should only endorse requisitions on methanol for use in mountaineering. For normal hiking trips, ethanol should be used. - The Danish EPA established in 1978 a dispensation scheme allowing for a certain number of recreational organizations to use methanol in prepared mixes with oils – for use in model planes. The recreational organizations cover: RC-unionen, Fritflyvningsunionen, Jydsk Fynsk Modelbåds Union, Bornholms RC klub, Dansk Automobilsports Union og speedway-kørsel indenfor Dansk Motor Union.
2010/1 LSF 21 on "Suggestion to alter the law on sustainable biofuels".	- The changes seem not to deal with methanol, even though methanol is mentioned in the law.
VEJ No. 9029 of 01/01/2002 on "Guidance no. 2, 2002. B-value guidance".	- B-values are set to protect the public from air pollution. They are to be seen as a limit value for the individual company's contribution to air pollution. - The B-value for methanol is 0.3 mg/m^3.
VEJ No. 10937 of 01/08/2007 on "Guidance on the limit value list 2007".	- Air pollution limit value for methanol is 200 ppm and 260 mg/m^3 – related to among others MAL codes etc. - NB: The limits are no longer valid, since they are replaced by Statutory Order 507. However, the list regarding 'Organic solvents' and the list regarding 'Substances and processes which are regarded as carcinogenic' are still valid.
VEJ No. 9027 of 04/02/2011 on "Guidance on nutrition labeling for prepackaged foods".	- Only requirements regarding a bortrifluorid-methanol complex.
VEJ No. 11047 of 01/03/1999 on "handbook on health preparedness"	- Methanol is listed as being kept on the shelves as 'antidote' in several hospitals in Århus.

NB: Only keywords are presented. For full description of the requirements please see the relevant document. Furthermore, a few of lesser important 'other legislative documents' mentioning methanol has been excluded (as for instance documents only mentioning methanol-compounds or where methanol is applied as a component in a test solution).

Within the context of the present mapping of methanol the most relevant/important rules regarding methanol seem to be:

- The Communication No. 14003, which concerns a dispensation scheme allowing for certain recreational organizations to use methanol was established due to an *excessive use* of methanol in these organizations. The dispensation scheme was established to ensure that the use of methanol would only take place in well-organized organizations.

- A B-value for methanol of 0.3 mg/m³ (related to the individual company's contribution to air pollution).

2.2.1.2 Substitution projects

On www.catsub.dk (a site presenting more than 300 examples of substitution projects) five projects are described concerning substation of methanol[2]. The five examples are described below.

1) A Danish company within the rubber and plastic industry had experienced problems with too large amounts of methanol in the air in their production hall. The solution was either increased ventilation or substitution of methanol. They attempted to substitute with water (which did not work) and finally ethanol, which presumably other similar companies had used with success. The final status of the substitution project is not described on the site.

2) Another Danish company (within the sector of laboratories and hospitals) successfully replaced methanol with ethanol – in their process of immune-blotting.

3) Substitution of methanol with ethanol was also the solution for another company, who used methanol in determination of hydrazine in water for boilers. After substation they simply used 96% ethanol in the same procedure.

4) The employees in a company were uncomfortable with using a metal glue product (Threebond) containing approx. 75% methanol. They thus switched to the metal glue K200 K-Klæber from Kemitura. They, however, doubt whether the change had any significant impact on the working environment.

5) The fifth company manufactures conveyer-belts, which need to be glued together. One of their glue-products contained methanol. The company asked BST (the occupational health service) to suggest substitution options to the company producing the glue. BST did so, and suggested a substitution to ethanol or a mix of ethanol and gamma-butyrolacton, which would decrease the risk by a factor of 40. The status of the substitution project is not known.

It is mentioned that in some cases methanol can be diluted with water, thus lowering the risk[3]. However, the examples above indicate that it is possible to substitute methanol with ethanol in certain cases.

2.2.1.3 Information campaigns

A general search for information campaigns related to methanol only resulted in a few hits – all concerning the aspartame-methanol issue, which is described in further details in later sections.

No other relevant information campaigns dealing with methanol have been identified.

2.2.1.4 Ecolabels

Contact to 'Ecolabeling Denmark' (the Danish Ecolabel Institute handling the Nordic Ecolabel as well as the EU Ecolabel) revealed that methanol is regulated in several criteria documents.

Methanol is regulated in pretty much of all of their technical/chemical criteria (i.e. criteria covering cleaning products, floor care products, etc.) primarily due to the classification of methanol and the fact that it is a VOC. The general picture is that they restrict the use of chemical substances/products which are classified with a certain number of risk phrases – and methanol is often covered by these risk phrases. As an example: In 'Chemical construction products' (such as

[2] http://www.catsub.dk/sog.aspx?sogeord=methanol
[3] http://employment.alberta.ca/documents/WHS/WHS-PUB_ch033.pdf

glue) methanol is not allowed, since '*No chemical substances must be assigned one of the following risk phrases or combinations thereof: R23, R24, R25, R26, R27, R28, R33, R39, R49, R48, R68*." Methanol is classified with the risk phrases R23, R24, R25 and R39.
The criteria behind 'Furniture and fitments" also restricts the use of methanol. In the criteria it is stated that "*Chemical products used in the production of Nordic Ecolabeled furniture and fitments must not be classified in accordance with table 2*". Table 2 lists – among others – chemical products classified as toxic, i.e. with risk phrases R23, R24, R25, R39 – which thereby covers methanol. However, according to the contact person from Ecolabeling Denmark it is possible to use a chemical product which contains methanol, however then the amount of methanol would be so small, that the overall chemical products is not classified with the risk phrases. Methanol is also indirectly regulated in the requirement of "*the content of VOC in glue must not exceed 3 % by weight*".

If the industry claims that it is not possible to avoid methanol during production, exemptions can be made.

2.2.2 Other 'legislative initiatives' in the EU

2.2.2.1 Illegal use of methanol in wines

According to www.eur-lex.eu there seems to have been some issues regarding (illegal) use of methanol in wine – especially in Italian wines. However, documents describing the full extent of the problem seem not publicly available.

2.2.2.2 Czech Republic banns sale of liquor with >20% alcohol due to methanol poisoning

According to an article[4] published on September 17, 2012 the Czech Republic has banned the sale of liquor containing 20% or higher content of alcohol. The reason was the death of at least 20 people (and dozen others being seriously injured) after consuming methanol-tainted spirits. According to the article the poisonings have raised questions about the effectiveness of the EU legislation and Czech safeguards against bootleg alcohol. One of the injuries was a 51 year old car factory worker, who bought a bottle of rum from a street kiosk. He had a few shots, but thought it tasted strangely. Four days later he became blind. Doctors are not optimistic he will ever see again. Alarm is growing since 8 people in Slovakia also fell ill after drinking plum brandy (bought in the Czech Republic). Poland in response to the crisis banned the import and sale of Czech-made spirits for 30 days. 23 people have now been arrested and the police officials believe that the tainted alcohol came from a single source. The Czech Republic is set to lose 40 million £ a month in liquor taxes as well as a daily loss of 10.7 million £ in revenue for bars, restaurants etc.

2.2.2.3 Italian, Polish and Finnish legislative initiatives

Italy, Poland and Finland have further restrictive requirements regarding the use of methanol in household products and for professional uses. However, documents describing the full extent of these requirements are not publicly available in English.

2.2.2.4 Suggestions to the EU Parliament on increasing amount of allowed methanol in fuels

According to a 'Parliamentary question' from February 2012[5] the reason for the limit of 3% methanol in fuels is not feasible since methanol is seen as an environmentally friendly fuel (during combustion it only produces CO2 and water). The Commission is asked to increase the allowed limit of methanol and furthermore equate it with ethanol. The answer from the Commission (by Connie Hedegaard) states that "*Adding a larger percentage of methanol can damage vehicle engines. It would also have a negative impact on vehicle warranties, drivability and durability, and also*

[4] http://www.nytimes.com/2012/09/18/world/europe/czechs-ban-hard-liquor-sales-after-methanol-poisonings.html?_r=0
[5] http://www.europarl.europa.eu/sides/getDoc.do?pubRef=-//EP//TEXT+WQ+E-2012-001342+0+DOC+XML+V0//DA

have an impact on such vehicle emissions. Moreover, there will be an increased gasoline vapor pressure when methanol is added, which can cause air quality problems. Finally, the energy content of methanol is about half the energy content of gasoline, making it less effective as an additive than ethanol, which has about two-thirds of the energy content of gasoline. The European Commission proposes not to increase the limit".

2.2.2.5 Suggestion to the EU Parliament on restricting use of methanol in washing fluids

Use of methanol in washing fluids is allowed in Finland. Since washing fluids containing methanol are cheaper than the alternatives (i.e. vodka or other alcoholic beverages), this caused an inappropriate use – unfortunately also as an intoxicating drug. This again caused the death of several hundred people, and the Parliament was asked (April 2010) as to what they intend to do regarding this issue[6]. No answer from the Commission has yet been published.

2.3 Deficiencies in current legislation

2.3.1 Illegal use of methanol containing washing fluids in Denmark

According to National Danish Statutory Order No. 857 of 05/09/2009 on "limitations in use of certain dangerous chemical substances and products for certain purposes" it is in § 5 stated that "Methanol must not be used in engine coolants, in anti carburetor freezing and deicing fluids (e.g. washing fluid).The prohibition does not apply to methanol-water mixtures for use in aircrafts." The Statutory Order is only valid in Denmark.

There are some indications of use of methanol in washing fluids. On an auto-index homepage[7] it is described how you can make your own washing fluid by use of methanol. They further state that typically washing fluids (bought in stores) contain between 5 and 10 % methanol. However, a further search after washing fluid products containing methanol revealed no hits. Thus, the problem seems not to be of large proportions – at least not in Denmark.

The problem with methanol in washing fluids may, however, be more significant in other EU countries, since the Statutory Order banning the use of methanol in washing fluids only applies to Denmark. It is up to the individual Member States to decide how they further regulate substances classified as acutely toxic in the CLP Regulation.

2.3.2 Methanol selected as a CoRAP substance

The Community Rolling Action Plan (CoRAP) specifies the REACH registered substances that are to be evaluated over a period of three years. Thus, CoRAP is part of the 'evaluation system' in REACH.

Methanol has been proposed as a CoRAP substance due to its high volume and wide dispersive use for both professionals and consumers, high exposure for workers and high release to the environment. The substance is furthermore toxic by every exposure route (oral, dermal, inhalation) (CoRAP, Methanol).

Poland has the task of preparing the substance evaluation on methanol, however, the evaluation is meant to take place in the years 2012 – 2014, thus no documents have yet been released.

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[6] http://www.europarl.europa.eu/sides/getDoc.do?pubRef=-//EP//TEXT+WQ+E-2010-2035+0+DOC+XML+V0//DA
[7] http://www.weindex.info/11/2012/05/hvordan-du-far-din-egen-sprinklerveske.html

3. Manufacture and uses

3.1 Production

3.1.1 How is methanol made?

Methanol can be made from a wide array of feedstocks, making it one of the most flexible chemical commodities and energy sources available today. To make methanol, you need first to create synthesis gas, which has carbon monoxide and hydrogen gas as its main components. While natural gas is most often used in the global economy, methanol has the distinct advantage of 'polygeneration' - whereby methanol can be made from any resource that can be converted first into synthesis gas. Through gasification, synthesis gas can be produced from anything that is or ever was a plant. This includes biomass, agricultural and timber waste, solid municipal waste, and a number of other feedstocks.

In a typical plant, methanol production is carried out in two steps. The first step is to convert the natural gas into a synthesis gas stream consisting of CO, CO_2, H_2O and hydrogen. The second step is the catalytic synthesis of methanol from the synthesis gas. Each of these steps can be carried out in a number of ways and various technologies offer a spectrum of possibilities which may be most suitable for any desired application.

Conventional steam reforming is the simplest and most widely practiced route to synthesis gas production:

$$2\ CH_4 + 3\ H_2O \rightarrow CO + CO_2 + 7\ H_2 \text{ (Synthesis Gas)}$$

$$CO + CO_2 + 7\ H_2 \rightarrow \mathbf{2\ CH_3OH} + 2\ H_2 + H_2O$$

This process results in a considerable hydrogen surplus, as it can be seen. If an external source of CO_2 is available, the excess hydrogen can be consumed and converted to additional methanol. This is just the most common of a number of ways to produce methanol (The Methanol Institute, 2012).

3.1.2 The most important producers – globally, the EU and in Denmark

According to exportpages.com the following producers of methanol exist on the global market:

TABLE 6
GLOBAL PRODUCERS OF METHANOL (SOURCE: EXPORTPAGES.COM).

Producer	Country
Alfa Aesar GmbH & Co.	Germany
Celanese Chemicals Europe GmbH	Germany
Red Triangle International Trading Co. Ltd.	China
Ciech S.A.	Poland
Advanced Technology & Industrial Co. Ltd.	China
Brenntag AG	Germany

China XianDing Chemical International Company	China
Fisher Scientific International Inc.	USA
Hansa Group AG	Germany
Jinan Haohua Industry Co. Ltd.	China
Sigma Aldrich Corp.	USA
Sumitomo Chemical Co. Ltd.	Japan
TCI Tokyo Chemical Industry Co., Ltd.	Japan
VWR International LLC	USA
WISTEMA Chemiehandel % Recycling GmbH	Germany

NB: Several more producers exist.

Recently (2008) a Methanol REACH Consortium has been established, in which the main manufactures of methanol have joined forces in order to ease their REACH compliance activities (presumably activities related to registration). On their webpage[8] they list the members, who can be seen as the main producers within the EU.

No producers of methanol have been located in Denmark.

3.1.3 Volume of methanol produced globally

The methanol industry spans the entire globe, with production in Asia, North and South America, Europe, Africa and the Middle East. Worldwide, over 90 methanol plants have a combined production capacity of about 75 million metric tonne. The global methanol industry generates $36 billion in economic activity each year, while creating over 100,000 jobs around the globe.

TABLE 7
WORLD AND CHINESE CAPACITY OF PRODUCING METHANOL (SOURCE: W.SEUERS – JJ&A EUROPE).

Mio.tonne/yr methanol Region	Capacity 2008	Capacity 2009	Capacity 2010	Capacity 2011	Capacity-expected 2012	Capacity-expected 2017
World	59.5	67.9	76.7	86.8	95.2	109.2
China	19.6	25.3	30.6	38.4	46.0	56.5

In 2010, global methanol *demand* totaled about 45.6 million metric tonne and is expected to exceed 50 million metric tonne in 2011, driven in large part by the resurgence of the global housing market and increased demand for cleaner energy. Worldwide, it is expected that 100,000 tonne of methanol are used as a chemical feedstock or as a transportation fuel - each day. Each day more than 80,000 tonne of methanol are shipped from one continent to another (The Methanol Institute, 2012).

Around 50 million tonne of methanol produced globally are, however, in direct mismatch to the amounts of methanol used within the EU (data from Euro stat - see section 3.2.2), which is reported to be approx. 55 million tonne in 2010. According to these figures the EU used more than the world production of methanol in 2010. Either there is a large difference between different years because of accumulation of methanol on stock or the large difference illustrates the difficulty of giving exact numbers for the global production of methanol.

[8] http://www.reachcentrum.eu/en/consortiumslt/consortia-under-reach/methanol-reach-consortium.aspx

According to W. Seuser - JJ&A Europe, China is the leading producer of methanol – approx. 50 % of the world's methanol is produced in China. Furthermore China imports approx. 3 mio. tonne of methanol each year. Iran has a capacity of producing 5 mio. tonne – which is 1/3 of the capacity in the Middle East.

3.1.4 Volume of methanol produced in the EU

It is stated on the homepage of ECHA that the total tonnage of methanol within the EU is between 1 mio. and 100 mio. tonne/year. However, this large range is not only for production of methanol, but also covers import of methanol to Europe.

According to data from W. Seuers - JJ&A EUROPE the amount of *produced* methanol in the EU is around 9 mio. tonne (in 2011) and is not expected to increase significantly in the coming years.

3.1.5 Volume of methanol produced in Denmark

Methanol is *not produced* in Denmark – however a number of companies use methanol during production of other products (see later).

3.2 Import/export

3.2.1 Import and export of methanol in Denmark

According to DST (Danish Statistics) Denmark imported/exported the following amount of methanol (as pure methanol) in the years from 2007 – 2011:

TABLE 8
IMPORT/EXPORT OF PURE METHANOL IN DENMARK FROM 2007 – 2011 (WWW.DST.DK; SITC KODER). 'USED IN DK' IS CALCULATED AS IMPORT MINUS EXPORT (SINCE NO PRODUCTION TAKES PLACE IN DENMARK

Year	Import (tonne)	Export (tonne)	Used in DK (tonne)
2007	61,679	635	61,044
2008	58,601	71	58,530
2009	37,487	46	37,441
2010	47,637	795	46,842
2011	47,573	5,367	42,206

According to DST (KN codes) methanol is also imported 'hidden' in products such as catalysts, reaction initiators, accelerators etc. – since these products are imported as a product diluted in methanol. A total amount of 770 tonne of these products was imported in 2011. However it is unknown how large a part of this volume is methanol. Pure methanol is also imported within a category named "Wood tar oils, resin acids, crude methanol, vegetable pitch, brewers pitch and similar". A total amount of 1431 tonne of these types of mixtures is imported in 2011 – however it is not possible to get information on how large a part 'crude methanol' constitutes of this amount. However these amounts constitute a very small part compared to the total import of pure methanol (as seen in the table above).

3.2.2 Import and export of methanol in the EU

According to Eurostat the following information is available regarding import and export of pure methanol into and out of the EU.

TABLE 9
IMPORT AND EXPORT OF PURE METHANOL WITHIN THE EU (SOURCE: EUROSTAT).

Year	Import (tonne)	Export (tonne)	Used in EU (tonne)
2008	67,159,387	1,346,462	65,812,925
2009	58,197,590	1,094,769	57,102,821
2010	56,753,743	1,559,599	55,194,144
2011	65,042,018	1,161,492	63,880,526

Thus the import of methanol in Denmark (47,573 tonne in 2011) equals 0.07 % of the total import into the EU.

As discussed earlier the reported use of 55 million tonne of methanol in the EU in 2010 is in direct mismatch to the earlier presented worldwide production of methanol of around 50 million tonne.

3.3 Use

According to the Methanol Institute (2012) methanol has been one of the world's most widely used industrial chemicals since 1800's. From paints and plastics, furniture and carpeting, to car parts and windshield washing fluid, methanol is a chemical building block used in making hundreds of products used in daily life. Methanol is also an emerging energy fuel for running cars, trucks, buses, and electric power turbines. According to SPIN methanol is also categorized under the label "very wide range of applications".

3.3.1 Main uses of methanol in Denmark in 2011

Schleicher et al. (2009) performed a rather extensive search on main uses of methanol in 2006 in Denmark. Schleicher et al. (2009) used data from SPIN as well as DST (Danish Statistics), combined with direct contact to a large number of Danish companies using methanol to provide not only identification of the main uses, but also estimates on their total yearly consumption of methanol (his figures for 2006 are presented in Table 10).

It is assumed that the main uses they identified in 2006 are still the main uses in Denmark in 2011. However, a further research has been performed to verify this, and potentially new uses have been added – as well as updated volume figures (if available) for 2011. Only information from companies which use methanol is presented here.

TABLE 10
MAIN USES OF METHANOL IN DENMARK IN 2011 (BASED ON SCHLEICHER ET AL. (2009) AND FURTHER DIRECT CONTACT TO NEW/ADDITIONAL USES IN THE FALL 2012.

Use category – 2011	Consumption (tonne) – 2011	Consumption (tonne) – 2006 (acc. to Schleicher)
Production of glue**	20,000 – 25,000	32,000
Production of biodiesel**	37,500	14,000
Production of medicine	210	1189
As solvent and a reagent** - primarily pesticide production	7,000 – 10,000	7,180
The Oil and Gas Industry	5,417	5,200
As raw material to produce hydrogen**	1000	Not found as main use in 2006.

Used in purification/cleaning of materials	285	Not found as main use in 2006.
As carbon source in waste water treatments	500*	Not found as main use in 2006.
Total	**79,912**	**59,569**

* Qualified guess from Helm Scandinavia who sells methanol to Danish Waste Water Treatments. However they believe that most waste water treatment facilities in Denmark use ethanol or other forms of carbon sources. ** The use volumes listed for 2011 represent an average over the recent years.

Schleicher et al. (2009) found (through contact with several main users of methanol) that besides the above mentioned main uses of methanol, other uses include:

- As rinsing agent in the plastic/rubber industry
- As carbon source in wastewater treatment plant with nitrogen removal
- As fuel for speedway motorbikes, go-karts, model airplanes etc. This amount may be relatively large, since it has been necessary to establish a dispensation scheme for the use of methanol in these types of products
- Some minor pharmaceutical companies may use small amounts of methanol for different purposes
- Denaturation of ethanol

According to the Danish Product Register there are also the following additional uses of methanol in Denmark (as of 2012):
- Biocides
- Binding agents
- Fuel additives
- Impregnating agents
- Laboratory chemicals
- Paint and lacquers
- Rust protection products
- Fillers

Within the present study it has been attempted to clarify the amounts used by these minor uses (if found, they are also listed in Table 10).

3.3.2 Main uses of methanol in EU
As presented in Figure 3 it can be seen that the (presumably) dominant uses of methanol in the EU are related to production of:

- Formaldehyde
- MTBE (Methyl t-butyl ether)
- DMT (Dimethyl Terephthalate)
- Methylamines
- Gasoline Blending & Combustion
- DME (Dimethyl ether)
- Acetic Acid
- Methyl Methacrylate
- Methanethiol
- Methyl Chloride
- Biodiesel
- Fuel cells

The data originates from W. Seuers – JJ&A EUROPE.

3.3.3 Dominant uses of methanol in the world

According to a Workplace Health and Safety (2010) the main uses of methanol worldwide are:

In the production of a number of chemical products, including:

- Formaldehyde
- Methyl t-butyl ether (MTBE)
- Acetic acid
- Methyl methacrylate
- Gasoline

As a solvent in:

- Antifreeze
- The oil and gas sector to prevent the formation of gas hydrates at low temperatures
- (and absorption agent) in gas scrubbers
- Drilling mud in oil fields
- Refrigeration systems
- Laboratories
- Base ingredient for a variety of oilfield chemicals such as corrosion inhibitors and demulsifiers

And as an ingredient in:

- Shellac
- Paint
- Varnish
- Paint thinner
- Plastics
- Inks
- Dyes
- Cements
- Nail polish remover
- Artificial sweeteners
- Automotive windshield washing fluid
- Motor fuel (fuel blend for race cars)

Data from W. Seuers - JJ&A EUROPE reveals the following volumes of methanol used (world-wide) in certain applications:

TABLE 11
VOLUMES OF METHANOL USED IN DIFFERENT WOLRD WIDE APPLICATIONS (W. SEUERS - JJ&A EUROPE).

Use category World-wide	2007 (1000 tonne)	2008 (1000 tonne)	2009 (1000 tonne)	20010 (1000 tonne)	2011 (1000 tonne)	2012E (1000 tonne)	2017E (1000 tonne)
Formaldehyde	15,084	15,159	14,163	16,284	17,571	18.290	22.786
Acetic Acid	4,004	4,278	4,244	4,985	5,190	5,440	6,628
MTBE	7,185	6,998	6,912	7,376	7,821	7,945	9,555
Methyl Methacrylate	1,330	1,329	1,262	1,409	1,462	1,516	1,854
DMT	488	487	467	453	457	463	495
Methanethiol	417	432	426	420	445	462	571
Methylamines	1,140	1,167	1,132	1,280	1,375	1,417	1,698
Methyl Chloride	1,685	1,713	1,692	1,781	1,858	1,929	2,467
Gasoline Blending & Combustion	2,798	3,091	4,905	6,158	7,143	7,656	10,521
Biodiesel	817	909	832	902	1,210	1,066	1,243
DME	933	1,825	3,338	3,978	4,265	4,374	5,635
Fuel Cells	7	10	5	5	6	7	9
Methanol-to-Olefins	5	7	7	702	2,479	2,959	9,833
Others	3,170	3,038	2,824	3,307	3,594	3,730	4,553

3.3.4 Examples of methanol concentration in typical products

A general search of product safety sheets containing methanol revealed the following examples of products containing methanol and the respective methanol concentration.

- Transparent building silicone (< 1% methanol)
- Glue (<0,2% methanol)
- Building silicone (<1 % methanol)
- Building foam (during hardening small amounts of methanol are released)
- Mounting glue (during hardening small amounts of methanol are released)
- Parquet glue (during hardening small amounts of methanol are released)
- Contact glue (0,1-1,1 % methanol)
- Sealants (<1 % methanol)
- Gelled solvent for cleaning epoxy paint from zinc coated holders (5-10%)

3.3.5 Historic development of volumes of use in Denmark 2000 – 2010

The table below describes the amount of methanol used in Denmark from 2000 – 2010. Data on a number of preparations (chemical products) is also presented. The data is from SPIN – the Nordic Database on Substances in Preparations in the Nordic Countries – and are non-confidential. SPIN builds on data from the national product registers.

TABLE 12
AMOUNT OF METHANOL USED IN DENMARK FROM 2000 – 2010 (SOURCE: SPIN).

Year	Amount (tonne)	Number of preparations
2000	9,178.6	1,175
2001	9,200.9	1,314
2002	11,753.1	1,422
2003	12,144.2	1,777
2004	15,961.5	1,891
2005	21,737	2,002
2006	35,572	2,082
2007	33,674.5	2,153
2008	27,933.6	2,025
2009	23,611.7	1,951
2010	23,005.3	2,029

It should here be emphasized that the data reported in SPIN builds upon data from the Danish Product Register – in which only companies using more than 100 kg methanol per year are included (and of course only if the companies remember to register). Furthermore, it is only 'dangerous chemical products' that are registered – thus a chemical product with a very low amount of methanol may not be registered, since the chemical product is not classified as 'dangerous'. Finally, data in SPIN is only presented if at least 4 companies have reported use in the respective category – this is due to competitive considerations. The large difference between the consumption data from SPIN i.e. the Danish Product Register (23,005.3 tonne in 2010) and the total reported use-volume (79,912 tonne in 2011) retrieved by direct contact to the dominant companies (see table Table 10) is due to the fact that some of the companies did not report the amount they used to the Product Register.

It should also be mentioned that the Danish Product Register does not contain information regarding content of chemicals in non-chemical products (e.g. computers, chairs, etc.) – it only contains information regarding chemical products (as for instance windscreen washing fluid). However, methanol is not expected to be found in non-chemical products due to its chemical properties (it is very volatile) and no chemical products containing above 10% methanol have been identified on the Danish market in this project.

3.3.6 Historic development of volumes of use in Scandinavia 1999 – 2010

The amount of methanol used in Sweden, Denmark, Finland and Norway respectively is presented in the figure below.

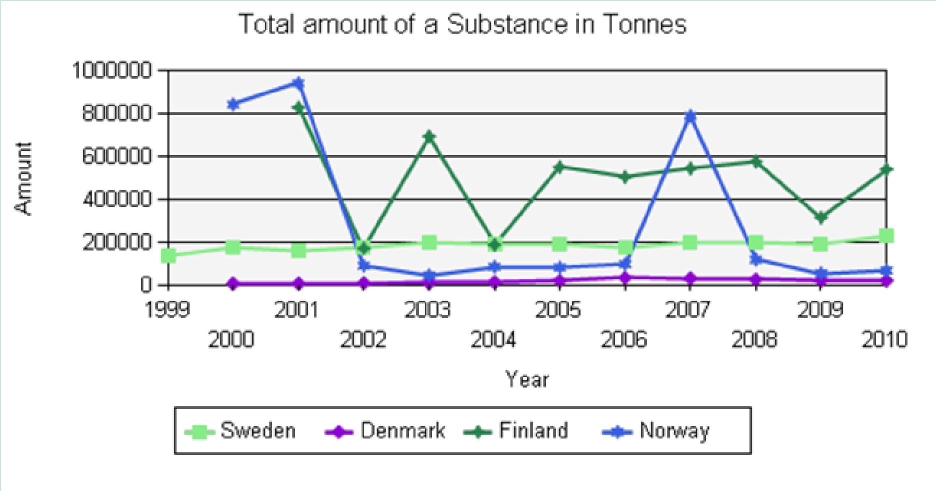

Figure 2

Amount of methanol used in Sweden, Denmark, Finland and Norway – from 1999 to 2010 (Source: SPIN).

3.3.7 Historic development of volumes of use in the EU 2007 – 2017

According to data from W. Seuers - JJ&A EUROPE the distribution of the use of methanol in the EU is as demonstrated in the figure below. The majority of the methanol is used in formaldehyde production. Secondly it is the use of methanol in the production of MTBE that dominates. Furthermore the increase in total demand in Europe (and Russia) is not expected to increase significantly during the coming years.

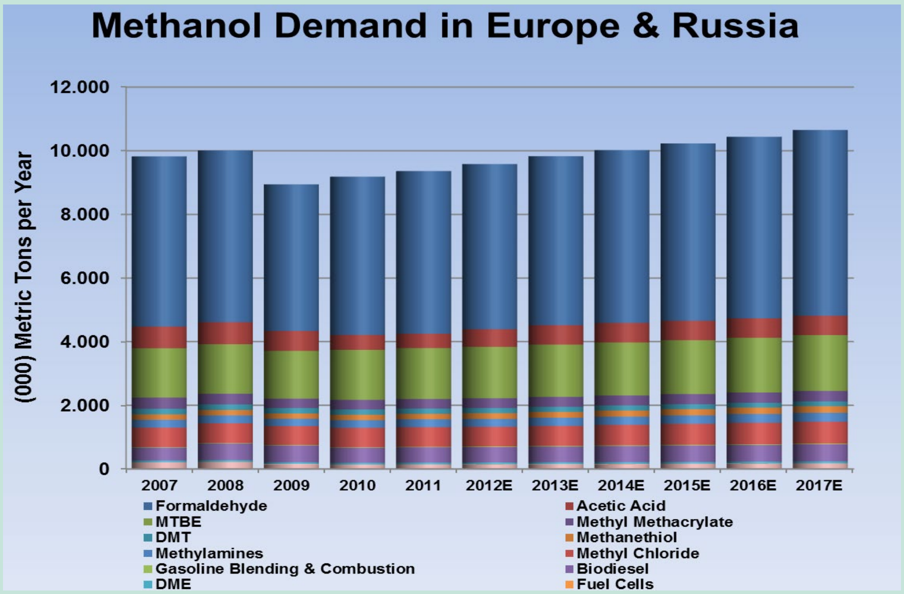

Figure 3

Historic development in use of methanol in Europe and Russia from 2007 – 2017 (Source: W. Seuers - JJ&A Europe).

3.3.8 Historic development of volumes of use globally from 2007 – 2017

According to data from M. Seuers - JJ&A EUROPE the distribution of the use of methanol globally is as demonstrated in the figure below.

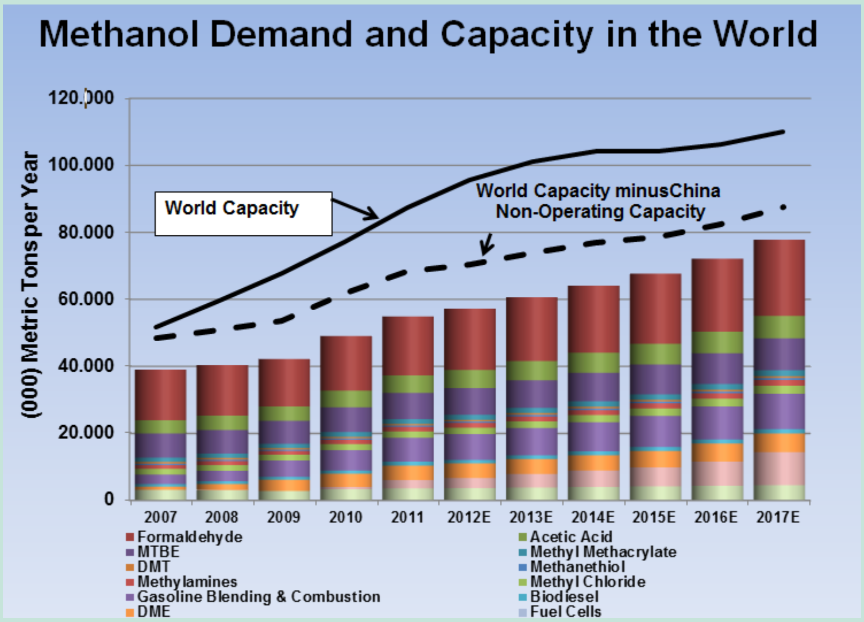

Figure 4

Historic development in the use of methanol globally from 2007 – 2017 (source: W. Seuers – JJ&A Europe).

3.4 Trends

3.4.1 Methanol instead of bioethanol in the transport sector

According to an article from December 2011[9] it is stated that China is investing heavily in methanol and DME as fuel for transport and in households. The same article also states that the Danish Government believes that methanol and DME are better suited for an energy system that is purely based on renewable energy. Methanol can be produced by thermal gasification of biomass, which subsequently is converted to liquid fuels such as methanol and DME. The article also describes that it is expected to be possible to produce methanol synthetically by pulling carbon atoms out of the smoke from combustion facilities and combine them with hydrogen. Therefore this indicates that the production and use of methanol are most likely to increase in the future – especially in China. This increase in the Chinese production of methanol is verified by data received from W. Seuser - JJ&A Europe that estimates an increase of the Chinese production of around 220% from 2010 to 2017.

3.4.2 Methanol producing facilities under consideration in Denmark

According to the article from December 2011[10] three organizations are currently (2011) considering establishing methanol production facilities in Denmark. Lars Thomsen is working on plans to establish a facility in Grenå which can convert 200,000 tonne of wood chips to 150,000 tonne of methanol per year. The company TK Energy in Køge has similar plans of establishing a methanol

[9] http://www.biopress.dk/PDF/FiB_38-2011_01.pdf
[10] http://www.biopress.dk/PDF/FiB_38-2011_01.pdf

facility. Their ultimate goal is to build a facility with a capacity of 1,000 MW for biomass and waste. The facility is expected to be ready within 10 years. Finally, DONG Energy has calculated that the economy in producing methanol seems reasonable.

3.4.3 Recent establishment of a 'Danish Methanol Union'

A Nordic Bio-Methanol Conference was held in Denmark on the 27th of October 2011. The topic was "Recognition of bio-methanol on equal footing with other green alcohols". The goal of the conference was to pave the way for the use of bio-methanol as the best alternative energy source. Recently the organization 'Danish Methanol Union' has been established – with the goal of promoting production and use of methanol in Denmark – partly based on agricultural waste and partly on recycling carbon dioxide in power plant smoke.

3.4.4 Increase in global methanol production expected

According to the Methanol Institute, the global production has passed the 50 million tonne per year and has been continuously growing every year. According to the Institute, the big growth, both in production and consumption, takes place in particular in China. The Chinese growth is in new areas like fuel (as blending or as DME) and MTO (methanol to olefins). According to W. Seuers & - JJ&A EUROPE the demand on methanol related to DME production (based on methanol) will increase significantly in the coming years. China has been in front when it comes to widespread commercialization of methanol fuels, but other countries are now making rapid progress.

As seen in the figure below the methanol demand in Asia is expected to increase significantly compared to the demand in Europe.

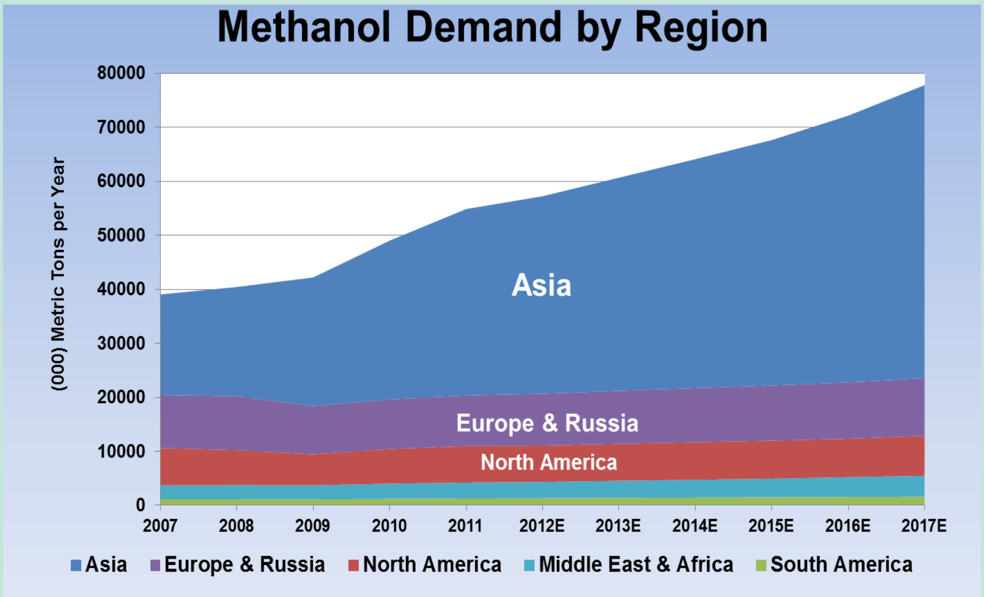

Figure 5

Expected development in methanol demand in Asia, Europe and North America (Source: W. Seuers – JJ&A Europe).

A report from GBI Research on 'Methanol Market to 2020'[11] presents a comprehensive analysis of the global methanol market covering all major parameters. According to W. Seuers – JJ&A

[11] http://www.marketwatch.com/story/methanol-market-to-2020-growing-fuel-applications-strong-demand-for-chemical-intermediates-and-cheaper-feedstock-from-the-middle-east-to-drive-growth-2012-06-28

EUROPE there is big potential in producing methanol for use in the transport sector. The shift to methanol should be very easy, since it only requires minor alterations in the engines (oil resistant parts should be changed to alcohol resistant parts).

3.4.5 Methanol a promising new component in fuel cells

At present, methanol is valued for its capability as a clean energy of the future. Methanol has been utilized as a direct fuel resource and as an additive (like MTBE). But, the application attracting the most attention now is the methanol-reformed type fuel cell. In this application, methanol is resolved to extract hydrogen, and the energy generated in the course of this reaction of hydrogen with oxygen in the air is harnessed as electricity. Automobiles using this power source will have high environmental performances due to greatly reduced CO_2 and any other exhaust gas emissions (according to the manufacturer). In addition, their energy efficiency will be superior to that of gasoline powered cars[12]. Thus, it seems that methanol potentially can play a more significant role in fuel cells in the future - perhaps also in Europe.

[12] http://www.mgc.co.jp/eng/products/lm/25.html

4. Waste management

4.1 Methanol's fate in 4 typical end-of-life treatments

In this section a short description of the fate of methanol in four typical end-of-life treatments is presented.

4.1.1 Methanol's fate in incineration facilities

Methanol is completely converted into CO_2 and water when burned in incineration facilities – according to the following formula:

$$2\ CH_3OH + 3\ O_2 \dashrightarrow 2\ CO_2 + 4\ H_2O$$

Thus the small amounts of methanol used as ingredient in different products and articles will not give cause to negative environmental effects when the products are burned in incineration facilities.

4.1.2 Methanol's fate when handled as 'dangerous waste'

In Denmark (and the EU), methanol is considered dangerous waste and thus must be handled as such. In practice it is the different municipalities that are responsible for making sure that dangerous waste from different companies are handled correctly. In Denmark Kommunekemi (which is a company authorized to handle dangerous waste) categorizes methanol as waste category C: Waste with high energy content (liquid waste with a calorific value above 18 MJ/kg and a water content below 50%) (source: direct contact to KommuneKemi). They dispose of the methanol waste by burning it (at temperatures between 1100 and 1300 ^{o}C). As described above burning of methanol result in the formation of CO_2 and water, thus no negative environmental impacts are associated with this. Examples of 'dangerous waste' containing methanol is waste from laboratories (where several different chemicals – including methanol - can be mixed in a container) or untreated biodiesel waste product.

In the US used or waste methanol is also considered a hazardous waste and must never be discharged directly into sewers or surface waters. It may only be disposed of at a licensed facility permitted to handle hazardous waste. Contaminated products, soil or water with methanol must be moved only by registered transporters in approved, properly labeled containers. The recommended disposal method for methanol is incineration for heating value recovery.

4.1.3 Methanol's fate when land filled

Methanol waste must not be land filled. However, it cannot be ruled out that certain products or articles with minor content of methanol may be land filled. When they decompose a small amount of methanol can be released to the atmosphere (as methanol is a VOC); however the degradation rate of methanol in air is rather high (half-life is a couple of days), thus the methanol will quickly be degraded.

4.1.4 Methanol's fate when recycled

The company SRS Engineering Corporation[13] has developed a methanol recovery system that recovers methanol from crude glycerin produced in the biodiesel production process. The system removes water and other contaminants from glycerin and recovers clean, dry methanol with a

[13] http://www.srsengineering.com/MethanolRecoverySystem.aspx

purity exceeding 99.5 %. Thus, 'recycling' of methanol is possible in certain circumstances. A search on the internet has not revealed other types of 'recycling' of methanol, however it may be possible that other recycling-methods have been developed. Land filling of organic waste produces methane which can be converted to methanol, however, this falls into the category of 'production of methanol' rather than recycling.

4.2 End-of-life treatment of the four most important uses in DK

The use of methanol in Denmark is described in section 3.3.1. Below the end-of-life treatment related to applications representing a use of above 1000 tonne of methanol per year is described further.

4.2.1 Production of glue

Contact to a glue manufacturer in Denmark revealed, that they do not have any production waste of methanol, since all methanol is used in the production and converted into other chemical substances. If during the process a fraction of non-used methanol remains, it is recycled back in the production line. The final product (glue) does not contain methanol, thus waste handling of the final product is of no importance.

4.2.2 Production of biodiesel

Contact to a biodiesel manufacturer in Denmark revealed that they do not have any production waste of methanol, since all methanol is converted to other chemicals in the production process. There is no residue of methanol left in the final product – biodiesel – thus end-of-life treatment of this is not relevant.

4.2.3 Use as solvent or reagent

Contact to a manufacturer of pesticides (the use of methanol as a reagent) revealed that they also convert the methanol to other chemical compounds, thus, as such they do not have methanol waste. They do, however, have some waste water which contains unreacted methanol, however, this is used as a carbon-source in their waste water treatment facility, where the methanol is 'consumed' by microorganisms. They further explain, that they receive large quantities of methanol in bulk-tanks, which is then pumped (through a closed system) into a storage facility. The workers that operate this pumping system wear necessary protective equipment (as described in the company's environmental management system). The company also has rules of how to handle spills.

4.2.4 Use in the oil and gas industry

Contact to a representative within the oil and gas industry revealed that methanol is used as a hydrate inhibitor – i.e. it is used to inhibit the formation of certain crystals, which are undesired. Methanol is added to prevent the formation, and afterwards the methanol is released to the ocean in a water solution. They have a permit to release the methanol to the ocean and each year report the amount of released methanol to the Danish Environmental Protection Agency. A very large percentage of the methanol consumed yearly ends up in the ocean (5161 tonne in 2011). The oil and gas industry also consumes a small amount of methanol (250 – 500 kg per day) as fuel in a process, where they remove the oxygen from the air. However, in this situation the methanol is burned, thus no waste is left.

5. Environmental effects and fate

5.1 Environmental effects in soil, water and air

The data in the following sections is (if not stated otherwise) based on information from IPCS from 1997 (IPCS, 1997). It is a globally recognized report regarding environmental and health effects of methanol.

5.1.1 Toxic effects on organisms in the environment

LC50 values in aquatic organisms range from 1,300 to 15,900 mg/L for invertebrates (48 h and 98 h exposures) and 13,000 to 29,000 mg/L for fish (96 h exposure). Methanol is thus of low toxicity to aquatic organisms and effects due to environmental exposure to methanol are unlikely to be observed, except in the case of spills.

Based on oral LD50 values of 0.4 – 14.2 g/kg for monkeys, rats, mice and rabbits (Rowe and McCollister (1981) in US EPA (1994)) it is unlikely that methanol would be toxic to terrestrial animals at environmental levels.

5.1.2 Losses into the environment

Given the high production volume, widespread use and physical and chemical properties of methanol, there is a high potential for large amounts of methanol to be released to the environment, primarily to air. If released to the atmosphere, a vapor pressure of 127 mm Hg at 25 ^{o}C indicates that methanol will exist solely in the vapor phase (HSDB, 2012). Here it should be mentioned that a study on VOC emissions in Denmark (Schleicher et al., 2009) estimated that methanol was released in an amount of 4,777 tonne in 2006. As comparison, the US release of methanol to the atmosphere was estimated to be 171.8 million lbs (77.9 ktonne) in 1993 (American Methanol Institute, 1997).

According to IPCS (1997) emissions of methanol primarily occur from miscellaneous solvent usage, methanol production, end-product manufacturing and bulk storage and handling losses. The largest source of emissions is the miscellaneous solvent use category. The US EPA reported in 1994 that methanol was the most released chemical to the environment (based on data from 23,630 facilities). Estimates of emissions from key processes are given below:

- It is estimated that 1.56 kg methanol is released (uncontrolled) per tonne of methanol produced by low-pressure synthesis of methanol from natural gas (in a model plant with a capacity of 450,000 tonne/year).
- It is estimated that 0.14 kg methanol is released (controlled) per tonne of methanol produced by low-pressure synthesis of methanol from natural gas (in a model plant with a capacity of 450,000 tonne/year).
- It is estimated that about 1% of the methanol used in the production of formaldehyde is released to the environment (during the production process by which formaldehyde is produced by either a metallic silver-catalyst process or a metal oxide-catalyst process).
- An LCA on biodiesel (Jensen et al., 2007) has shown a release of 0.19 kg methanol to the water and 0.01 kg methanol to air per 975 kg biodiesel produced (furthermore 109 kg methanol is used as input to the production process).

Since Denmark has no production of methanol, the information regarding release of methanol per tonne of methanol produced is less important. However, we do in Denmark produce glue by use of approx. 25,000 tonne of methanol. Within this process methanol is converted to formaldehyde. Thus, assuming that all 25,000 tonne of methanol are converted to formaldehyde, this corresponds to a release of 250 tonne of methanol yearly. Denmark also uses approx. 35,000 tonne of methanol to produce biodiesel. Assuming that the release-figures from the LCA on biodiesel (from animal fat) are valid for the entire biodiesel production in Denmark, this corresponds to a release of (0.19/109*37,500,000) 65.4 tonne of methanol to the water and (0.01/109*37,500,000) 3.4 tonne of methanol to the air. However, it is not known whether this amount of methanol to water in fact is waste water from the biodiesel factory – waste water that in Denmark is treated in a waste water treatment facility, where the content of methanol is in fact positive because it helps the microorganisms convert other contaminants to harmless substances.

The global losses of methanol to the air are hence expected to be large, but due to the low toxicity of methanol and high degradation rate in air the environmental effects are assumed to be low, as methanol are degraded to CO_2 and water.

5.1.3 Biodegradation and half-life values

A large number of microorganisms are capable of using methanol as a growth substrate (they completely mineralize methanol to carbon monoxide and water), thus methanol is generally readily biodegraded.

Vapor phase methanol is degraded in the atmosphere by reaction with photochemically-produced hydroxyl radicals; the half-life for this reaction in air is estimated to be 17 days (HSDB, 2012).

If released to soil, methanol is expected to have very high mobility based upon a measured Koc of 2.75. Volatilization from moist soil surfaces is expected to be an important fate process based upon a Henry's Law constant of 4.55X10-6 atm-cu m/mole. Methanol may also volatilize from dry soils based upon its vapor pressure. Biodegradation of methanol in soils is expected to occur rapidly based on half-lives in a sandy silt loam from Texas and a sandy loam from Mississippi of 1 and 3.2 days respectively (HSDB, 2012). Methanol is thus readily biodegradable in soil and sediments, both under anaerobic and aerobic conditions (IPCS, 1997).

Methanol is also readily biodegradable in water and sewage sludge. Studies have showed rapid biodegradation of methanol by sewage organisms - between 66 and 95% within five days (IPCS, 1997). Methanol volatilization half-life in a model river has been estimated to 5.3 days.

5.1.4 Bioconcentration factors and bioaccumulation

Bioconcentration factors (BCF's) of methanol are experimentally measured in aquatic organisms to 0.2. Other studies report a BCF of <10 (for the golden ide) and others again a BCF of 1 (for a carp). A BCF of 28,400 has been reported for a green alga, however it is suggested that this high BCF is anomalous compared to those of other aquatic organisms, probably due to the fact that methanol is metabolized by the algae and the C14-label, which is measured to calculate the BCF value, is incorporated into the algae in metabolic forms other than methanol. Thus, in general the BCF values indicate that methanol does not bioaccumulate in aquatic organisms.

5.2 Main points related to environmental effects of methanol

According to the IPCS criteria document on methanol (1997) the effects of methanol on the environment can be comprised in the following:

- Methanol is **readily degraded in the environment** by photo-oxidation. Half-lives of 7-18 days have been reported for the atmospheric reaction of methanol with hydroxyl radicals.

- Methanol is **readily biodegradable** under both aerobic and anaerobic conditions in a wide variety of environmental media. Many genera and strains of microorganisms are capable of using methanol as a growth substrate.
- Generally **80% of methanol in sewage systems is biodegraded** within 5 days.
- Methanol is a normal growth substrate for many soil micro-organisms, which are capable of **completely degrading methanol to carbon dioxide and water**.
- Methanol is of **low toxicity** to aquatic and terrestrial organisms and does not bioaccumulate.
- Effects due to environmental exposure to methanol are unlikely to be observed, unless it is released to the environment in large quantities, **such as a spill.**

In summary, the IPCS report concludes that unless released in high concentrations, methanol would not be expected to persist or bioaccumulate in the environment. Low levels of release would not be expected to result in adverse environmental effects'. However, care should be taken to prevent spills of large quantities of methanol, in particular spills that reach surface waters.

6. Human health effects

6.1 Health effects of methanol

The data in the following sections is (if not stated otherwise) based on information from IPCS from 1997 (IPCS, 1997). It is a globally recognized report regarding environmental and health effects of methanol.

The toxicity of methanol appears when formate (a toxic metabolite of methanol) generation occurs at a rate that exceeds its rate of metabolism. Since people's metabolism rate is different, there is a wide variability in the toxic dose. Two important aspects governing the toxic impact of methanol are 1) concurrent ingestion of ethanol, which slows the entrance of methanol into the metabolic pathway and 2) the content/status of folate, which governs the rate of formate detoxification.

6.1.1 Inhalation, oral and dermal uptake

Inhalation of methanol is the most common route of entry in an occupational setting. Studies have showed that methanol is rapidly absorbed after inhalation. Around 60-85% of inhaled methanol is absorbed in the lungs of humans. Inhalation studies suggested that an 8-hour exposure to 3,990 mg/m^3 (3,000 ppm) methanol would be necessary before a gradual accumulation of methanol would occur in the body. In comparison the occupational threshold limit value for methanol is in Denmark set at 260 mg/m^3 (200 ppm)[14]. The occupational threshold limit value therefore has to be exceeded with a factor of 15 or more before a gradual accumulation of methanol would occur in the body. Acute inhalation of methanol vapor concentrations below 260 mg/m^3 should not result in formate accumulation above endogenous levels (IPCS, 1997).

Methanol is rapidly absorbed from the gastrointestinal tract with peak absorption occurring in 30-60 minutes depending on the presence or absence of food in the stomach. Ingestion of methanol has been the primary route of exposure in many cases of acute poisoning.

Methanol has an anomalously high diffusion rate through epidermis (the skin). Methanol is hence also marked as a substance that is permeable through skin in the Danish Occupational Threshold Limit value list (Grænseværdilisten[15]). The permeability of epidermis for methanol is 10.4 mg/cm^2 per hour. Skin absorption rate studies have showed that an average of 0.192 mg $methanol/cm^2$ per minute is absorbed through direct contact of the skin to methanol. No other adverse effects of methanol have been reported in humans except minor skin and eye irritation at exposure well above 260 mg/m^3 (200 ppm) (IPCS, 1997).

6.1.2 Distribution and excretion

Methanol distributes readily to organs and tissues in direct relation to their water content. In all mammalian species studied, methanol is metabolized in the liver by oxidative steps to form formaldehyde, formic acid and CO_2. Methanol clears from the body with a half-life of 1 day or more for high doses (> 1 g/kg) and about 3 hours for low doses (< 0.1 g/kg). Methanol is excreted unchanged in the urine and breath. The time for excretion is dependent on the combined action of both direct excretion and metabolism.

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[14] http://arbejdstilsynet.dk/~/media/at/at/04-regler/05-at-vejledninger/c-vejledninger/c-0-1-graensevaerdilisten/c-0-1-graensevaerdilisten-2007%20pdf.ashx

[15] http://arbejdstilsynet.dk/~/media/at/at/04-regler/05-at-vejledninger/c-vejledninger/c-0-1-graensevaerdilisten/c-0-1-graensevaerdilisten-2007%20pdf.ashx

6.1.3 Deadly dose

The deadly one-time dose for humans by ingestion is set to 30 – 250 ml, however as little as 15 ml of a 40% solution has proven deadly. Yet, survival has also occurred by ingestion of up to 600 ml methanol. In animals (rodents) the acute toxicity of methanol is very low – so low that the substance does not fulfill the normal criteria for being classified as a health hazard. The explanation is a different and much quicker metabolic rate in animals (Jensen, 2003). Inhalation of methanol (12 hours exposure of 4000 – 13000 ppm methanol) has also resulted in death (occupational exposure). According to IPCS (1997) the lethal dose of methanol for humans is not known for certain. The minimum lethal dose of methanol in the absence of medical treatment is between 0.3 and 1 g/kg. The minimum dose causing permanent visual defects is unknown.

6.1.4 Short term exposure

Methanol has been recognized as a human toxic agent since the end of the 19th century. The majority of methanol poisonings has resulted from the consumption of adulterated alcoholic beverages. In 1951, Georgia, USA, 323 people consumed whiskey contaminated with 35-40% methanol – 41 of them died. Several other similar cases exist. Nearly all of the available information on methanol toxicity in humans relates to the consequences of acute rather than chronic exposures. Although ingestion dominates as the most frequent route of poisoning, inhalation of high concentrations of methanol vapor and percutaneous absorption of methanolic liquids are as effective as the oral route in producing acute toxic effects, because of its high permeability through skin (HSDB, 2012).

Acute methanol toxicity in humans evolves in a fairly defined way. First a transient mild depression of the central nervous system appears (similar to that of ethanol, but to a much lesser degree). Then follows an asymptomatic latent period, which occurs most commonly about 8-24 hours after ingestion. The latent period is followed by a metabolic acidosis with toxicity to the visual system. Physical symptoms typically include headache, dizziness, nausea and vomiting, followed in more severe cases by abdominal and muscular pain and difficult periodic breathing, which may progress to coma and death – usually from respiratory distress. Death may occur if patients are not treated for metabolic acidosis and blindness may result even if treatment for metabolic acidosis is performed. There is a relatively large degree of variability in the reaction towards methanol, which may be due to simultaneous ingestion of ethanol (which onset the poisoning). The difference may also be due to different levels of folate in the diet (IPCS, 1997).

In treating methanol poisoning a 3-step procedure is common: 1) administration of hydrogen carbonate to combat metabolic acidosis, 2) administration of ethanol to compete as a substrate for alcohol dehydrogenase and 3) haemodialysis to remove methanol from the blood (ICPS on methanol, 1997).

6.1.5 Long term exposure

Information on chronic methanol exposures is limited, however few studies suggest that extended exposure to methanol may cause effects qualitatively similar to those observed from relatively high levels of acute exposure, including in some cases CNS and visual disorders (IPCS, 1997). The most noted health consequences of longer term exposure to lower levels of methanol are a broad range of effects on the eyes. The minimum dose causing permanent visual defects is, however, unknown (HSDB, 2012). Chronic exposure to methanol vapor concentrations of 480-4000 mg/m^3 (365-3080 ppm) has resulted in headache, dizziness, nausea and blurred vision (IPCS, 1997).

The rate of metabolic detoxification, or removal of formate (a toxic metabolite from methanol), is vastly different between rodents and primates and is the basis for the dramatic differences in methanol toxicity observed between rodents and primates. The acute and short term toxicity of methanol varies greatly between different species, toxicity being highest in species with a relatively poor ability to metabolize formate. In such cases of poor metabolism of formate, fatal methanol poisoning occurs as a result of metabolic acidosis and neuronal toxicity, whereas, in animals that readily metabolize formate, consequences of CNS depression (coma, respiratory failure, etc.) are usually the cause of death. Sensitive primate species (humans and monkeys) develop increased blood formate concentrations following methanol exposure, while resistant rodents, rabbits and dogs do not. Humans and non-human primates are uniquely sensitive to the toxic effects of methanol. Overall methanol has a low acute toxicity to non-primate animals (HSDB, 2012).

6.1.6 Most important human exposures to methanol

6.1.6.1 Occupational inhalation of methanol

The most important route of occupational exposure to methanol is inhalation. Sources of occupational exposure include the dissipative emissions of methanol primarily occurring from miscellaneous solvent usage, methanol production, end-product manufacturing and bulk storage and handling (IPCS, 1997).

6.1.6.2 Accidental ingestion of contaminated beverages or fuels

Human exposure to large acutely toxic amounts of methanol via the oral route has principally been noted in a number of individuals, generally resulting through accidental or intentional consumption of methanol of contaminated alcoholic beverages (IPCS, 1997).

The extent of this problem seems to vary considerably dependent on the country. Finland and the Czech Republic have had several incidents of death due to intake of methanol (several hundred in Finland and recently (2012) 20 deaths in the Czech Republic). However, the problem does not seem to be of large proportions in Denmark. According to the Danish 'Poison Control Hotline' (a telephone service offering immediate guidance for poisoning emergencies to all Danes) Denmark experienced 1 case of poisoning due to methanol in 2010, 3 cases in 2011 and so far 2 cases in 2012. The primary causes for the poisoning were (equally divided between) deliberate intake of fuels meant for use in the kitchen, accidental intake of fuel meant for use in model race-cars (by sucking fuel up through a pipe for transfer to another car, etc.) and finally accidental intake of fuel for model race-cars (children who taste the liquid). Besides these incidents a number of less severe exposures have been registered. These cases cover methanol spill on the skin or in the eyes – related to laboratory work or refueling of model race cars.

6.1.7 TDI value for methanol

According to US EPA[16] methanol has a TDI value (non-carcinogen tolerable daily intake) of 0.5 mg/kg (oral).
According to IRIS[17] a NOEL value of 500 mg/kg/day exists for decreased brain weight.
A rather extensive study from Finland (Finnish Institute of Occupational Health, 2009) collected information regarding DNEL (derived no effect values) related to methanol, and prepared the following preliminary DNEL values for workers as well as consumers – in different exposure scenarios:

[16] http://www.popstoolkit.com/tools/HHRA/TDI_USEPA.aspx
[17] http://www.epa.gov/iris/subst/0305.htm

Way of exposure	Worker	Consumer
Acute (15 min) inhalation exposure (systemic effects)	DNEL=270 mg/m3	DNEL=232 mg/m3
Acute dermal exposure (when exposure occurs only via the skin)	DNEL=1,2 mg/kg (max 15 min exposure, total dermal exposure per day DNEL=9,6 mg/kg)	DNEL=1,2 mg/kg (acute max 15 min exposure)
Acute total exposure (inhalation + skin)	DNEL=1,2 mg/kg	DNEL=1,2 mg/kg
Acute local exposure (iho/hengitystiet)	*	*
Acute oral exposure	No relevant. Is connected to misuse.	No relevant. Is connected to misuse.
Long-term inhalation exposure (systemic effects)	DNEL= 67,5 mg/m3 (4 h/d)	DNEL= 27 mg/m3 4 h/d exposure (windscreen fluid scenario); chronic environment exposure DNEL= 4,5 mg/m3
Long-term dermal exposure	DNEL= 9,6 mg/kg	No relevant
Long-term total exposure (mg/kg/d)	DNEL= 9,6 mg/kg	no developed here because no need for this endpoint in our scenarios
Long-term oral exposure	No relevant. Is connected to misuse.	No relevant. Is connected to misuse.
Long-term local exposure	*	*

* Critical effect is caused by absorption through skin or inhalation. Therefore no DNEL value is set for local effects.

Figure 6

Preliminary DNEL values for methanol – workers and consumers (Finnish Institute of Occupational Health, 2009).

The Finnish study also concludes that a preliminary DNEL value for continuous environmental exposure is 4.5 mg/m^3. This exposure is not likely to cause any increase in blood methanol concentration above the endogenic and nutritional concentrations, and it corresponds to the limit values set for air in the USA.

6.1.8 Acute Exposure Guideline Values (AEGL)

AEGLs are intended to describe the risk to humans resulting from once-in-a-lifetime, or rare, exposure to airborne chemicals in the U.S.A. The values are developed in order to help both national and local authorities, as well as private companies, dealing with emergencies involving spills, or other catastrophic exposures. The National Advisory Committee for the Development of Acute Exposure Guideline Levels for Hazardous Substances (AEGL Committee) is involved in developing these guidelines[18].

Below are presented the AEGL values for methanol as prepared by the US EPA.

[18] http://www.epa.gov/opptintr/aegl/index.htm

SUMMARY TABLE OF PROPOSED AEGL VALUES FOR METHANOL [a]						
Classification	**10-Minute**	**30-Minute**	**1-Hour**	**4-Hour**	**8-Hour**	**Endpoint (Reference)**
AEGL-1 (Nondisabling)	670 ppm (880 mg/m³)	670 ppm (880 mg/m³)	530 ppm (690 mg/m³)	340 ppm (450 mg/m³)	270 ppm (350 mg/m³)	No headache or eye irritation (Batterman et al., 1998; pers. commun. Franzblau, 1999; 2000; Frederick et al., 1984; NIOSH, 1980; 1981)
AEGL-2 (Disabling)	11000 ppm [b] (14000 mg/m³)	4000 ppm (5200 mg/m³)	2100 ppm (2800 mg/m³)	730 ppm (960 mg/m³)	520 ppm (680 mg/m³)	No developmental toxic effects in mice Rogers et al. (1993; 1995, abstract; 1997); Rogers (1999, personal communication)
AEGL-3 (Lethal)	#	14000 ppm [b] (18000 mg/m³)	7200 ppm [b] (9400 mg/m³)	2400 ppm (3100 mg/m³)	1600 ppm (2100 mg/m³)	Lethality in humans after oral exposure (AACT, 2002)

[a] Cutaneous absorption may occur; direct skin contact with the liquid should be avoided.
[b] The 10-minute AEGL-2 value and the 30-minute and 1-hour AEGL-3 values are higher than 1/10 of the lower explosive limit (LEL) of methanol in air (LEL = 55,000; 1/10th LEL = 5500 ppm). Therefore, safety considerations against the hazard of explosion must be taken into consideration.
[#] The 10-minute AEGL-3 value of 40,000 ppm is higher than 50% of the lower explosive limit of methanol in air (LEL = 55,000 ppm; 50% of the LEL = 27,500 ppm). Therefore, extreme safety considerations against the hazard of explosion must be taken into account.

Figure 7

AEGL values for methanol (NAS/COT, 2005).

The table shows that the occupational threshold limit value of 200 ppm (8-hour average) will ensure no effects/symptoms from methanol exposure.

6.1.9 Combination effects

Regarding the issue of combination effects involving methanol, the only observed effect is the positive effect of ingesting ethanol together with methanol. Ethanol delays the metabolic rate of methanol and thus lowers the toxic impact.

A study has investigated a potential combination effect of methanol and formate. The study concluded that exposure to combinations of methanol and formate had less effect (developmental effects of formate) than would be expected based on simple toxicity additivity. Thus, in this case there seems to be no negative impact caused by combination effects (Andrews et al., 1998).

6.2 Main points related to health effects of methanol

A summary of the most relevant aspects is presented below:

- Methanol is more toxic to humans than animals (which can be problematic since the classification system is based on studies on animals).
- The most pronounced effect of methanol is damage to the eyes.
- Methanol is readily absorbed through dermal contact, ingestion or inhalation.
- Methanol is rather quickly excreted from the body.

- Few data available on chronic exposure to methanol, however, effects are considered similar to effects related to acute exposure.
- According to IPCS (1997) no studies have been reported on methanol in the peer-reviewed literature on reproductive and developmental effects. Likewise with chromosomal and mutagenic effects and carcinogenic effects.
- Folate-deficient individuals might be at greater risk from inhalation of low concentrations of methanol, compared to normal individuals. Folate-deficient individuals cover pregnant women, the elderly, individuals with poor-quality diets, alcoholics and individuals on certain medications or with certain diseases (IPCS, 1997).

IPCS (1997) concludes that a conventional risk assessment of methanol is not feasible and that an alternative approach should be an evaluation based on blood levels of the most toxic metabolite (formate). Since formate occurs naturally in humans, it would seem reasonable to assume that normal background levels should not pose any risk to health and consequently that levels of human exposure that do not result in levels of blood formate above background levels could be considered to pose insignificant risk. In this respect, based on information from limited studies in humans, it might be concluded that occupational exposure to current exposure threshold limit values (around 260 mg/m^3) or single oral exposure to approximately 20 mg/kg body weight would fall into this category (IPCS, 1997) – i.e. be safe.

In continuation of this it should be mentioned that studies in humans and non-human primates exposed to concentrations of methanol ranging from 13 to 2601 mg/m^3 (10 to 2001 ppm) and the widely used occupational threshold exposure limit value of 260 mg/mg^3 (200 ppm) suggest that exposure to methanol vapor during the normal use of methanol fuel does not pose an unacceptable risk to healthy adults. General population exposures to methanol through air (although infrequently measured) are over 1000 times lower than occupational limits (IPCS, 1997).

The IPCS report on methanol suggests the following in order to protect human health in terms of exposure to methanol:

- Methanol and methanol mixtures should be clearly labeled with a warning of the acute toxicity of methanol. Labels should use the description "methanol".
- Storage, process and drying plants should be designed to protect against fire and explosion risks and exposure of personnel to methanol.
- Workplaces where methanol is present should be provided with adequate ventilation to minimize inhalation exposure. Where necessary, personnel handling methanol should be provided with suitable protective clothing to prevent skin contamination.
- Clinicians should be aware of the latent period and signs and symptoms following exposure to methanol, particularly by ingestion. Consideration associated with the existence of sensitive subgroups should be recognized, including those at increased risk of folate deficiency.
- To avoid misuse, methanol used as fuel should be denatured and should contain a color additive.

7. Monitoring data and exposure

7.1 Monitoring levels

Methanol occurs naturally in humans, animals and plants. It is a natural constituent in blood, urine, saliva and expired air. The average intake of methanol from natural sources varies, but limited data suggests an average intake of considerable less than 10 mg methanol per day (data from 1977 and 1986) (ICPS, 1997). This corresponds to 0.17 mg/kg bw/day (assuming a body weight of 60 kg) and is thus below the US EPA TDI value of 0.5 mg/kg and well below the lowest calculated DNEL of 1.2 mg/kg as presented in section 6.

7.1.1 Exhaled air

Methanol has been detected in the expired air of normal healthy humans ranging from 0.06 – 0.32 µg/liter (1963).

7.1.2 Blood

Blood methanol concentrations of > 500 mg/l are associated with severe acute clinical signs of toxicity (IPCS, 1997). The normal blood concentration of methanol from endogenous sources (i.e. from processes within the body) is less than 0.5 mg/l. However, dietary sources may increase blood methanol levels. Generally, effects on the central nervous system appear above blood methanol levels of 200 mg/l, ocular symptoms appear above 500 mg/l and fatalities have occurred in untreated patients with initial methanol levels in the range of 1500 – 2000 mg/l (IPCS, 1997).

7.1.3 Urine

A mean urinary methanol level of 0.73 mg/l (range 0.3-2.61 mg/l) in unexposed individuals has been detected (IPCS, 1997).

7.2 Risk evaluation of exposures from different sources

7.2.1 Background air

In 1994 methanol was listed as one of the 189 hazardous air pollutants under the Clean Air Act Amendment of 1990. In a US EPA summary (1993) median methanol levels of 6-60 µg/m^3 were found in 52 samples in the USA. In dense traffic sites in Stockholm measurements of up to 94 µg/m^3 were reported (1985) (ICPS, 1997). General population exposures to methanol through air (although infrequently measured) are over 1000 times lower than occupational limits (IPCS, 1997).

7.2.2 Background water

Data on occurrence of methanol in water, particular finished drinking water is limited. However, methanol was detected in finished drinking water at 12 locations in the USA from 1974-1976. Furthermore, methanol was detected in the USA at a mean level of 22 µg/l in rainwater (1985) and levels of up to 80 mg/l were detected in wastewater effluents from a chemicals manufacturing facility in the USA (however no methanol was detected in associated river water or sediments). A high level of 1050 mg/l was detected in condensate waters discharged from a coal gasification plant in North Dakota, USA (1985) (IPCS, 1997).

7.2.3 Food

The two most important sources of background body burdens for methanol are diet and metabolic processes. Methanol is available in the diet principally from fresh fruits and vegetables, fruit juices, fermented beverages and diet foods (primarily soft drinks). The artificial sweetener aspartame is widely used and (on hydrolysis) 10% by weight of the molecule is converted to free methanol, which is then available for absorption (IPCS, 1997). The methanol content of fresh and canned fruit juices varies considerably and may range from 1-640 mg/l. Methanol levels of 27 mg/l (beer), 321 mg/l (wines) and 220 mg/l (spirits) respectively have also been found (IPCS, 1997).

Beverages totally sweetened with aspartame typically contain 0.5 – 0.6 mg aspartame/ml or approximately 195 mg/350 ml soft drink. Puddings use about 100 mg/serving and cereal products about 60 mg/25 ml. The methanol body burden following ingestion of these products could vary from 6-20 mg, but according to IPCS (1997) if aspartame was used to replace all sucrose in the diet, its average daily ingestion would be 8.5 mg/kg, which would be equivalent to 0.85 mg/kg methanol and is thus above the US EPA TDI value of 0.5 mg/kg. However, this data is from 1981/1986, and the use of aspartame has increased significantly since then. It should also be mentioned that according to a UK Aspartame Awareness Campaign[19] the NOAEL value on aspartame does not take into account the fact that 10% of it is converted into methanol in the body. Thus, the organization calls for a revision of the NOAEL value of aspartame.

7.2.4 Methanol in fuels

An increased number of people could be potentially exposed to environmental methanol as a result of the projected increased use of methanol in gasoline. Exposures would principally arise from exhaust, evaporative emissions and normal heating of the engine. Simulation models based on 100% of all vehicles powered by methanol-based fuels predict concentrations of methanol in urban streets, expressways, railroad tunnels or parking garages ranging from a low of 1 mg/m^3 (0.77 ppm) to a high of 60 mg/m^3 (46 ppm). Predicted concentrations during refueling of vehicles range from 30 to 50 mg/m^3 (23-38.5 ppm). For comparison and reference purposes a current occupational exposure limit for methanol in many countries is 260 mg/m^3 (200 ppm) for an 8-h working day. The simulated methanol exposures are therefore well below the occupational threshold limit values for methanol and health effects are hence not expected. However there are uncertainties in the form of lack of complete data. The potential expanded use of methanol in automotive fuels would also increase the potential for dermal exposure in a large number of people (IPCS 1997).

7.2.5 Loading and unloading work related to transport of methanol

The Finnish study (Finnish Institute of Occupational Health, 2009) calculated, based on measured values compared with their preliminary DNEL values, that overall there was no risk associated with exposure to methanol from loading/unloading work related to transport of methanol.

7.2.6 Manufacturing of different products with methanol

According to Finnish Institute of Occupational Health (2009) the majority of methanol in Finland is used as a raw material in formaldehyde production. The Finnish study attempted to create an exposure scenario, which simulated manufacturing processes (assuming that it was 'closed processes'). They operated with acute exposure scenarios (15 min.) and long-term exposure scenarios (8 hour) and found that there was a need for focus on dermal protection – however the scenarios were originally set without protection equipment, which may be assumed to be used normally.

[19] http://www.aspartame-awareness-campaign.co.uk/information.html

7.2.7 Use of methanol in waste water treatment

The Finnish study also evaluated the exposure related to use of methanol in waste water treatment. In Denmark 500 tonne of methanol are estimated to be used in waste water treatment. Inhalation exposure information for workers obtained via measurements was compared to preliminary DNEL values for long term exposure (of 68 mg/m^3) and they concluded that both in terms of inhalation and dermal exposure, there was a need for personal protection. However, again the exposure scenario was set without the use of protective equipment.

7.2.8 Manufacturing of windshield washing fluids

The Finnish study also evaluated methanol exposure related to manufacturing of windshield washing fluid, since windshield washing fluids containing methanol are available on the Finnish market. They concluded that there was a need for local exhaust ventilation and respiratory protection and protective gloves.

7.2.9 Use of methanol as an industrial solvent in extraction processes

The exposure information used is based on pharmaceutical industry use, but similar extraction processes can be used in other industries – for example the manufacturing of raw materials needed in the cosmetics and foodstuff industries. The results varied according to the model used for evaluation (EUSES or Ecetoc). The EUSES model resulted in the need for protective equipment related to dermal exposure (Finnish Institute of Occupational Health, 2009). Similar results were seen when evaluating the use of methanol as solvent in different fields of industry.

7.2.10 Laboratory use of methanol

The Finnish study also examined exposures to methanol related to laboratory use of methanol. However, in this scenario they found no problems (probably due to the fact that laboratories have strict rules regarding protective equipment).

7.2.11 Consumer use of windshield washing fluid

The Finnish study also prepared a preliminary health risk characterization for consumer use of methanol containing windscreen washing fluids (a washing fluid containing 24% methanol). However, this is not relevant in Denmark, since this product is not allowed on the Danish market. They concluded that there was a need for protection against dermal exposure and they also found problems related to inhalation. Since they do not expect consumers to be able to take ‘further risk management measures’, they suggested that the methanol content should be lowered in windshield washing fluid.

7.2.12 Use of methanol based fuels in speedway, drag racing etc.

According to the Finnish study methanol is used as 100% fuel in three speedway motor cycle classes, three drag racing classes and five tractor pulling classes. They found that – if not wearing gloves – there could be a risk related to methanol spillage on the skin when filling the methanol tanks. Thus protective gloves would be needed.

8. Information on alternatives

8.1 Existing and future alternatives

In this section alternatives to the most dominant uses of methanol in Denmark are investigated and described if available. The investigation is based on direct contact to companies representing the dominant uses of methanol. The direct contact is supplemented by research of alternatives presented on the internet. If possible, environmental, health and economic aspects related to the alternatives are described as well.

8.1.1 Alternatives to methanol in the production of glue

Direct contact to a glue manufacturer in Denmark revealed that they do not know of any relevant alternatives to methanol that can be used in the glue production. This is due to the specific chemical process from which they manufacture glue.

8.1.2 Alternatives to methanol in the production of biodiesel

In terms of production of biodiesel some alternatives to methanol can be used. Making biodiesel is defined chemically as a reaction between an alcohol and a long chain fatty acid. Methanol is an easy alcohol to use, however it is possible to use other types of alcohols, for instance ethanol or ethyl alcohol and isopropyl alcohol. However you need to have an alcohol with very low water content in order for the process to be efficient[20]. Direct contact to a biodiesel manufacturer in Denmark revealed that in practice these other types of alcohols are not really an alternative to methanol, since methanol has some process-related advantages (among these a fast reaction rate), that makes methanol the absolute best choice. Furthermore methanol is cheaper to use. According to the Danish biodiesel manufacturer all biodiesel manufacturers in the world use methanol.

8.1.3 Alternatives to methanol used as solvent or reagent

As described in section 2.2.1.2 Substitution projects methanol can in some cases be replaced by ethanol. This was the case for a company within the rubber and plastic industry, which had experienced problems with too large amounts of methanol in the air in the production hall. They changed to ethanol, however the status (and rate of success) of the substitution project is unknown. Another Danish company (within the sector of laboratories and hospitals) successfully replaced methanol by ethanol – in their process of immuneblotting. Substitution of methanol by ethanol was also the solution for a third company, who used methanol in determination of hydrazine in water for boilers. After substation they simply used 96% ethanol in the same procedure. The examples above indicate that it is possible to substitute methanol by ethanol in certain cases. It is not possible within the scope of this project to estimate the economic benefit/cost of changing to ethanol.

Contact to a manufacturer of pesticides (where methanol is used as a reagent) revealed that they do not have any alternative to methanol, since methanol is used in their chemical processes due to the specific chemical properties of methanol. Since methanol is the simplest alcohol, it would not be the same product they end up with if they change to another alcohol. They do have production lines that use ethanol; however, the product here is then quite different. Furthermore, they state that even though methanol is more toxic as a substance than ethanol, the final product based on methanol is less toxic than the final product based on ethanol.

[20] http://make-biodiesel.org/Ingredients/methanol-for-biodiesel.html

8.1.4 Alternatives to methanol used in the oil and gas industry

Contact to a representative within the oil and gas industry revealed that they do have an alternative to the use of methanol as a hydrate inhibitor. It is possible to use monoethylen glycol (MEG) instead, which they also do in some cases. However, the environmental 'profile' of MEG is somewhat similar to methanol, thus there is no environmental advantage linked to using MEG instead of methanol. Furthermore, there are some advantages of using methanol, namely that:

- Methanol besides being able to hinder the formation of the crystals also is able to thaw crystals once they are formed. MEG cannot do this.
- If using MEG a much larger volume is needed than if using methanol.
- Methanol will to a certain degree divide between the phases, whereas MEG primarily will remain in the water phase. It is an advantage, that methanol divides between the phases.
- Methanol is better capable of reaching a starting 'hydratplug' in a pipeline due to its volatility.
- Methanol is seen as a 'green chemical' within the industry. And the industry has many years of experience of handling the use of methanol in an environmentally responsible and safe way.
- Additionally, it is a very expensive task to change from methanol to MEG, once the production line is setup – since all pumping systems, tanks etc. should be changed.

9. Overall conclusions

In this section potential hotspots are described. The potential hotspots are identified through a comparison of information presented throughout the report.

It must be emphasized that the identified hotspots are *potential* – i.e. that it seems that it *might* be areas that need further focus/analysis in order to clarify whether there are issues that need to be regulated further.

The section below starts with a summary of the 'most important elements' from the different sections in the report. This is done in order for the reader to get a better understanding of why certain areas have been identified as potential hotspots.

Finally, it should be mentioned that the present survey of methanol would be relevant for the Polish Authorities, which are responsible for preparing the CoRAP evaluation of methanol.

9.1 Main points from the different sections

9.1.1 Main points from the regulatory sections

- Methanol is not allowed for use in deicing fluids (washing fluids) – except for water-methanol mix solutions, which are allowed to be used in aircrafts (DK).
- Methanol is not allowed for use in engine coolants or in solutions used for preventing the freezing of carburetors - except for water-methanol mix solutions, which are allowed to be used in aircrafts (DK).
- It is not allowed to sell products containing methanol in a concentration above 10% to the general public (with certain exceptions, as for instance hospitals, dentists, etc.) (DK).
- There are rules regarding safe transport of methanol and for avoiding spills (for companies using at least 500 tonne) (DK).
- There are rules regarding safe storage of methanol (as it is a VOC). The larger quantities the stricter rules (DK).
- Limit values regarding content of methanol in alcoholic beverages (EU).
- Methanol is mentioned as a possible theme for future development of alternative fuels (EU).

Other regulatives, DK, EU, global:

- The Communication No. 14003, which concerns a dispensation scheme allowing for certain recreational organizations to use methanol was established due to an *excessive use* of methanol in these organizations. The dispensation scheme was established to ensure that the use of methanol would only take place in well-organized organizations.
- An air pollution limit value for methanol of 200 ppm (or 260 mg/m^3).
- A B-value for methanol of 0.3 mg/m^3 (related to the individual company's contribution to air pollution).
- Substitution projects have shown some (unproved) success with replacing methanol by ethanol (as solution agent, presumably).
- Ecolabels often restrict the use of methanol due to its categorization or through the criteria 'the content of VOC in glue must not exceed 3 % by weight'.

- 20 deaths in Czech Republic due to methanol-tainted alcohol (sep. 2012) led to a ban on sale of alcohol in the Chezc Republic (and Poland). There was a critique of the EU legislation not being sufficient.
- Finland also has problems with death of several hundred people due to methanol poisoning.
- Commission did not allow increase in methanol content in fuels.

9.1.2 Main points from the production and use sections

- Methanol is selected as a CoRAP substance, i.e. a report will be released in 2014 regarding a new evaluation of methanol. Furthermore a new extensive toxicological review of methanol is currently being prepared by the US EPA (draft is available, but must not be cited or quoted). It should be released in 2013.
- Some companies (main users) did not report their use of methanol to the Danish Product Register, which means that the numbers reported to the Danish Product Register are too low.
- The contacted dominant users of methanol in Denmark do not expect a significant increased consumption during the coming years. Increase in consumption in the EU is not expected in the coming years either; however increase in worldwide production is expected, especially in China (due to heavy investment in methanol as fuel for transport).
- Yet, three Danish pilot-projects regarding production of methanol are underway and a Danish Methanol Union has recently been established, with the aim of paving the way for use of bio-methanol as the best alternative energy source.
- Import of methanol in Denmark constitutes 0.07% of the total import into the EU.
- The dominant uses of methanol in Denmark (above 1000 tonne/year) are:
  - Production of glue
  - Production of biodiesel
  - Production of pesticides (and use as solvent)
  - Use in the oil and gas industry

9.1.3 Main points from the waste management section

- Methanol waste is classified as 'dangerous waste' and is thus treated by authorized facilities which burn the methanol waste. During incineration methanol is converted to CO2 and water, thus with no negative environmental effects.
- The 'normal' burning of consumer products containing small amounts of methanol (since products with large amounts of methanol are not allowed to be sold to the consumer) causes no environmental problems.
- Some companies reuse methanol (back into the production process) or use it as carbon-source in their waste water treatment facility.
- The majority of the dominant uses of methanol all concern the conversion of methanol to other chemical products – thus the waste-handling issue seems less important. Some though use waste-methanol in their waste water treatment facility, while others (laboratories) send the waste to proper treatment at KommuneKemi (where it is burned).

9.1.4 Main points from the environmental effects section

- Methanol is of low toxicity to aquatic and terrestrial organisms.
- Methanol mainly evaporates to air, but the degradation rate is high (half life a couple of days).
- Environmental effects are unlikely except in case of a large spill.
- Bioaccumulation is low.
- Methanol is readily biodegraded/degraded in the environment (water, soil, sediment, air).

9.1.5 Main points from the health effects section

- Methanol is more toxic to humans than animals (which can be problematic since the classification system is based on studies on animals).
- The most pronounced effect of methanol is damage to the eyes.
- Methanol is readily absorbed through dermal contact, ingestion or inhalation.

- Methanol is rather quickly excreted from the body.
- Few data available on chronic exposure to methanol, however effects are considered similar to effects related to acute exposure.
- According to IPCS (1997) no studies have been reported on methanol in the peer-reviewed literature on reproductive and developmental effects. Likewise with chromosomal and mutagenic effects and carcinogenic effects.
- Folate-deficient individuals might be at greater risk from inhalation of low concentrations of methanol, compared to normal individuals. Folate-deficient individuals cover pregnant women, the elderly, individuals with poor-quality diets, alcoholics and individuals on certain medications or with certain diseases (IPCS, 1997).
- The extent of poisoning due to accidental or intentional intake of methanol seems to vary considerably dependent on the country. Finland and the Czech Republic have had several incidents of death due to intake of methanol (several hundred in Finland and recently (2012) 20 deaths in the Czech Republic), whereas the problem does not seem to be of large proportions in Denmark (1 case in 2010, 3 cases in 2011 and so far 2 cases in 2012).
- IPCS's suggestions of how to protect human health from exposure to methanol primarily focus on correct labeling, adequate ventilation, use of suitable protective equipment and denaturation of methanol to avoid misuse.
- To avoid misuse, methanol used as fuel should be denatured and should contain a color additive.

9.1.6 Main points from the monitoring section

- Methanol intake derived from use of aspartame in food could be problematic. A rough calculation has shown, that if aspartame was used to replace all sucrose in the diet, its average daily ingestion would be 8.5 mg/kg, which would be equivalent to 0.85 mg/kg methanol, which is above the US EPA TDI value of 0.5 mg/kg.
- No risk related to loading/unloading of methanol, laboratory use of methanol or use of methanol as common fuel.
- Need for ensuring use of protective equipment in exposure scenarios related to manufacturing of products with methanol (including windshield washing fluid); use of methanol in waste water treatment; use of methanol as solvent in the extraction processes and use of methanol based fuels in speedway, drag racing etc.
- Need for lowering the content of methanol in windscreen washing fluids, since consumers cannot be expected to wear protective equipment (however, the product studied contained 24% methanol, which is a very high amount).

9.2 Potential environmental hotspots - conclusions

9.2.1 Important to avoid spill – uncertain whether other EU member states regulate this

As the IPCS report concludes, effects due to environmental exposure to methanol are unlikely to be observed, unless it is released to the environment in large quantities, such as a spill. They suggest that care should be taken to prevent spills of large quantities of methanol, especially spills to the surface water.

However, as presented in the sections regarding legislation on methanol, there is a Danish Statutory Order (Statutory Order No. 20 of 12/01/2006 on "control with the working environment in terms of risk related to larger accidents with dangerous substances") that regulates in order to prevent large accidents – i.e. spills. It seems that this Statutory Order is linked to a minimum Directive, which means that (at least some of the rules) apply to other Member States. However, it could be investigated whether these rules indeed apply to other EU member states in a sufficient manner.

9.2.2 No obvious environmental problems related to the dominant uses of methanol in Denmark

Contact to the dominant users of methanol in Denmark did not reveal any significant environmental problems related to their use of methanol. For most part, methanol is used in chemical processes and converted to other chemical substances, thus methanol waste is minimum. Furthermore, when methanol is used (at least in pesticide production) it is transferred through closed piping systems. In cases where methanol is present in the waste water it is actually beneficial, since the microorganisms in the waste water treatment facilities make use of methanol in their process of cleaning the water.

9.2.3 No obvious environmental problems related to content of methanol in products

In Denmark it is forbidden to sell products containing large amounts of methanol. Thus, consumer products, which end up in either landfills or in incineration plants do not contain large amounts of methanol, and the amount contained is by incineration converted to CO_2 and water, and in landfills to emissions to the air, where the methanol is rather quickly degraded. Thus, no obvious environmental concerns are related to the content of methanol in consumer products in Denmark. Even though the content of methanol may be higher in products in other countries, the products are still not expected to cause environmental concerns due to the environmental properties of methanol.

9.3 Potential health related hotspots - conclusions

9.3.1 Evaluate the need for new classification

Italy has proposed a new classification for methanol. The new classification defines methanol as toxic to reproduction. The background information for this suggested altered classification should be evaluated and commented, bearing in mind that methanol is much less toxic for animals than for humans and that classification is often based on animal studies. It should also be taken into consideration that folate-deficient individuals might be at greater risk from inhalation of low concentrations of methanol, compared to normal individuals. Folate-deficient individuals cover pregnant women, the elderly, individuals with poor-quality diets, alcoholics and individuals on certain medications or with certain diseases. The fact that the minimum dose causing permanent visual defects is unknown should also be taken into consideration. Also important to bear in mind is the fact that IPCS concludes that a conventional risk assessment of methanol is not feasible and that an alternative approach should be an evaluation based on blood levels of the most toxic metabolite (formate).

9.3.2 Evaluate whether EU legislation regarding prevention of ingestion of methanol-contaminated alcoholic beverages is sufficient

A number of countries (Finland, Poland, the Czech Republic) has experienced problems with people dying from ingestion of methanol contaminated alcoholic beverages. Latest (September 2012) 20 people died in the Czech Republic and concerns were raised regarding whether the EU legislation is sufficient in this area. This does not seem to be a problem in Denmark.

9.3.3 Make sure that protective equipment is used in several use scenarios

The majority of methanol is used in manufacturing of other products – i.e. a chemical conversion of methanol to form other chemical compounds. Only a minority of methanol ends up as ingredient in consumer products (and the content is restricted – at least in Denmark), thus there does not seem to be any health issues related to consumer products - with the exception of windscreen washing fluids from Finland containing 24% methanol – however, this product would not be allowed on the Danish market.

However, there are some indications of the importance of making sure that the correct protective equipment is used – especially in the exposure scenarios investigated in the Finnish study (Finnish Institute of Occupational Health, 2009). They found a need for using protective equipment (the exposure scenarios were assumed not to include protective equipment) in the following scenarios:

- manufacturing of products with methanol (including windshield washing fluid);
- use of methanol in waste water treatment;
- use of methanol as solvent in the extraction processes and
- use of methanol based fuels in speedway, drag racing etc.

Thus, it could be relevant to inform relevant groups of the need for protective equipment.

9.3.4 Investigate further whether there is a problem related to exposure to methanol from food sweetened with aspartame

As described previously, there may be a problem related to the intake of methanol from aspartame in food (10% of the aspartame is converted to methanol in the body). A rough calculation has shown that if aspartame was used to replace all sucrose in the diet, it would correspond to an average daily ingestion of 0.85 mg methanol/kg (we assume the source means bodyweight), which is above the US EPA TDI value of 0.5 mg/kg (IPCS, 1997). Of course it is not a realistic scenario to assume that *all* sucrose in the diet is replaced by aspartame, however, the data is from 1981/1986 and may not be representative for today's scenario (perhaps we currently eat more/less sugar in our diet?). Searches on the internet have shown, that there is an ongoing debate regarding health risks associated with the use of aspartame and that several organizations express concern regarding the use of aspartame. It should be mentioned that according to a UK Aspartame Awareness Campaign[21] the NOAEL value on aspartame does not take into account the fact that 10% of it is converted into methanol in the body. Thus, the organization calls for a revision of the NOAEL value of aspartame.

[21] http://www.aspartame-awareness-campaign.co.uk/information.html

10. Abbreviations and acronyms

AEGL - Acute Exposure Guideline Values
BCF – Bioconcentration factor
BST - The Occupational Health Service in Denmark
CLP Regulation – Regulation (EC) No 1272/2008 of 16 December 2008 on classification, labeling and packaging of substances and mixtures.
CNS – Central nervous system
CoRAP - Community Rolling Action Plan
Danish EPA – Danish Environmental Protection Agency
DST – Danish Statistics
DME – Dimethyl ether
DMT – Dimethyl terephthalate
DNEL - Derived No Effect Values
EUSES – European Union System for Evaluation of Substances
ECHA – European Chemical Agency
GHS - Globally Harmonized System
IPCS – International Programme on Chemical Safety
IRIS – Integrated Risk Information System
LOUS – List of Unwanted Substances
MAL code – Measured Technical Working Hygienic Air Requirements
MeOH - Methanol
MEG - Monoethylen glycol
MTO - Methanol to olefins
MTBE – Methyl tert-butyl ether
NOEL – No Observed Effect Level
PBT – Persistent, bioaccumulative and toxic
vPvB – Very Persistent and very bioaccumulative
REACH – Registration, Evaluation, Authorisation and Restriction of Chemicals
SPIN – Substances in Products In Nordic countries
TDI – Tolerable Daily Intake
US EPA – United States Environmental Protection Agency
VOCs - Volatile Organic Compounds

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Survey of Methanol (Cas no. 67-56-1)

Survey of methanol
This survey is part of the Danish EPA's review of the substances on the List of Undesirable Substances (LOUS). The report presents information on the use and occurrence of methanol, internationally and in Denmark, information on environmental and health effects, on alternatives to the substances, on existing regulation, on monitoring and exposure, waste management and information regarding ongoing activities under REACH, among others.

Kortlægning af methanol
Denne kortlægning er et led i Miljøstyrelsens kortlægninger af stofferne på Listen Over Uønskede Stoffer (LOUS). Rapporten indeholder blandt andet en beskrivelse af brugen og forekomsten af methanol, internationalt og i Danmark, en beskrivelse af miljø- og sundhedseffekter af stofferne, og viden om alternativer, eksisterende regulering, moniteringsdata, eksponering, affaldsbehandling og igangværende aktiviteter under REACH.

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