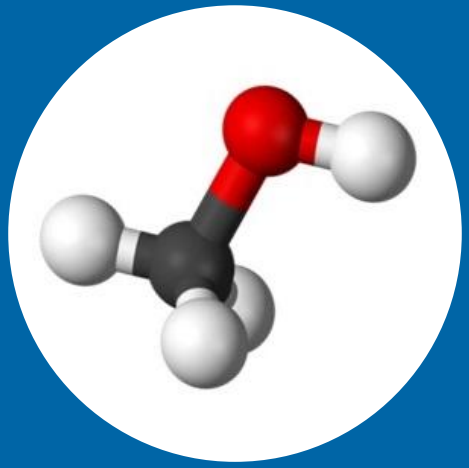
Evaluation of Methanol



MethaShip

Methanol as fuel for engines in passenger shipping

Methanol Technical Workshop

Copenhagen, 20. March 2018

MethaShip

MEYER WERFT
PAPENBURG 1795

MEYER WERFT at a glance

- Family owned in 6th generation
- 3200 employees in Papenburg
- Two ship building docks, laser centre
- 1986: first cruise ship new build

MEYER WERFT
PAPENBURG 1795

MEYER group

MEYER TURKU
SHIPYARD 1737

NEPTUN WERFT
ROSTOCK 1850

EMS PreCab

PIIKKIO WORKS

MAC Hamburg
MARINE AIRCONDITIONING CENTRE

Portfolio

Cruise ships

River cruise ships

(Cruise)ferries

Passenger ships

Research ships

Island ferries

Gas tankers

Livestock carriers

Container ships

Content

(1) MethaShip project

(2) Methanol ship design

(3) Some property highlights

(4) Sustainability & infrastructure

(5) Conclusion

MethaShip is …

- Nationally funded German research project
- Partners from Shipbuilding, ship-safety, marine engines, methanol trading & production
- Project from 09/2014 to 05/2018

→ **Examine methanol as fuel for cruise ships and RoPax ferries.**

Associated partners:

Motivation

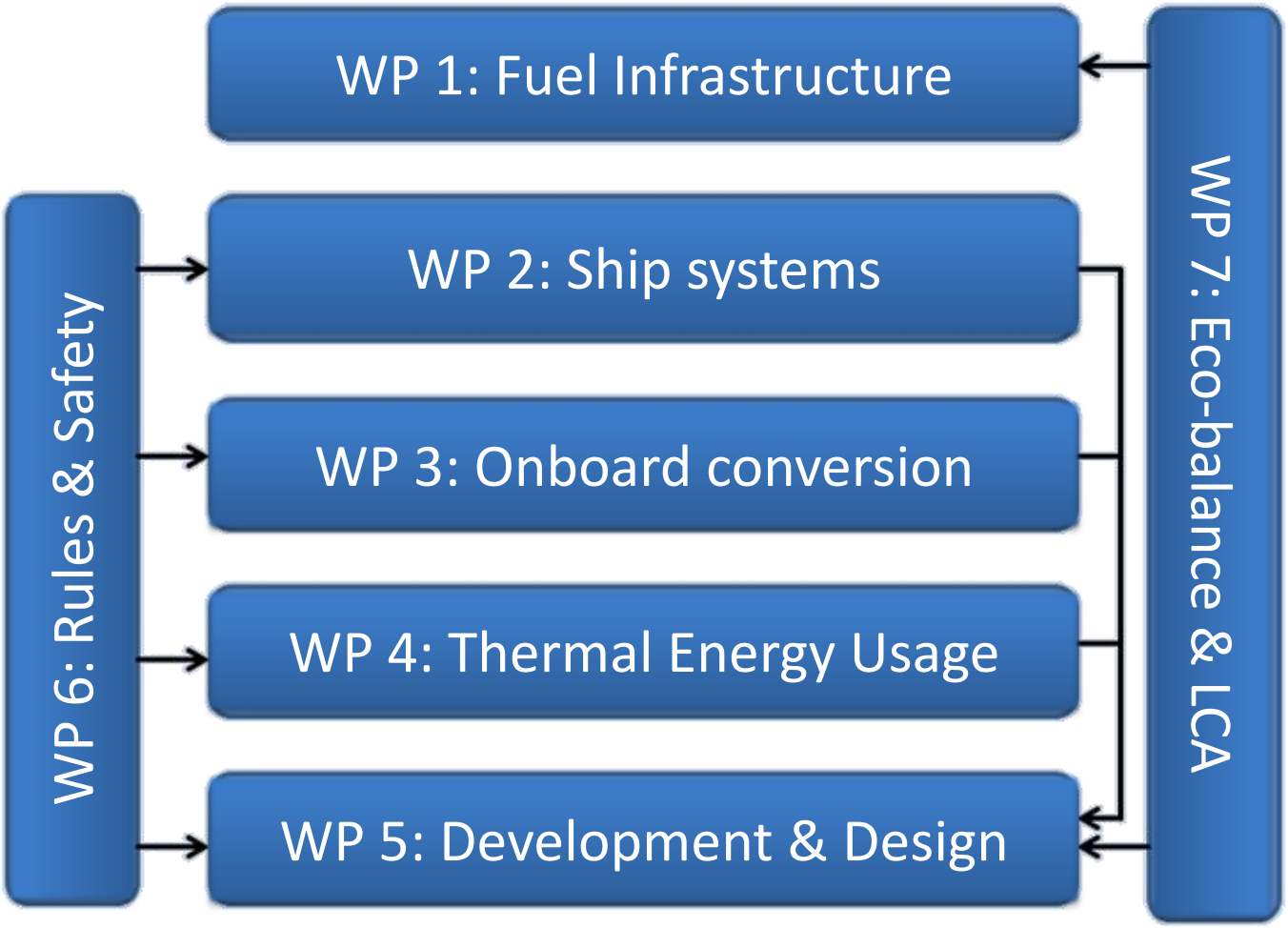
- Avoid emissions by use of clean fuels
- Environmental awareness
- Operate more eco- and energy-efficient

- Alternative fuel that is “practicable”

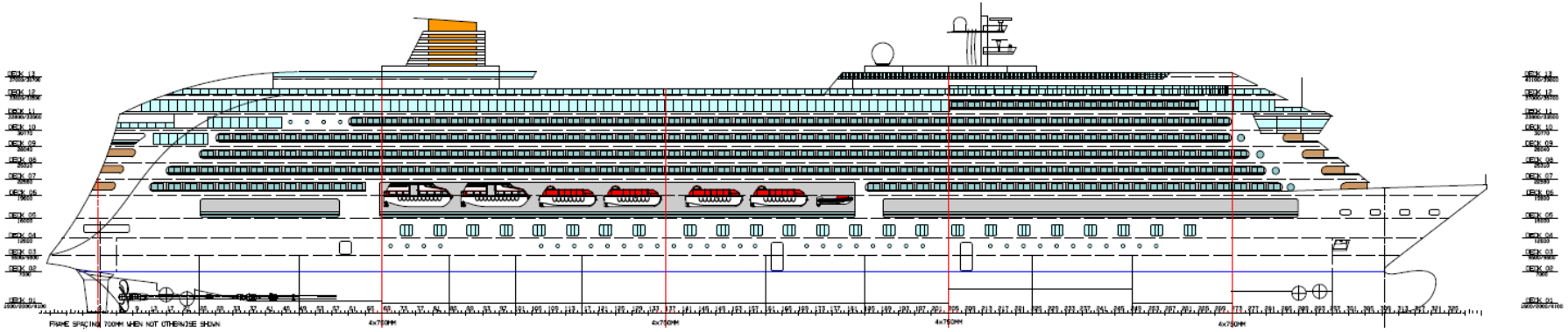
- Evaluate Methanol regarding sustainability (Paris agreement)

- Support the IMO rule development

Work Packages

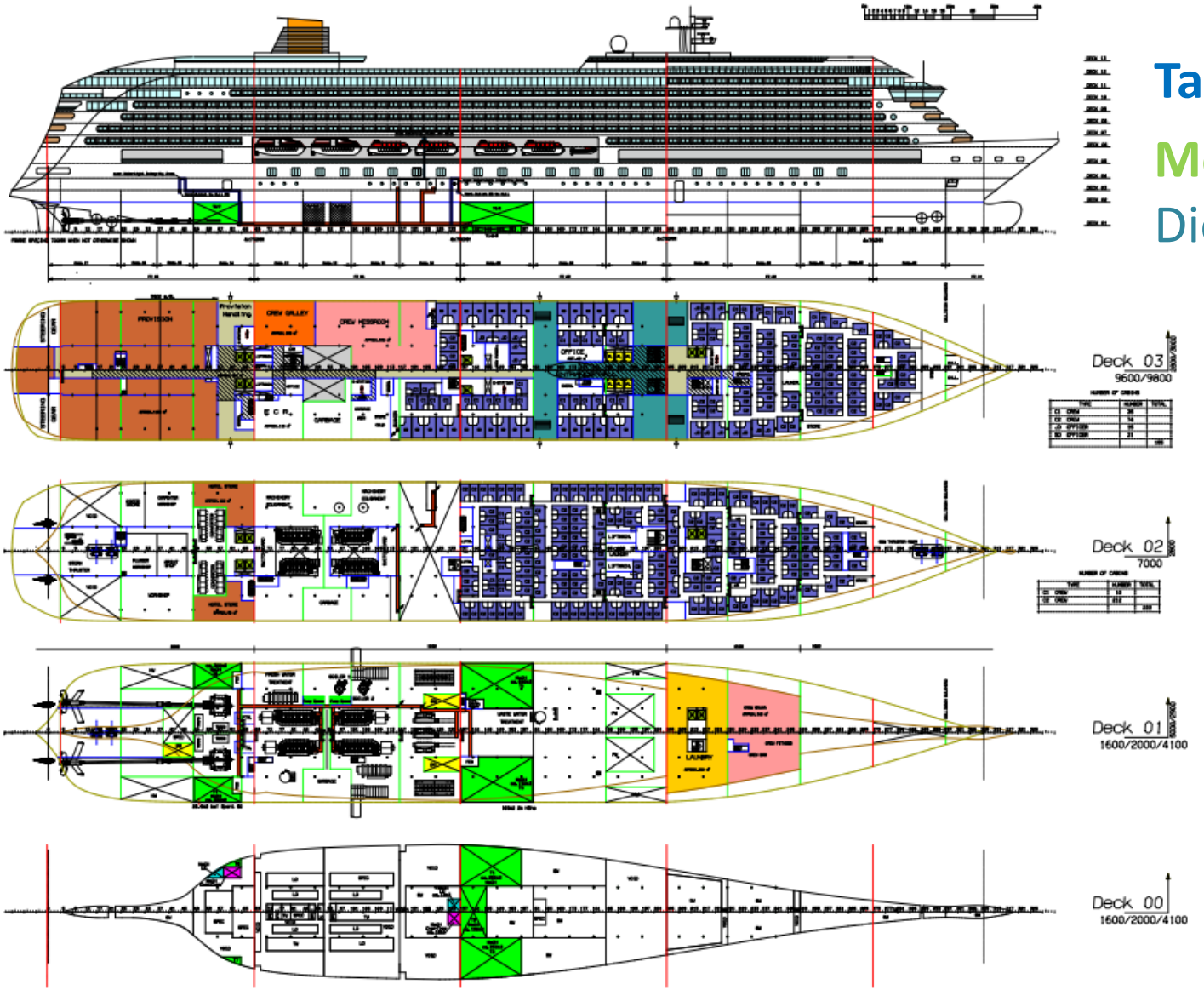


Methanol cruise ship



Main data	
Length	238.0 m
Width	32.2 m
Tonnage	62 800 GT
Passengers	2050 + 570 Crew
Engines	4 x 9 MW medium speed engines
Main fuel	Methanol

GAP cruise ship



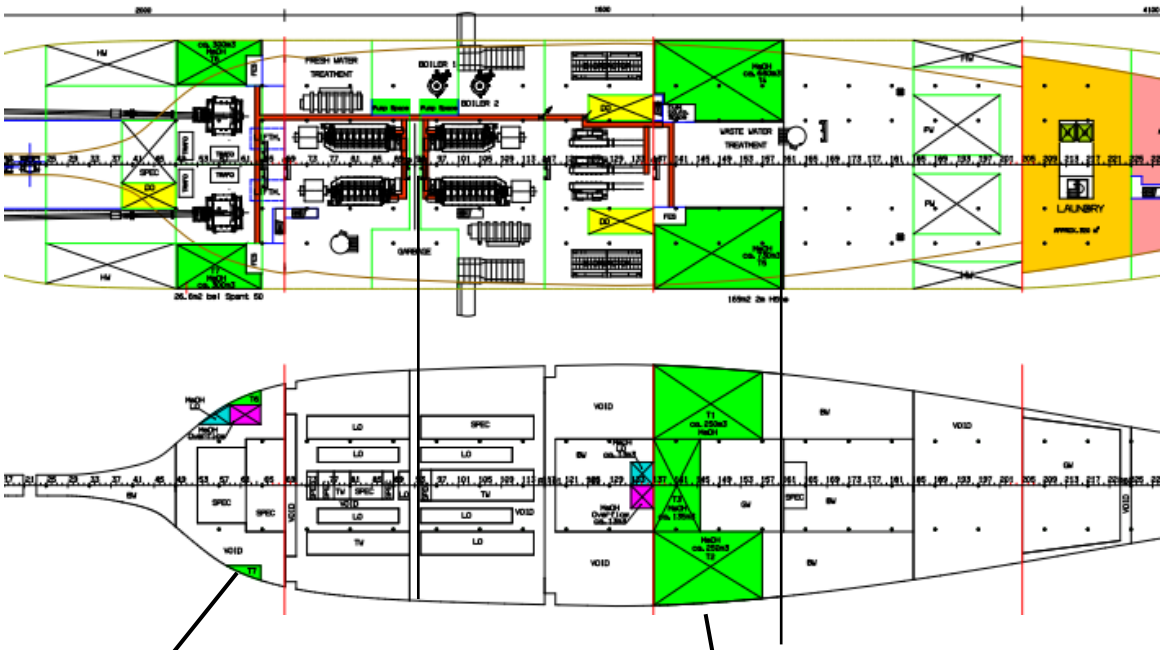
Tank plan:

MeOH Storage

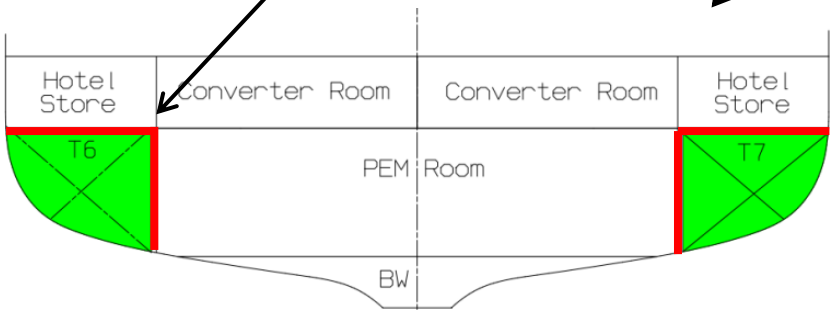
Diesel (Pilot)

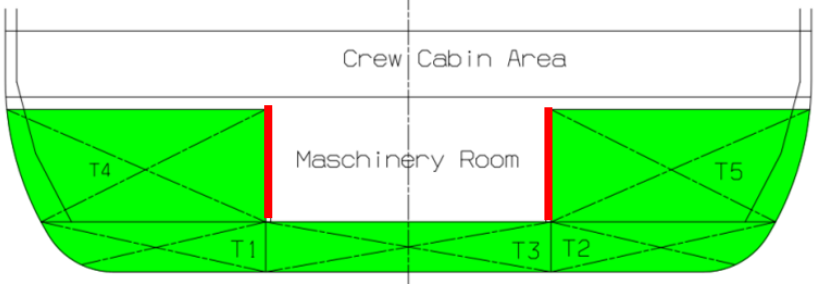
Examplary tank arrangement

- Ambient conditions
- Room saving, structural tanks
- In hull & double bottom
- Mild steel



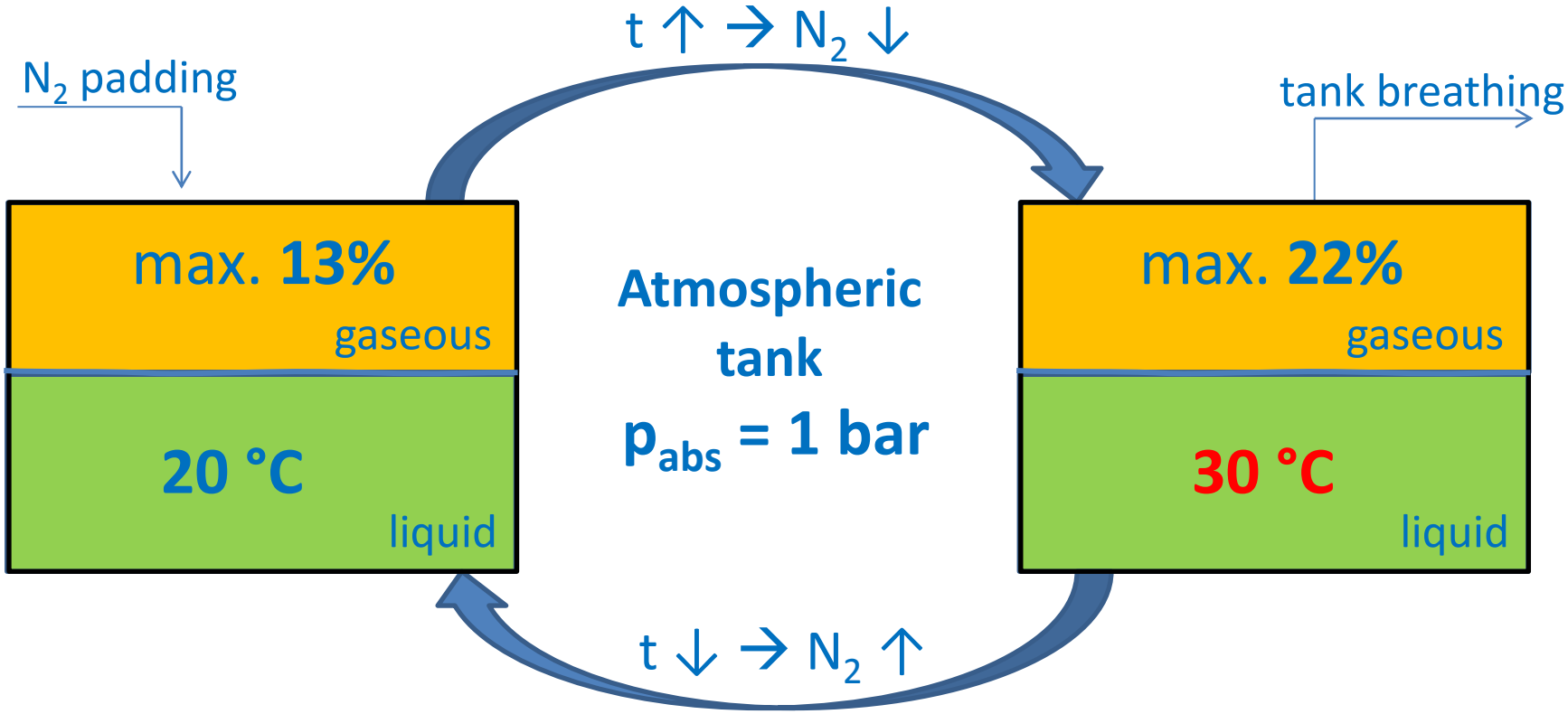
secondary barrier





Tank atmosphere

- Methanol content in gas phase depends on temperature

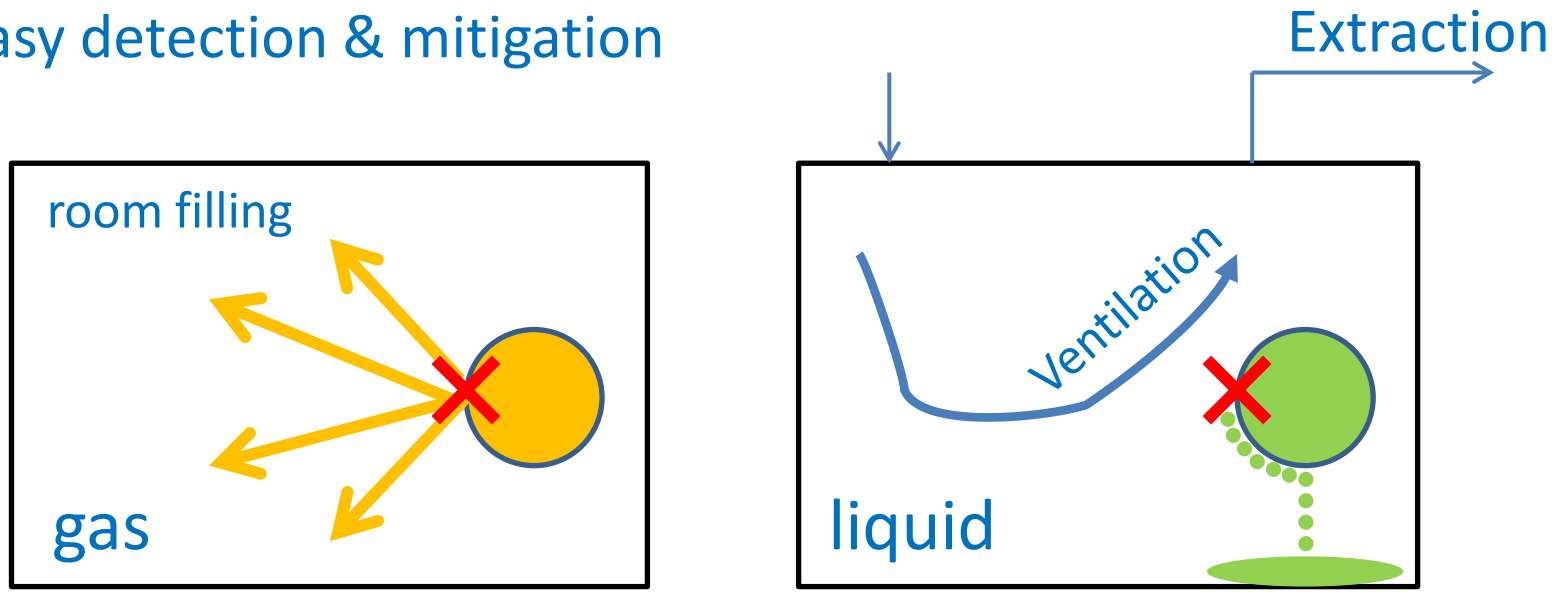


Evaporation is slow process (*not boiling!*). Little "driving force".

Spreading & mitigation

Crucially different behaviour of gas and liquid fuel

- immediate pressure release
- less medium released
- locally bound
- easy detection & mitigation



Methanol is to be treated as “liquid fuel system”

IMO Rule Recommendations

Documents to IMO CCC Sub-Committee

- **CCC 3/INF.23** "Information on a German project called MethaShip"
- **CCC 3/3/1** "Proposals […] for safety of ships using […] alcohol as fuel"
- **CCC 4/3/4** "Boundaries for methyl and ethyl alcohol-fuelled ships"

IMO INTERNATIONAL MARITIME ORGANIZATION

E

SUB-COMMITTEE ON CARRIAGE OF CARGOES AND CONTAINERS
3rd session
Agenda item 3

CCC 3/3/1
1 July 2016
Original: ENGLISH

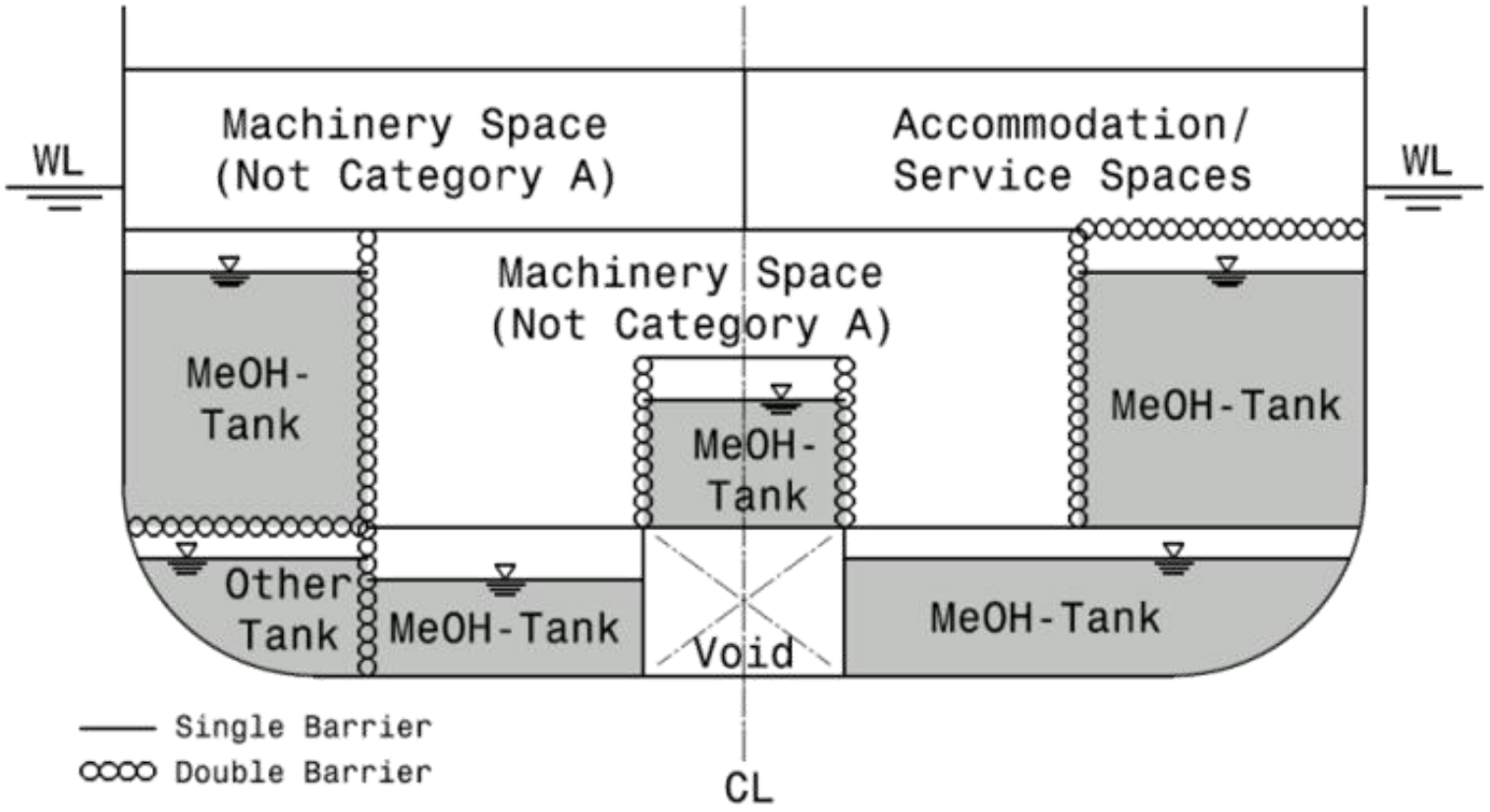
AMENDMENTS TO THE IGF CODE AND DEVELOPMENT OF GUIDELINES FOR LOW-FLASHPOINT FUELS

Proposals for further amendments to the draft technical provisions for the safety of ships using methyl/ethyl alcohol as fuel, based on findings from the German project MethaShip

Submitted by Germany

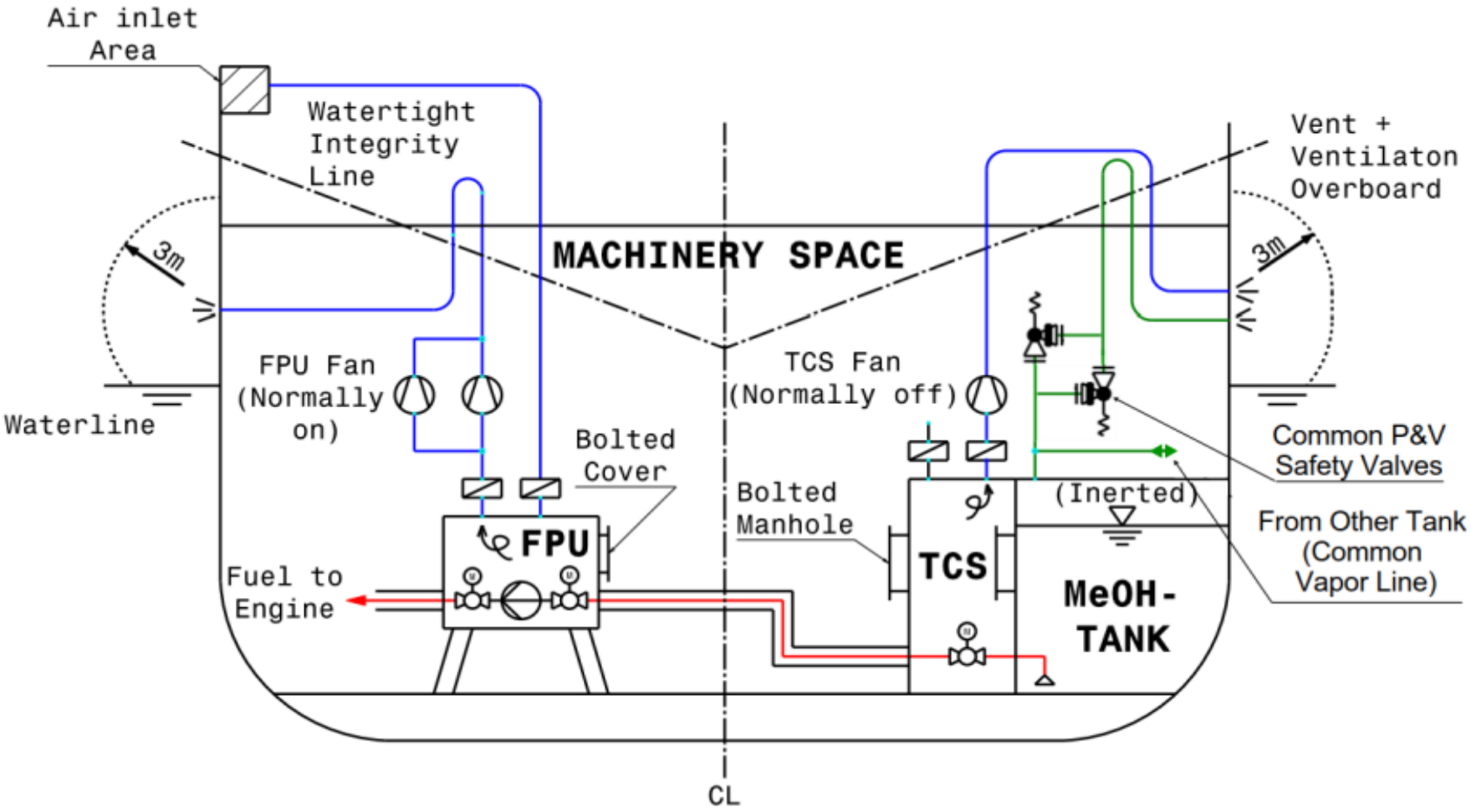
IMO Rule Recommendations

Application of Secondary barriers



IMO Rule Recommendations

Vent & Ventilation arrangement



Conclusions ship design

The beneficial properties of methanol result from being liquid.

- No potential of pressure build-up
- Slow evaporation
- Easy and safe spill mitigation (ventilation)
- Detection from 2 ppm onwards (MAC: 200 ppm for 8 h)

  → ideal for preventive surveillance
- … and many more: water soluble (mitigation), bio degradable, ESD-protected spaces, vent outlets, small hazardous zones, high auto-ignition temperature, high heat capacity, …)

By physics, Methanol is superior to fuels not naturally liquid.

Hazard comparison

	METHANOL	DIESEL	GASOLINE
Hazard pictograms (CPL)			
Signal word: (CPL)	Danger	Danger	Danger
Hazard statements (CPL)	H225 Highly flammable liquid and vapour. H301 Toxic if swallowed. H311 Toxic in contact with skin. H331 Toxic if inhaled. H370 Causes damage to organs.	H226: Flammable liquid and vapour. H304: May be fatal if swallowed and enters airways. H315: Causes skin irritation. H332: Harmful if inhaled. H351: Suspected of causing cancer. H373: May cause damage to organs through prolonged or repeated exposure. H411: Toxic to aquatic life with long lasting effects	H224: Extremely flammable liquid and vapour. H304: May be fatal if swallowed and enters airways H315: Causes skin irritation H340: May cause genetic defects H350: May cause cancer H361: Suspected of damaging fertility or the unborn child H336: May cause drowsiness or dizziness H411: Toxic to aquatic life with long lasting effects
Precautionary statements (CLP)	P210 - Keep away from heat. - No smoking P280 - Wear protective gloves, protective clothing, eye protection, face protection P304+P340 - IF INHALED: remove victim to fresh air and keep at rest in a position comfortable for breathing P303+P361+P353 - IF ON SKIN (or hair): Remove/Take off immediately all contaminated clothing. Rinse skin with water/shower P301+P310 - IF SWALLOWED: Immediately call a POISON CENTRE or doctor P403+P235 - Store in a well-ventilated place. Keep cool	P201: Obtain special instructions before use P210: Keep away from heat/sparks/open flames/hot surfaces – No smoking P240: Ground/bond container and receiving equipment P241: Use explosion-proof electrical/ventilation/ lightning equipment P242: Use only non-sparing tools P243: Take precautionary measures against static discharge P260: Do not breathe dust/fume/gas/vapours/spray P264: Wash hands thoroughly after handling P270: Do not eat, drink or smoke when using this product P273: Avoid release to the environment P280: Wear protective gloves/clothing/eye protection P301+P310: IF SWALLOWED: Immediately call a POISON CENTER or doctor/physician P302+P352: IF ON SKIN: Wash with plenty of soap and water P303+P361+P353: IF ON SKIN (or hair): Remove/Take off immediately all contaminated clothing. Rinse skin with water/shower P304+P340: IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing P308+P313: IF exposed or concerned: Get medical advice/attention P312: Call a POISON CENTER or doctor/physician if you feel unwell P331: Do NOT induce vomiting P332+P313: If skin irritation occurs: Get medical advice/attention P370+P378: In case of fire: Use water spray or foam for extinction P391: Collect spillage P403+P233: Store in a well-ventilated place. Keep container tightly closed P403+P235: Store in a well-ventilated place. Keep cool P405: Store locked up P501: Dispose of contents/container in accordance with local/regional/national/international regulation	P201: Obtain special instructions before use P202: Do not handle until all safety precautions have been read and understood P210: Keep away from heat/sparks/open flames/hot surfaces - No smoking P233: Keep container tightly closed P240: Ground/bond container and receiving equipment P241: Use explosion-proof electrical/ventilation/ lightning equipment P242: Use only non-sparing tools P243: Take precautionary measures against static discharge P261: Do not breath fume/gas/mist/vapours/spray P264: Wash hands thoroughly after handling P271: Use only outdoors or in a well-ventilated area P273: Avoid release to the environment P280: Wear protective gloves/clothing/eye protection P301+P310: IF SWALLOWED: Immediately call a POISON CENTER or doctor/physician P302+P352: IF ON SKIN: Wash with plenty of soap and water P303+P361+P353: IF ON SKIN (or hair): Remove/Take off immediately all contaminated clothing. Rinse skin with water/shower P304+P340: IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing P308+P313: IF exposed or concerned: Get medical advice/attention P312: Call a POISON CENTER or doctor/physician if you feel unwell P331: Do NOT induce vomiting P332+P313: If skin irritation occurs: Get medical advice/attention P370+P378: In case of fire: Use water spray or foam for extinction P391: Collect spillage P403+P235: Store in a well-ventilated place. Keep cool P405: Store locked up P501: Dispose of contents/container in accordance with local/regional/national/international regulation

Hazard Statements describe **hazards of chemical substances** and mixtures by standardized phrases.
Precautionary Statements give advice for the **safe handling**.

Methanol not classified “more dangerous” than other fuels.

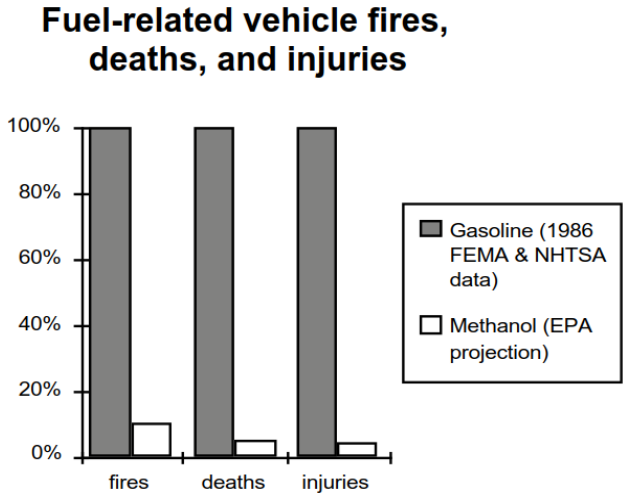
U.S. EPA – fire safety

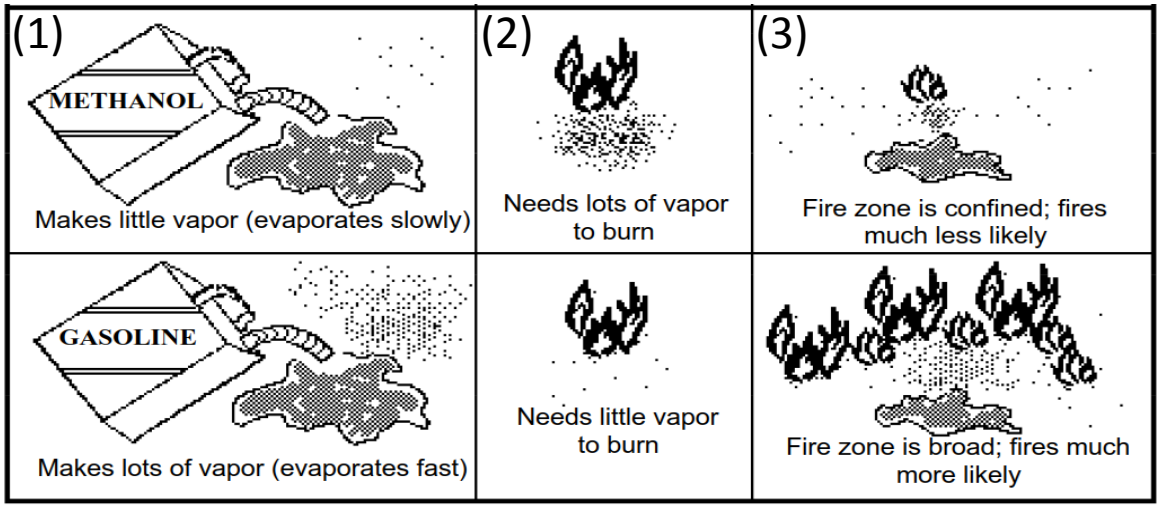
EPA 400-F-92-010

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF MOBILE SOURCES

Methanol's advantageous over gasoline

- (1) lower volatility
- (2) higher flammability requirements
- (3) lower vapour density
- Less severe (heat release $^1/_8$ th , burning 75% slower)





Superior fire safety over Gasoline

Flammability and Toxicity

TABLE 6-1 HAZARD SUMMARY[a]	M100	Gasoline
Flammability		
Ease of Occurrence		
Open & Restricted Areas	4	9
Enclosed Spaces	8 (2-4) [b]	2
Relative Hazard if Fire		
Fire Severity	3	10
Ease of Extinguishing	7	10
Flame Visibility	8	1
Toxicity		
Inhalation-Low Conc.		
Toxicity	3	10
Ease of Occurrence	10	10
Inhalation - High Conc.		
Toxicity	10	10
Ease of Occurrence	3	4
Skin Contact.		
Toxicity	9	8
Ease of Occurrence	3	3
Ingestion		
Toxicity	10	10
Ease of Occurrence	8(2) [c]	3

Table adapted from Machiele, 1998; [a] 1-No concern. 2 to 3 = Low Level concern. 4 to 6 = moderate concern. 7 to 8 = high-level concern. 9 to 10 = extreme hazard. [b] Numbers in parenthesis reflect hazard reductions resulting from design changes. [C] Number in parenthesis incorporates the lowered likelihood of ingestion due to the presence of additives.

Source: Malcolm Pirnie, Inc. , Technical Memorandum

MeOH overall less dangerous than Gasoline, which everyone knows from daily life.

A case of poisoning

Occupational Medicine, Volume 42, Issue 1, 1 January 1992, Pages 47–49, https://doi.org/10.1093/occmed/42.1.47
A. Downie ✉, T. M. Khattab, M. I. A. Malik, I. N. Samara
Published: 01 January 1992

Abstract

Methanol (CH_3OH) is a chemical feedstock of increasing importance as well as a commonly used solvent. In the early 1980s methanol production was introduced at a new petrochemical complex in the Saudi port of Jubail. A case is presented of a consultant supervising tank cleaning prior to methanol loading. He wore positive pressure breathing apparatus but no protective clothing. After 2–3 hours working in the confined space of the tank, he worked on deck and continued to wear his methanol-soaked clothing which eventually dried out. Visual symptoms of acute methanol toxicity presented some 8 hours after exposure. The appropriate treatment (with ethanol provided by the ship bond) was carried out in hospital and the individual recovered completely. Most reported cases of methanol toxicity are social in origin, arising from ingestion. This particular case, though unusual, does present some interesting lessons.

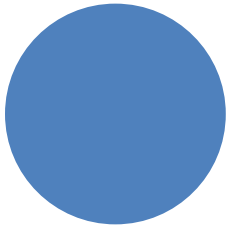
Easy and reliable treatment with full recovery.

Lethal dosis (fish)

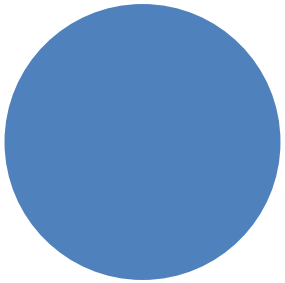
(LC50, LC=Lethal Concentration):
Concentration in water, at which half the population died within a specified test duration.

Methanol[1]
15400 (mg/l)

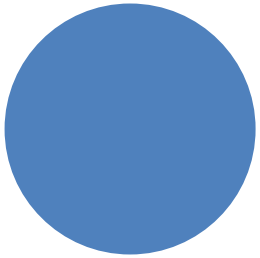
Methane[5]
49,9 (mg/l)



Heavy Fuel Oil[3]
79 (mg/l)



Diesel[4]
65 (mg/l)



Gasoline[2]
8,2 (mg/l)

Methanol better than
- **Diesel** by factor **240**
- **Gasoline** by factor **1900**

[1] ECHA, European Chemicals Agency, registration dossier Methanol
[2] Petrobras/Statoil ASA, Safety Data Sheet, ECHA registration dossier Gasoline
[3] GKG/ A/S Dansk Shell, Safety Data Sheet
[4] ECHA, European Chemicals Agency, registration dossier Diesel
[5] ECHA, European Chemicals Agency, registration dossier Methane

Effect dosis (algae)

(EC50, EC = Effect Concentration):
Concentration in water, at which half the population shows change in growth rate after a specified test duration.

Methanol[1]
22000 (mg/l)

Methane[5]
19,4 (mg/l)

Heavy Fuel Oil [3]
1 (mg/l)

Diesel[4]
78 (mg/l)

Gasoline[2]
3,1 (mg/l)

Methanol better than
- **Diesel** by factor **280**
- **HFO** by factor **22000**

[1] ECHA, European Chemicals Agency, registration dossier Methanol
[2] Petrobras/Statoil ASA, Safety Data Sheet, ECHA registration dossier Gasoline
[3] GKG/ A/S Dansk Shell, Safety Data Sheet
[4] ECHA, European Chemicals Agency, registration dossier Diesel
[5] ECHA, European Chemicals Agency, registration dossier Methane

MeOH spill simulations

Simulation 1 [8]:

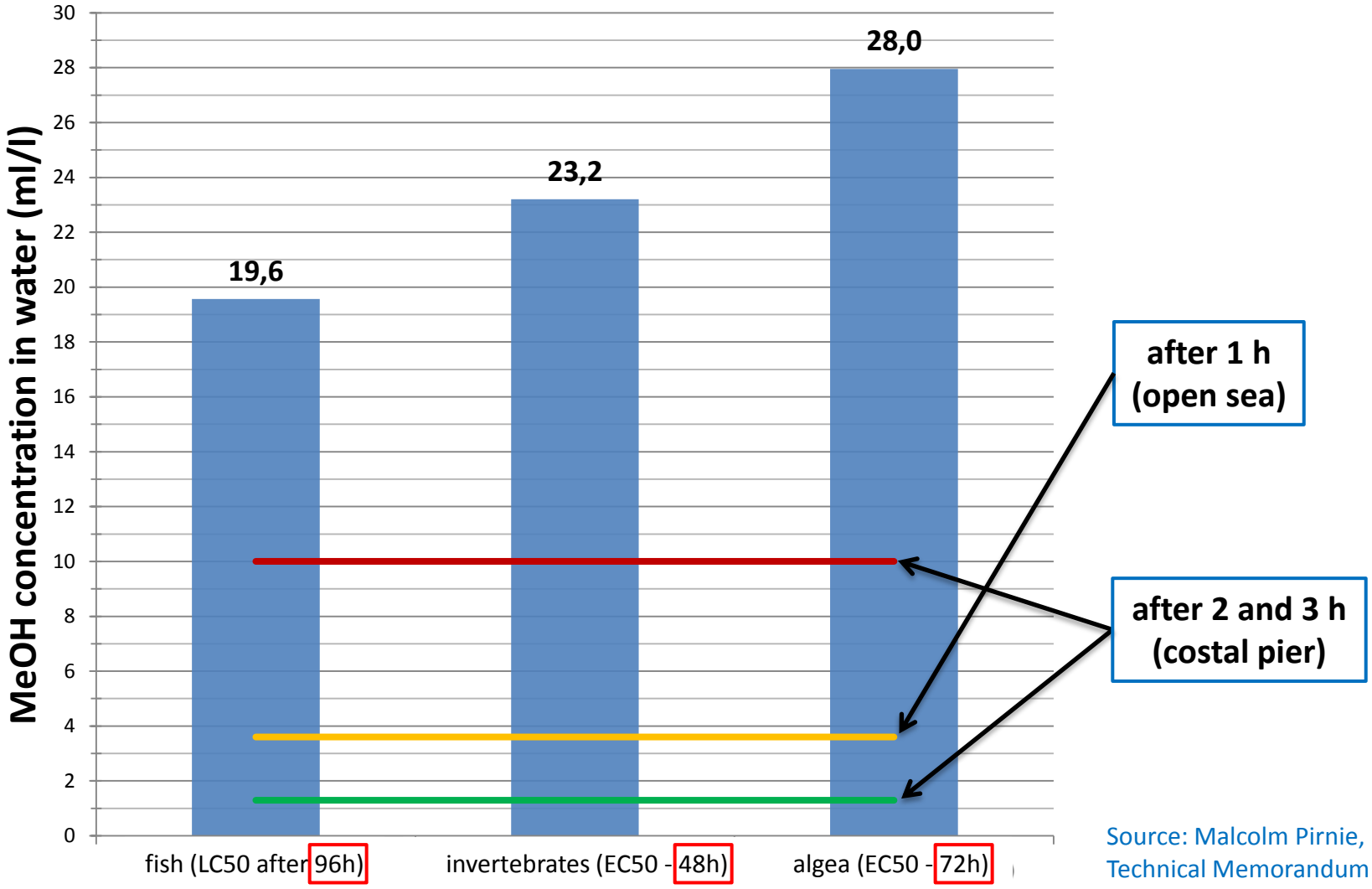
- Release of 10,000 tons Methanol at **open sea**
  - Concentration of 0,36 % after 1 hour

Simulation 2 [8]:

- Release of 10,000 l/h from a **coastal pier**
  - Concentration < 1 % after 2 hours
  - Concentration of 0,13 % after 3 hours

[8] Malcolm Pirnie, Inc., Technical Memorandum

Comparison to LC/EC50 values



Source: Malcolm Pirnie, Inc., Technical Memorandum

Methanol dilutes so rapidly that EC/LC times will not even be reached.

Impact of accident

	Maritime accident	Maritime accident	Simulation
Ship	Erika	Tanio	-
Fuel	Heavy Fuel Oil	Heavy Fuel Oil	Methanol
Released amount	19 000 t	13 500 t	10 000 t
Affected coastline	400 km	200 km	0 km
Total damage:	$914M	-	-
Cleaning	$100M	$50M	$0
Fishing industry	$98,3M	-	-
Tourist industry	$400-500M	-	-
Claim for damages	$120M	$17M	-
Killed birds	≈ 60,000	≈ 40, 000	-> 0

Source: economic, social and environmental effects of the „Prestige“ oil spill; international scientific seminar

Quotations

„Even in the event of a large scale spill these times of exposure are unlikely to occur due to the rate at which methanol dissipates.“

Source: Plasma Fusion Center, Massachusetts Institute of Technology

„Methanol is significantly less toxic to marine life than petroleum fuels, and many of the effects of short term exposure are temporary and reversible.”

„[…] and the U.S. Department of Energy considers gasoline to be ‘overall’ more hazardous to health than neat methanol.“

Source: Malcolm Pirnie, Inc. , Technical Memorandum

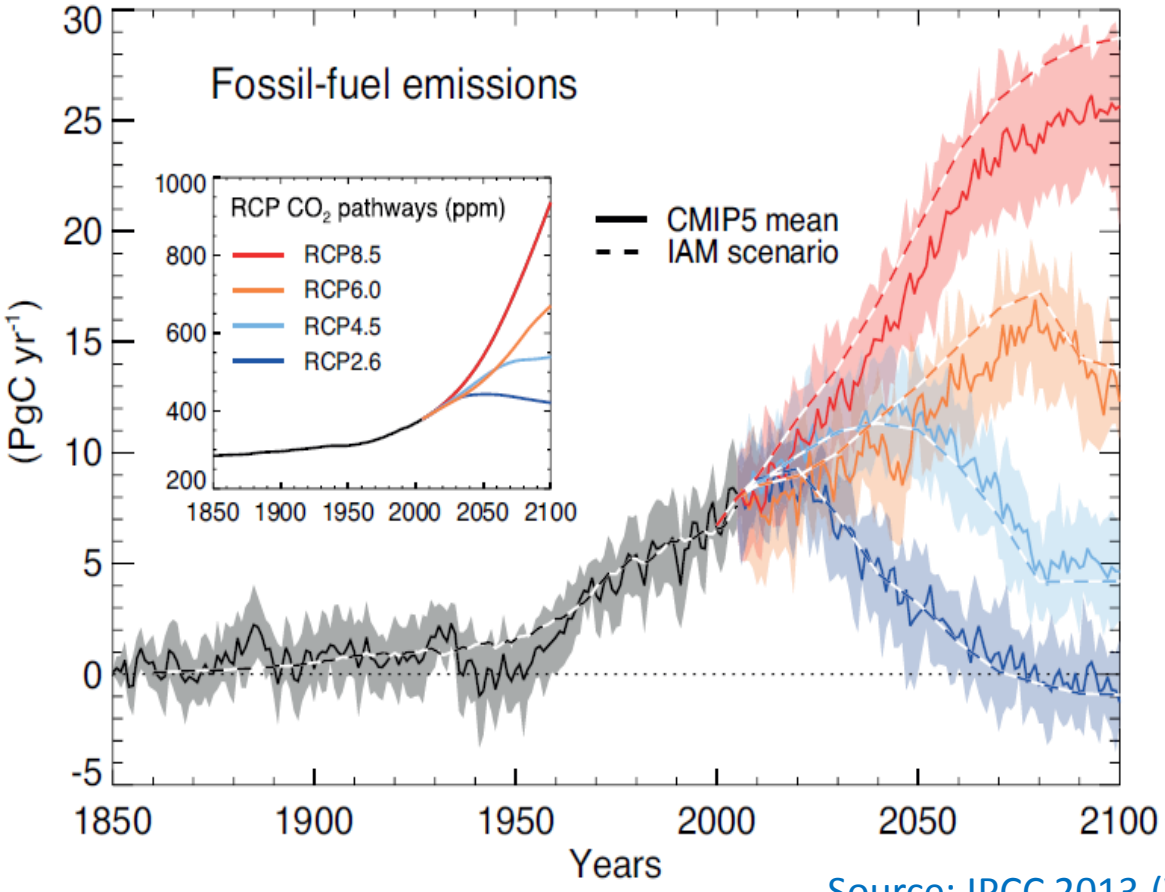
Conclusion Properties MeOH

- For humans not more poisonous than diesel or gasoline
- Poisoning is reliably treatable by simple means. In particular Methanol is not carcinogenic
- Far less hazardous to the environment than gasoline, diesel or heavy fuel oil. Large scale spills at sea would rapidly disperse
- Aquatic plants and bacteria biodegrade Methanol readily and rapidly without residue
- No Global Warming Potential, unlike LNG (methane slip)

Major challenge “climate change”

2°C-limit (acc. RCP 2.6) requires

- **Peak of CO_2** by 2025, **negative emissions** towards 2070



Source: IPCC 2013 (WGI), SPM, page 27

Conclusions LCA

- **Today**: Methanol from natural gas or coal
  → No advantage in Life Cycle Assessment

- **Future** renewable production: Alcohols best in LCA

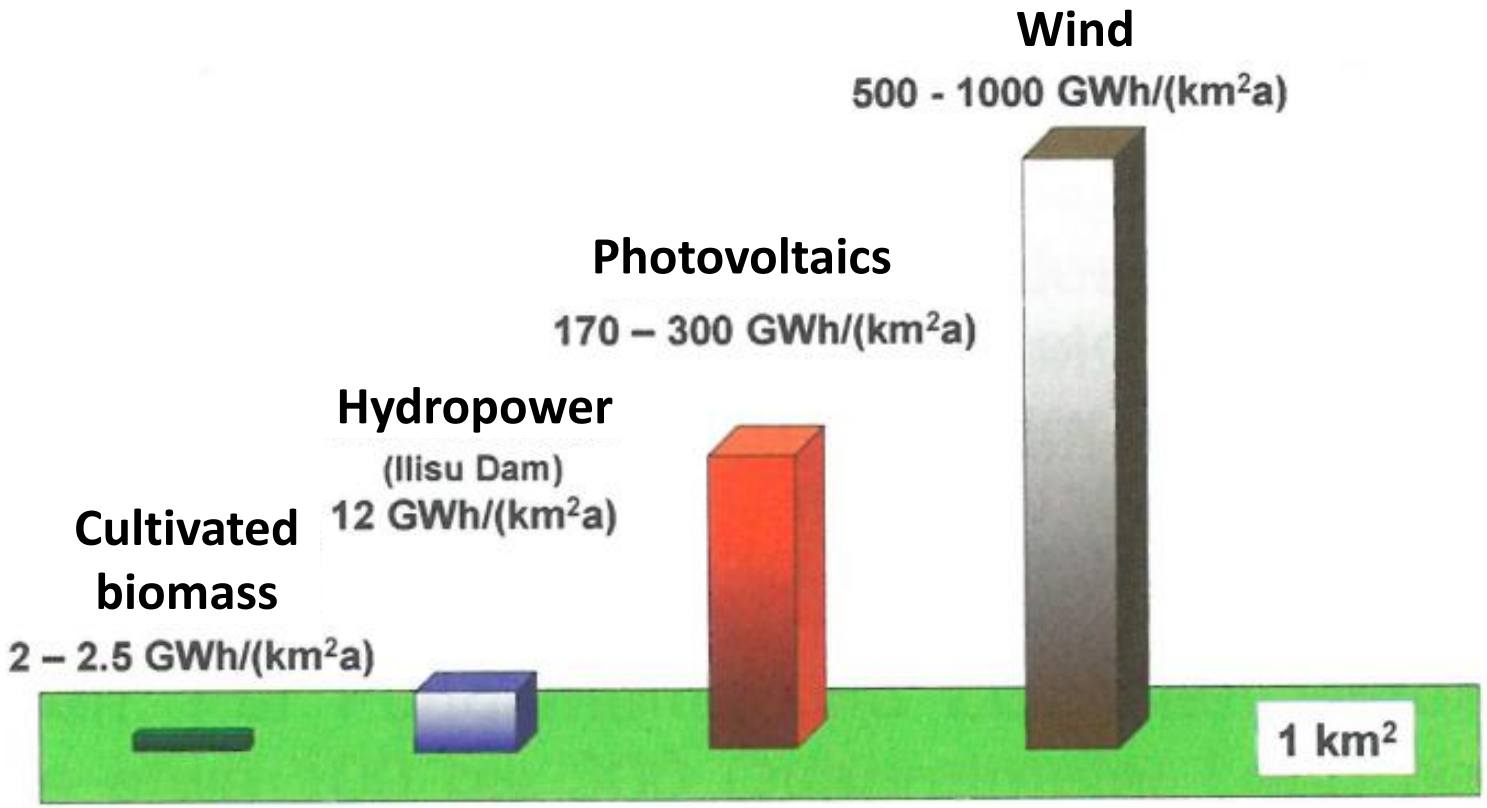
- Wind & solar becomes primary energy source in global scale
  → Fast steps towards renewable methanol needed

- Industrial scale production of Methanol since 1923 (BASF)

Great outlook for Methanol to become the favoured E-fuel

Power to X

Power yield from comparison



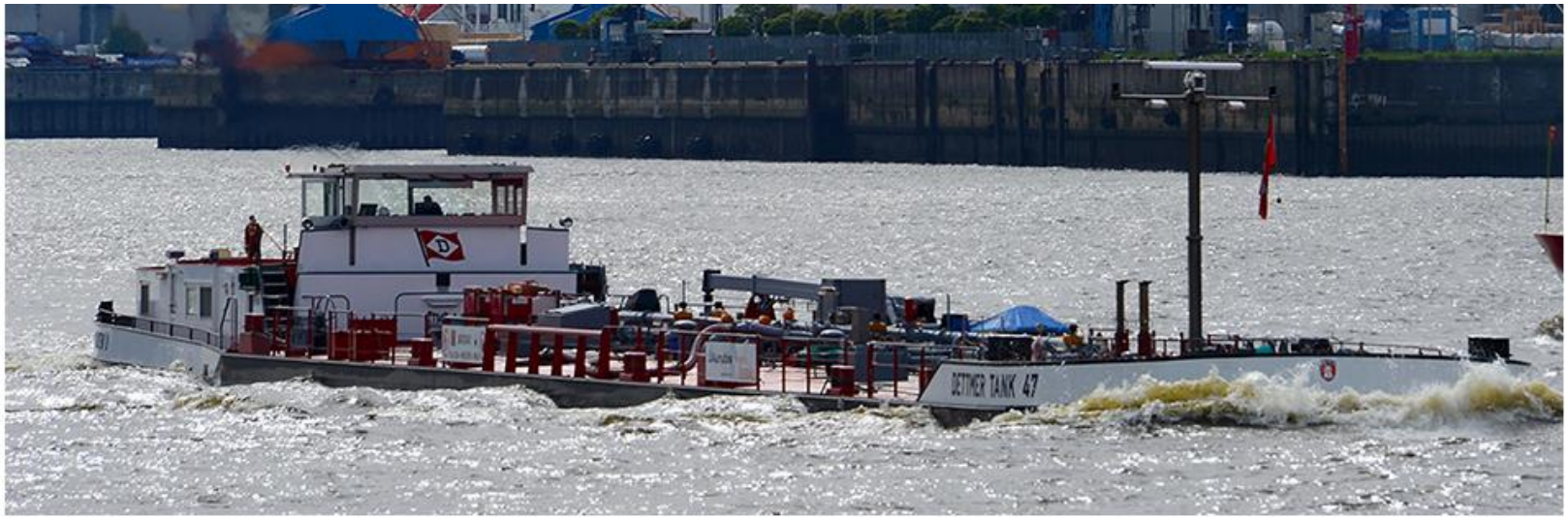
Source: „Energiewende zu Ende gedacht“, Ulf Bossel, 2014

Sun & Wind yield substantially more, sensible land use compulsory.

Infrastructure

- Infrastructure plays a major role (*costs!*)
- Methanol infrastructure already present

  → It can vastly be extended by adjustments to existing tanks.



- Bunkering workshop conducted

A world wide spread fleet could practically be existent.

Conclusion

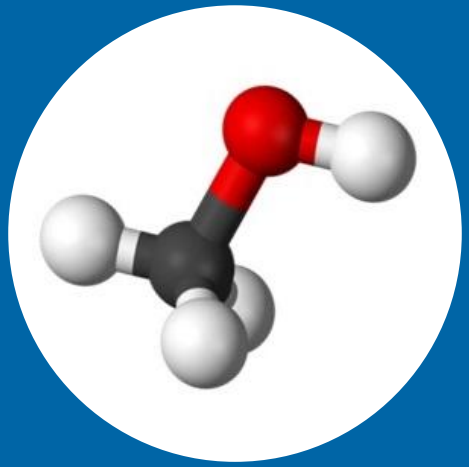
- Physics of Methanol surpasses other alternative fuels
- Ship design: Easy, advantages, practicable, understandable
- Methanol should be treated as **“liquid fuel system”**

- Compelling environmental properties

- Most promising in LCA when renewably provided

- Infrastructure could become a key enabler

Appeal: Utilise Methanol’s advantages



Thank you for your attention.