





Industrial H2 and Liquid H2 /Organic Carriers













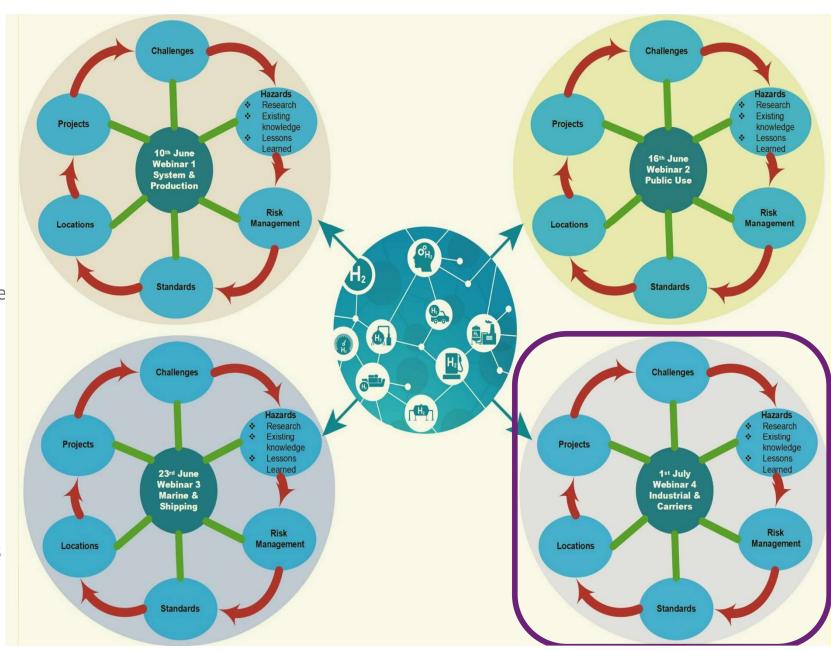






Webinar 4 – 1st July Hydrogen: Industrial H2 and Liquid H2 /Organic Carriers

- H2 use in glass furnace firing: Andrew Keeley, NSG and Clare Dunkerley, OSL
- Green NH3 as hydrogen carrier: Nikolaj Knudsen, Haldor Topsøe
- 3. Safety Aspects of Alternatives for Hydrogen Transport and Storage: Gianluca Carigi, MES International



Webinar Programme

	Session	Approximate Timing
	Introduction from S&LP SIG host	5 min
Speaker 1	Andrew Keeley and Clare Dunkerley: H2 use in glass furnace firing.	25 minutes
	Panel discussion	10 minutes
Speakers 2	Nikolaj Knudsen, Haldor Topsøe: Green H2 and H2 Carrier	20 minutes
	Panel discussion	10 minutes
Speaker 3	Gianluca Carigi, MES International: Safety Aspects of Alternatives for Hydrogen Transport and Storage	20 minutes
	Panel discussion	10 minutes
	Question and answer session	20 minutes

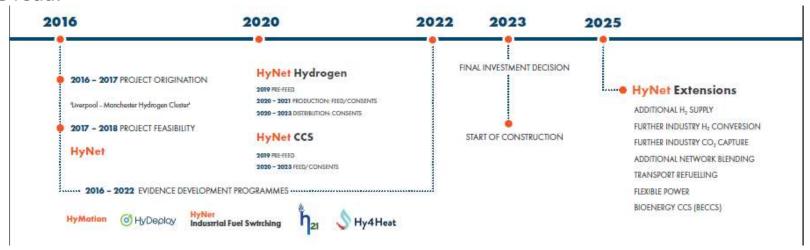






HyNet

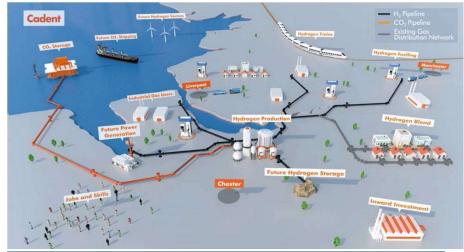
- HyNet North West project key part of transition to 'net zero' greenhouse gas emissions by 2050.
- Led by Progressive Energy
- Project started in 2016 with feasibility study.
- Together with carbon capture and storage (CCS), these technologies have the potential to reduce carbon dioxide emissions by 10 million tonnes every year by 2030 – the equivalent of taking four million cars off the road.

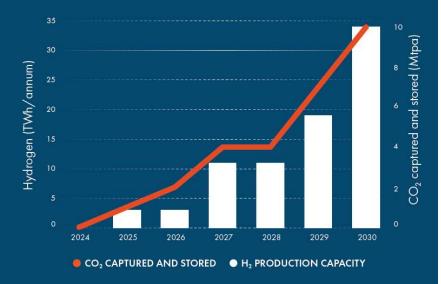


Current phase of development building the evidence

HyNet

- Proposal is to generate 'Blue' hydrogen at facility on Essar site at Stanlow
 - Hydrogen generated from methane with CO₂ captured and stored in redundant gas fields in Liverpool Bay.
 - Hydrogen supplied to industrial users in North West (Unilever, Jaguar Land Rover, Encirc & NSG.
- £5.2m BEIS funding for hydrogen firing trials at Essar, Dunphy,
 Unilever and NSG to be completed by March 2021. Also separate
 £7.5m funding for hydrogen generation FEED study.
- Aim for project to go live in 2025.
- Firing 100% hydrogen instead of natural gas at Greengate would reduce CO₂ emissions by ~80%. Remaining CO₂ emissions from decomposition of carbonates.
- Announced to press on 17th February by North West Hydrogen Alliance
- BBC North West and Granada were on site at Greengate interviewing Matt Buckley following announcement of the go ahead for trials.

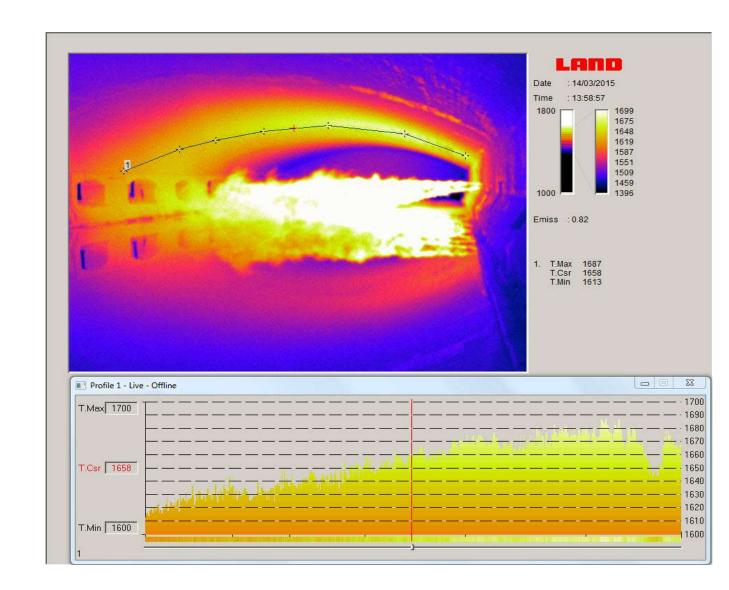




Potential major reduction in CO₂ emissions

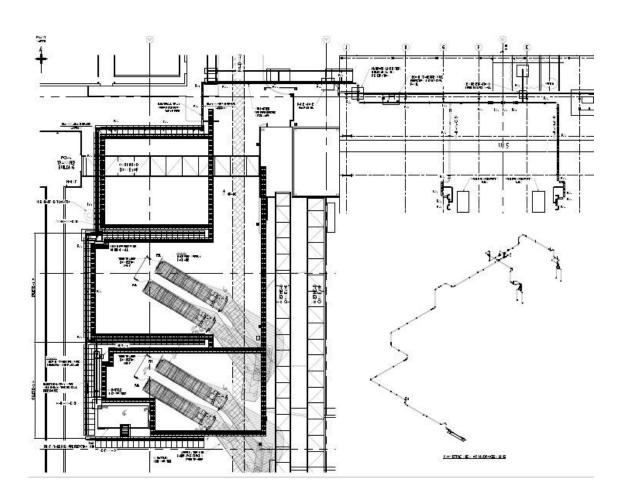
Glass Furnace

- Cross fired furnace –
 reverse firing direct every
 20 minutes
- 8 ports
- Heat transfer direct from flame to furnace structure and glass melt
- Converting the first port to fire hydrogen
- H2:NG fired on port 1 with H2 increasing from 20 to up to 100% depending on performance
- CFD modelling carried out before agreeing trials



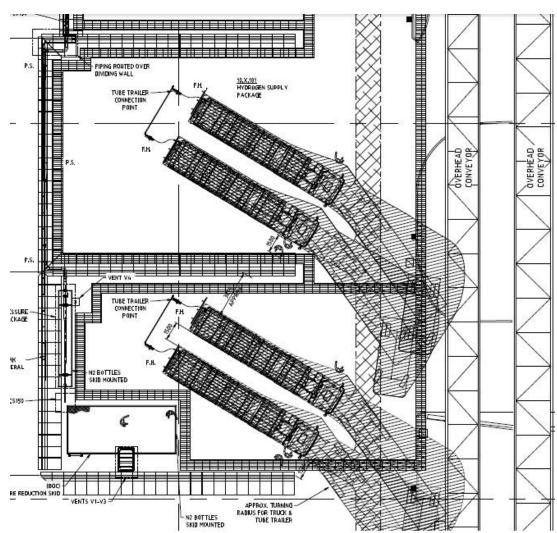
HyNet Trial Installation

- Designed by OSL
- Two configurations
 - Port 1 trials
 - Trials to assess maximum hydrogen percentage
 - Series of 8 hour trials
 - Manual control
 - All ports (HyDeploy)
 - 15% hydrogen by volume on all ports
 - 5 day continuous trial
 - Fully automatic control

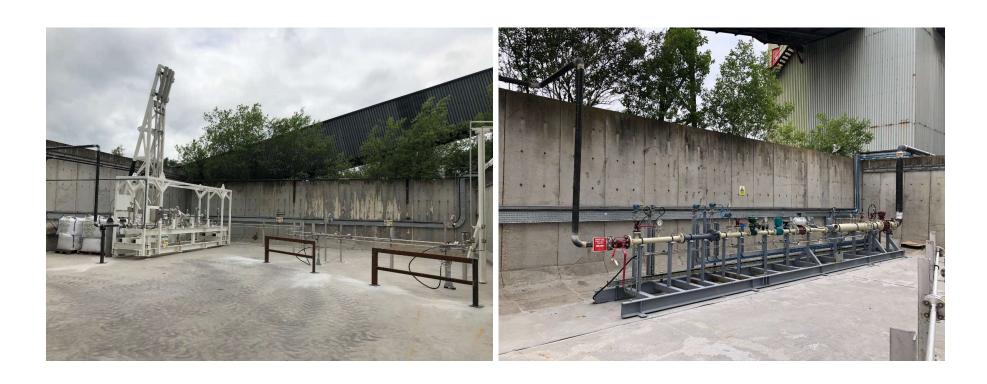


HyNet Trial Installation

- Hydrogen delivered in tankers at 228 bar pressure
- BOC skid reduces pressure to 10 bar
- Orbital skid reduces pressure to ~0.5 bar for port 1 trials
- Pair of tankers on line at a time
- At full flow using 1 tanker every 40 minutes.



BOC Skid & Flow control Skids



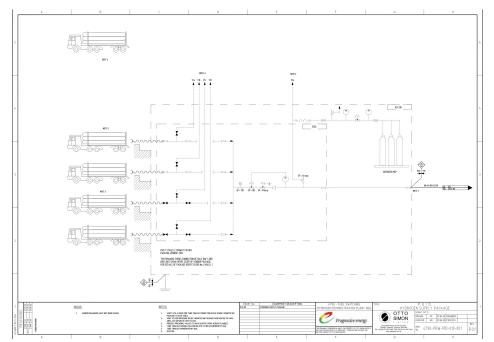
HyNet Trial

- Port 1 trials
 - Hydrogen reversal valves
 - Flow control valve start to close before reversal (to minimise pressure spike)
- All port trials
 - Reconfigure to add u/s individual port control valves
 - New GC to measure composition of mixture
 - Wobbe from new GC used in DCS instead of current value
 - No change for the operator



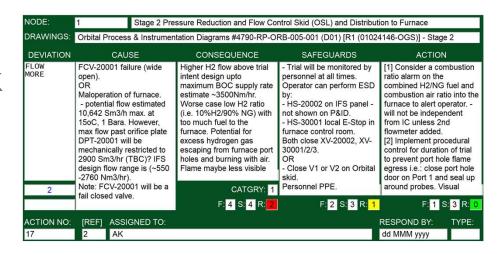
Hazard Studies 1 & 2

- Identifying inherent hazards of dealing with Hydrogen - flammability, diffusivity, buoyancy, hydrogen embrittlement.
- Identifying potential building, infrastructure, layout and transport issues.
- Paying attention to ventilation, hydrogen accumulation at high points, leak detection.
- Pinpointing key activities, such as changeover of duty to/from hydrogen and blends and purging.
- Agreement of risk tolerability criteria, regulations, standards, codes and guidance.



HS3/HAZOP

- Qualitative consequence and frequency allocation to enable risk ranking and provide link to next stage risk analysis (FTA/LOPA)
- Identification of gaps in risk tolerability – requirement for new safeguards
- Action monitoring for close-out requiring evidence

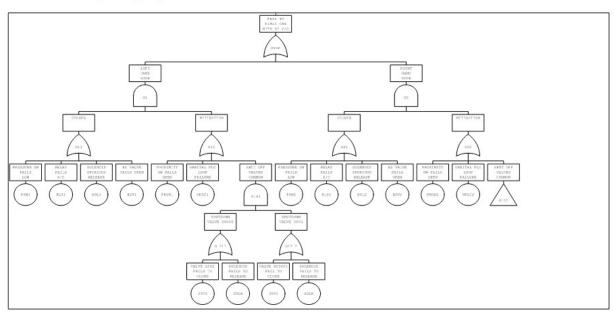


		A	В	С	D	E	F	G	н
5	Catastrophic > 5 fatalities (1 offsite)	1	1	1	2	2	2	2	2
4	Major 1 onsite	0	1	1	1	2	2	2	2
3	Severe disabling	0	0	1	1	1	2	2	2
2	Serious LTI	0	0	0	1	1	1	2	2
1	Significant First aid	0	0	0	0	0	1	1	2
0	Negligible	0	0	0	0	0	0	0	0
Qualitative descriptions of frequency of event		Unknown – No recorded instances	Very Rare - Has happened within the industry internationally	Rare - Has happened within the industry nationally	Very Unlikely - has been recorded within the same company/ organisation worldwide	Unlikely - has been recorded within the same company/ organisation nationally	Possible - may occur within the expected lifetime of the plant	Likely - may occur more than once within the expected lifetime of the plant	Common – may occur multiple times per year at facility
Times between occurrences (years)		10,000,000	1,000,000	100,000	10,000	1000	100	10	1
Times per		1.0 x 10 ⁻⁷	1.0 x 10 ⁻⁶	1.0 x 10 ⁻⁵	1.0 x 10 ⁻⁴	1.0 x 10 ⁻³	1.0 x 10 ⁻²	1.0 x 10 ⁻¹	1.0 x 10 ⁻⁰
Risk Categor	ry	Broadly Acceptable		Tolerable if ALARP		Intolerable			

LOPA/FTA

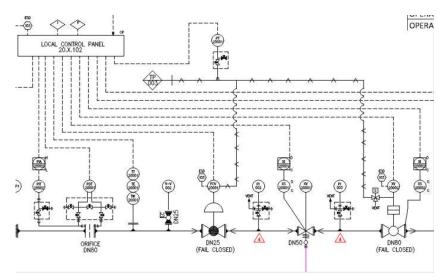
- Three Scenarios
 - High hydrogen flowrate
 - H₂ reversal failure
 - Overpressure of NG line with H₂
- Preliminary LOPAs
 demonstrated that the
 methodology was not
 granular enough and moved
 to an FTA approach
 supported by David Smith at
 Technis
- FTA demonstrated all risks fell within tolerable limits.

FIGURE 3.2 - Failure to changeover Hydrogen flow



Protection of Gas Network

- Backflow of hydrogen into the gas grid was an initial concern but with the safeguards put in place in the design, the risks were deemed tolerable.
- Unexpected issue with backpressure in NG distribution line.
 - Likelihood of over pressure in the natural gas line if the hydrogen blending system continued to inject hydrogen during a reversal is high.
 - NG Supply pipework rated at 5 barg, protected with mechanical slam-shuts at 4.3 and 5 barg.
 - The risk of fully isolating gas flow to site due to over-pressurisation of the line from the HyDeploy trial is unacceptable.
 - Solution is to reduce setpoints on Orbital slam-shuts from 4.5 to 4.3 barg to increase margin above line pressure drop.

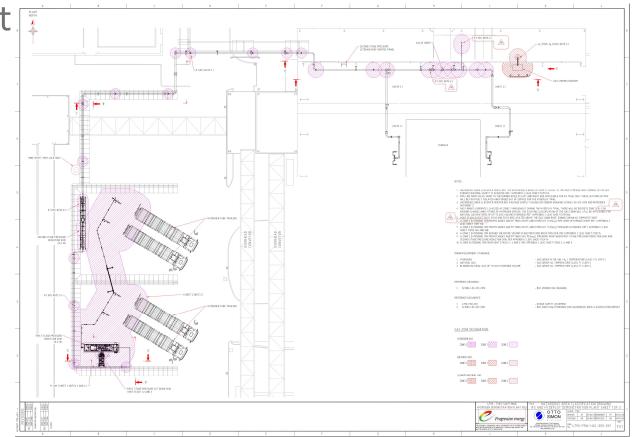


1	DEVIATION	CAUSE	CONSEQUENCE	SAFEGUARDS	ACTION
10	PRESSURE HIGH	Control downstrean pressure to 4.5 Barg to protect NG pipework rated at 5 Barg.	Overpressure downstream pipework up to 10 Barg. Hydrogen supply pipework is rated to class 150 (~19.8Barg). Natural gas supply pipework rated ~5Barg. Potential for DN150 rupture and combined H2 / NG release inside furnace building. Ctgy: [1] Freq. [4] Svrty: [5] Risk:	- PS-20007 high pressure switch closes XV-20002 closes at 5.45 Barg Pneumatic slamshut XV-20001 closes at 5.8 Barg QA-30001 high gas detection alarm @10% LEL alerts operator QA-30001 high high gas detection @25% LEL trips H2 isolation valves. Freg: [1] Svrtty: [5] Risk: [1]	Consider lowering the setpoint for the PRV-20001 for operational / blending purpose; and verifying during commissioning. Review setpoints for the instrumented PS-20007 and the Pneumatic slamshut XV-20001 to protect the NG pipeline (must no exceed 5 Barg).
	ACTION NO: 4	ASSIGNED TO: AD TYPE: 2			
11	PRESSURE LOW	PRV-20001 failure (fully closed).	See No Flow.		

DSEAR

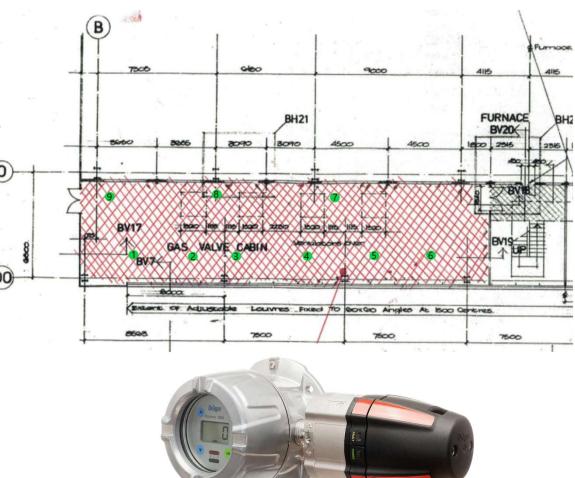
DSEAR Risk Assessment

- Ignition Hazard Assessment
- Dangerous Substances Physical Hazards Assessment
- HAC Flammable
 Materials List
- LEAC Sheet
- HAC Drawings



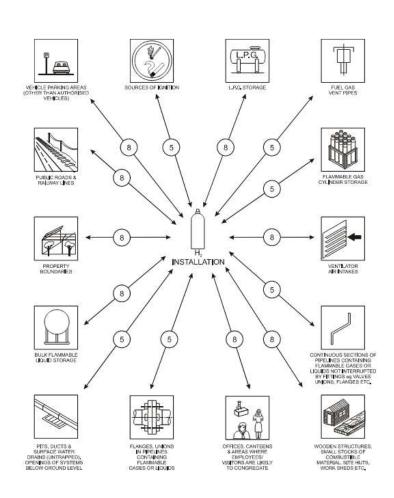
Gas Detection and Fire Risk Assessments

- Fire Risk Assessments conducted
- Ventilation Assessments in furnace room including air flow monitoring
- No accumulation of hydrogen or NG within furnace room unless a overy large leak.
- Hot surfaces = auto-ignition
- Gas Cabin has 9 Gas Detectors installed
- Hydrogen Detectors are crosssensitive to NG
 - Move from 10% LEL to 20% LEL detection



Layout

- BCGA Code of Practice CP33 for initial layout purposes.
- Reviewed against hazardous areas
- Location of relief valve on BOC Skid
 - Minimum distance from conveyer
 - Modelling carried out by BOC using PHAST
 - Generated a worst case scenario
- Noise from let-down station
 - Proximity to site boundary
 - Calculated at circa 81dB
 - Monitored during commissioning

















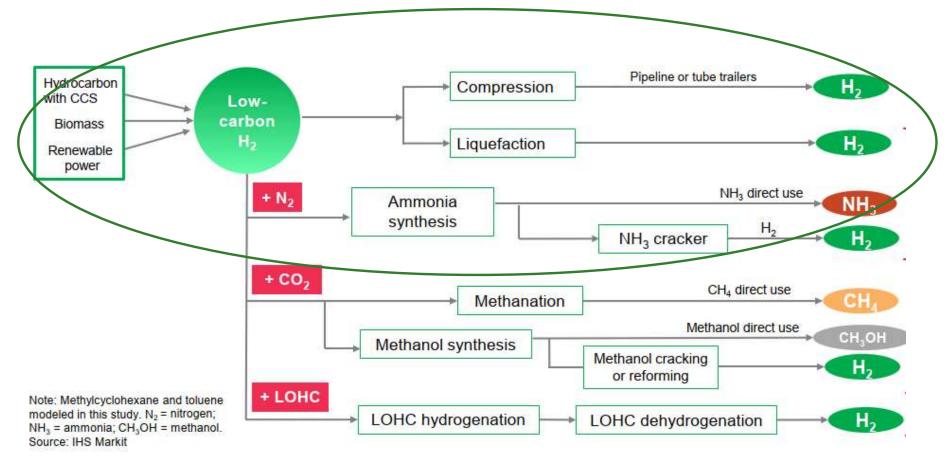


What we offer

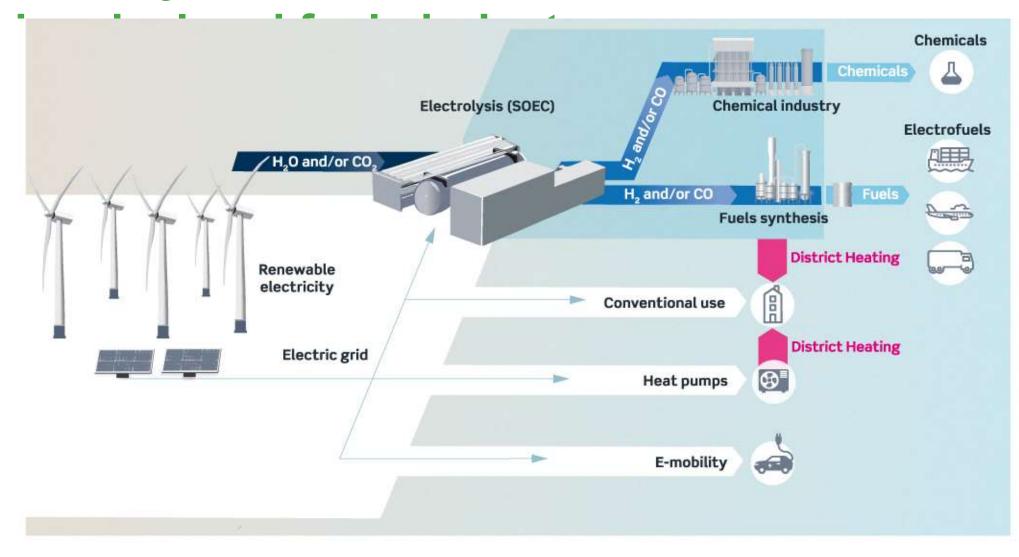
Complete solutions for a decarbonized world



Low carbon Hydrogen transport pathway



Electrolysis enables electrification of the



Ammonia as an energy vector Efficient Green Energy Storage and Transportation

- Carbon free clean fuel
- Abundant feedstock
- Low pressure energy storage
- H₂ carrier
- Ammonia synthesis is efficient in OPEX and CAPEX
- Proven, acceptable safety history for over 75
 years (inhalation hazard, must be handled
 professionally)
- Energy density 15.5 MJ/L (half of diesel, 32-36 MJ/L)
- Produced and traded world wide



Hydrogen or Ammonia Challenges and Advantages

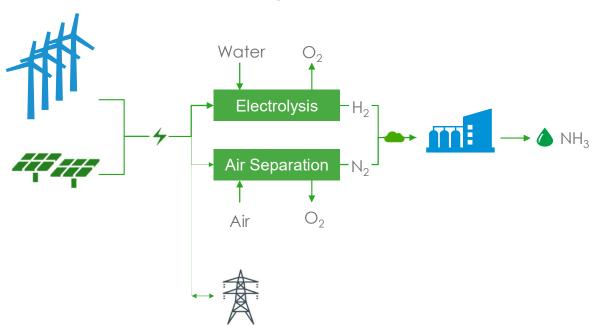
	Liquid H2	Ammonia
Infrastructure	Needs further development and construction for large scale	Possibility to utilize the currently available infrastructure for propane
Purpose (utilization)	hydrogen combustionFuel cell	Direct combustionFuel cell (after dehydrogenation and purification)Direct fuel cell
Challenges	 Requires very low temperature (about -250 °C) High energy requirement for cooling/ liquefaction Liquefaction can consume about 15% of the energy brought by hydrogen Difficult for long term storage Requires boil-off control (0.2-0.3%/d in well insulated tanker and up to 3%/d in truck) 	 Lower reactivity compared to hydrocarbons Requires treatment due to toxicity and pungent smell Treatment and management by certified engineers Consumes energy input in case of cracking and purification
Advantage	Risk of leakageHigh purityRequires no dehydrogenation and Purification	Possible for direct usePotentially be the cheapest energy carrierExisting ammonia infrastructure and regulation

Green ammonia

Dynamic operation by Topsoe

Decreasing capital investment cost

From renewable energy to electrolysis to synthesis

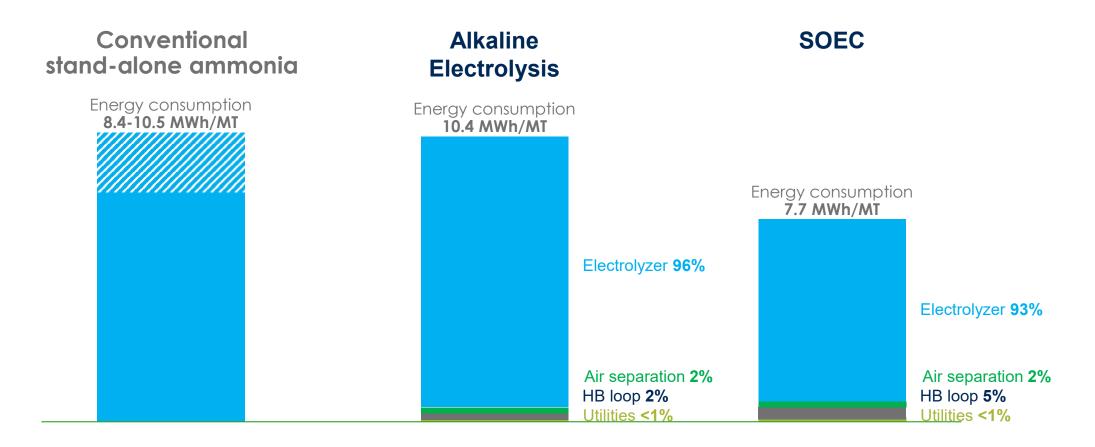


Advantages Power-to-ammonia

- Fully flexible operation
- No hydrogen storage
- Store energy as NH3
- Grid balancing

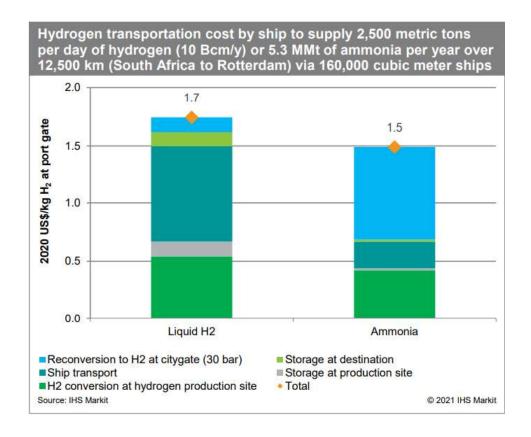
Different Technology Routes to Ammonia

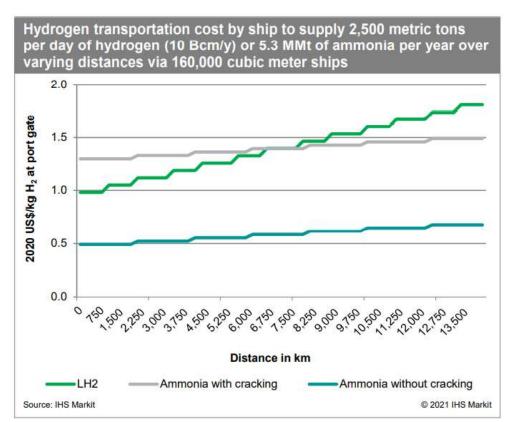
Energy consumption



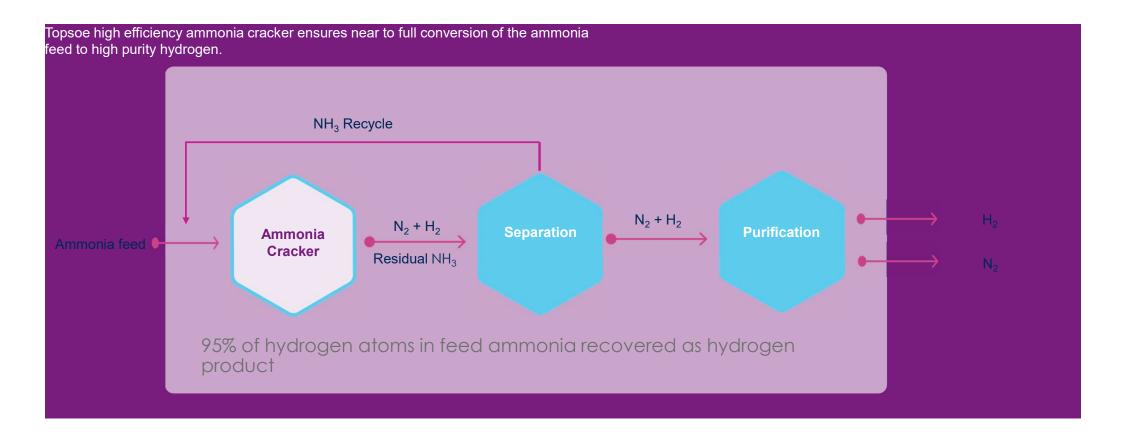
Ammonia as hydrogen carrier

Cost distribution

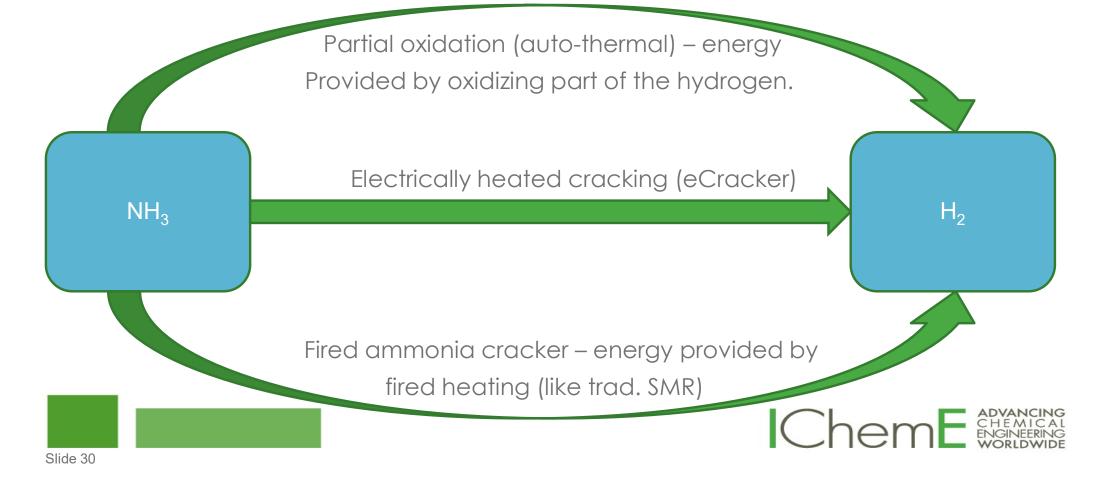


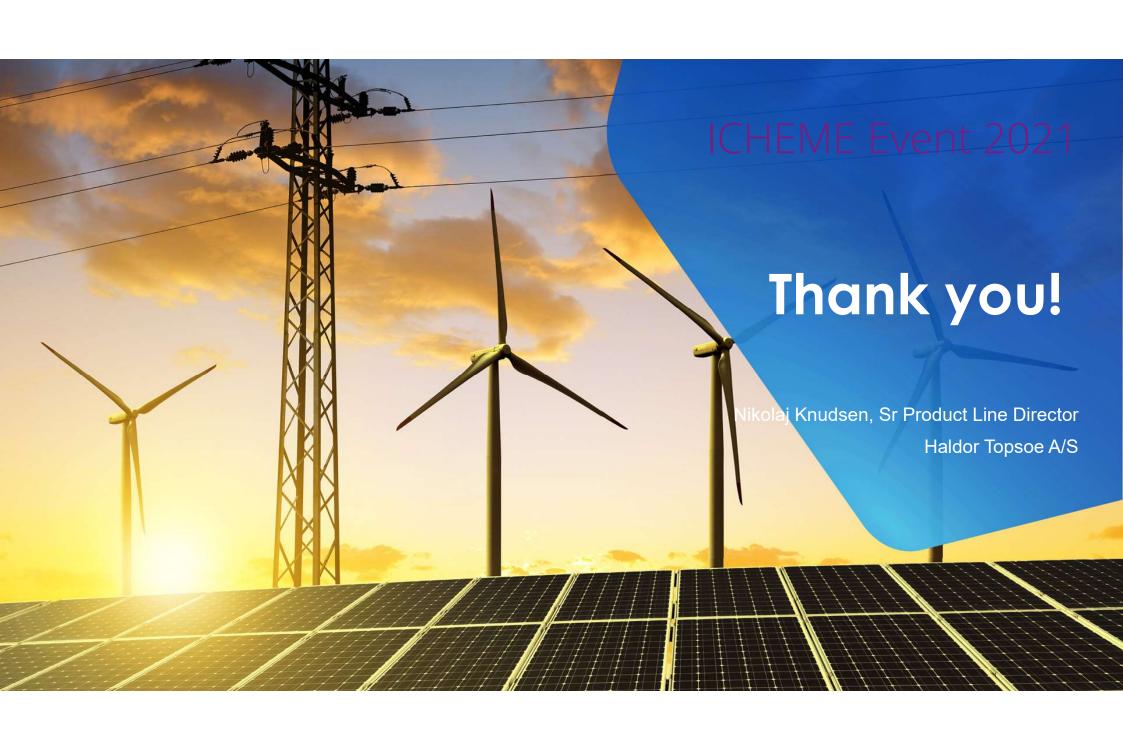


How it works



Catalytic decomposition of ammonia Endothermic – need energy to run























Monaco Engineering Solutions

Safety aspects of alternatives for hydrogen transport

Jul 2021

Gianluca Carigi

Introduction to MES



- Established in 2006 continuously expanding
- Approved with major International Operators and EPC Contractors
- Affiliated with IChemE, FABIG, SARS and Energy Institute
- Active members of the Energy Industries Council (EIC) and represented at the EIC Board
- Highly qualified and experienced specialists.
- Around 150 consultants globally, with large pool of associates
- Diverse academic background and professional experience (e.g. consultancy, EPC, Operator, etc.)
- · Chartered engineers and Fellows
- Operator approved chairpersons
- TUV certified and functional safety experts
- Presented / published at major conferences / events (e.g. IChemE Hazards, Mary O'Connor, ASSE)

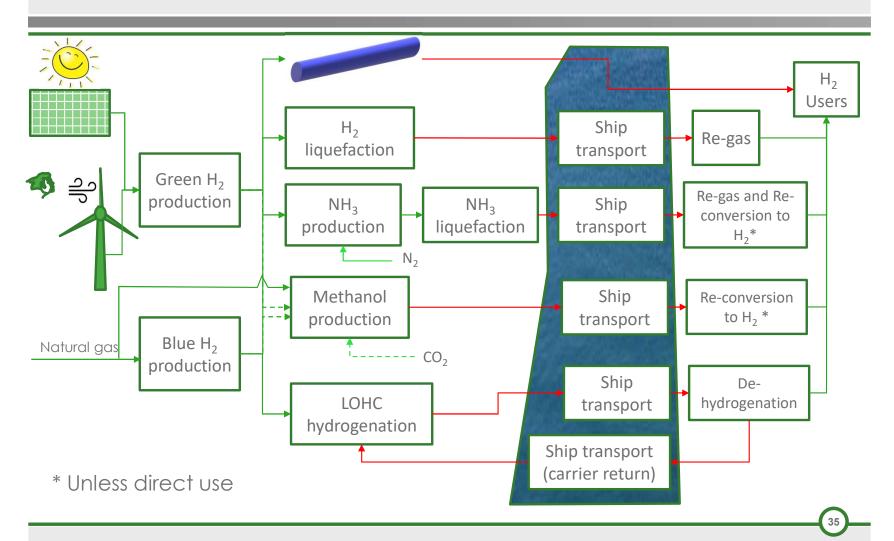
International consultancy provider of HSE, Asset Integrity, CFD, Cyber Security & Technical Engineering Services



Clean Energy, Renewables, Oil & Gas, Petrochemical, Refining, Chemical, Manufacturing and Transportation Industries

Hydrogen transport





Liquid hydrogen



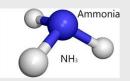
- For liquid H₂, heat liberated in ortho/para transition is large (670 kJ/kg whilst latent heat of vaporisation is 446 kJ/kg) requiring boiloff system to be designed for this
- The thermal conductivity 120-190K can be 30-50% for para-H₂
- Supercritical H₂ in cryogenic conditions: heat coefficient unpredictable in turbulent to laminar transition and lower in laminar regime
- Significant inventories & Tanks location wrt to H₂ production
- Pipe and components designed for temperature fluctuation from ambient to cryogenic H₂
- Tanks maintained at positive pressure to avoid air ingress (solidified air can plug pipes and jam valves)
- Avoid traces of O₂ in the liquified gas and ensure adequate purging prior to operation
- Positive removal of N₂ if used for purge (so avoid it becoming solid during operations). (Using He is expensive)

Liquid hydrogen



- Adequate design of boil-off system. Protections against pressure generated when liquid vaporises and dispersion from vent to consider buoyance of vented gas
- Personnel protection against cold T
- Release con solidify ambient air: O₂ enrichment following a release lowering ignition energy and increase detonation hazards (mixtures a shock-sensitive)
- Cryogenics spill management (avoiding splash off, pool management, effect on adjacent facilities) and protection
- Loading and offloading systems (quick release couplings)
- Risk of Rapid Phase Transition (RPT), e.g. when released on water
- Management of storage on ships/ boil off/ fuel system
- Re-vaporisation systems (conditions management/ ortho-para transition)
- Potential use for LH₂ refuelling stations in urban area (population, congestion/ confinement)

Ammonia Hazards





- Hydrogen present in large quantities (in integrated complexes)
- Ammonia is highly toxic (IDLH 300 ppm)
- Large quantities of ammonia produced (e.g. 1000 MTPD), storage tanks and export pipeline to jetty
- Ammonia refrigeration loop can be a significant risk contributor (large amount of equipment + significant liquid inventories)
- Pumps in export/ recirculation can also have a large leak frequency

Dispersion

- Depends on type of release (pressurised gas jet, two-phase jet, liquid leakages)
- Two-phase jet has typically 3 zones (expansion, entrainment and passive)
- Liquefied NH₃ releases generally results in a cold cloud (heavier than air)
- Affected by near-field obstacles (impact can cause significant rainout)
- Distance for hazardous concentrations can be significant (e.g. LC50 can reach 1400m for large releases (but quickly dissipates once the source term ceases).
- Weather conditions greatly affect the distance reached
- Jets are visible (visibility increases with relative humidity)

Ammonia Risk Mitigation



- Minimise potential leak sources
- Strategically located isolation valves & risk based leak requirements
- Depressurisation to dedicated ammonia flares
- Open layout/ no barriers
- Leak containment around equipment and diked areas
- Early detection of leakages (suggested using gas detector mapping techniques. Consider CFD gas dispersion for better predictions)
- Personnel to be equipped with portable gas detectors
- Shelters in place/ breathing apparatuses locations (onsite and offsite)
- Provisions for dilution of ammonia releases (e.g. water spray curtains + monitors adjusted to fog mode)
- Distance between production and liquefaction/ storage (e.g. against hydrogen explosions and fires) vs. extra sectionalisation
- PFP on major ammonia inventories which can be exposed to fires
- Fast emergency response is key Appropriate onsite and offsite ERP

Ammonia export

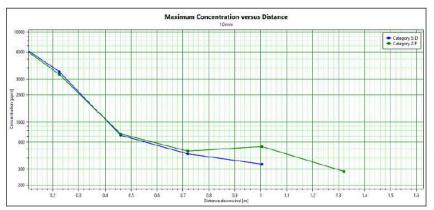


- Prevention of vehicle impact
- Consider pipeline leak detection system (or FO line detection to isolate the PL and stop storage and circulation pumps)
- Water tender coverage for NH₃ export pipeline leaks (but no direct water application to pools)
- Consider sectionalisation of export pipeline to limit inventories
- Gas detection at jetty
- Measures to prevent spillages during ship loading (e.g. loading arms / hoses provided with dry break couplings)
- QRA and ERP to cover loading and on-ship releases

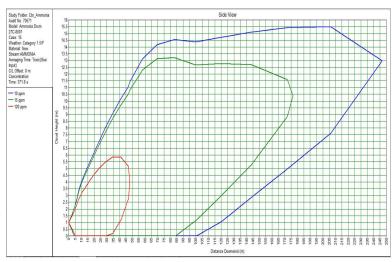
Ammonia detection



Conc vs distance graph - Ammonia IDLH (300ppm) at 1m



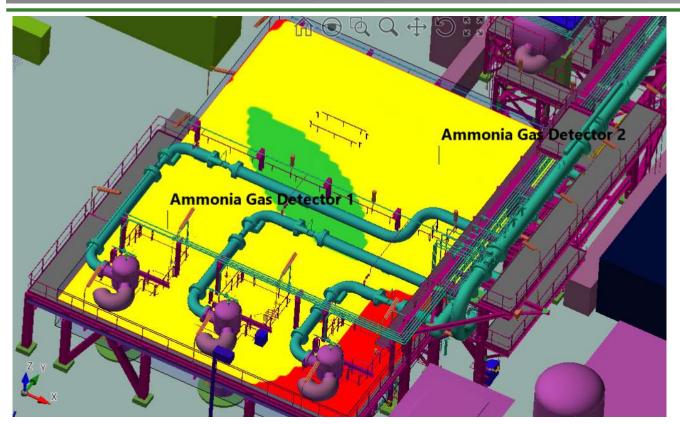
For streams with NH_3 conc. 6000ppm the distance to IDLH is $\geq 1m \rightarrow$ detection for sources with NH_3 conc. >5000 ppm



IDLH 300 ppm → Detection level 120 ppm

Ammonia detection





MES F&G
mapping
Tool shows
good coverage
for alarm only.
If shutdown is
required more
detectors
needed

F&G mapping can be coupled with CFD gas dispersion when congestion and/or confinement are present

NH₃ material aspects

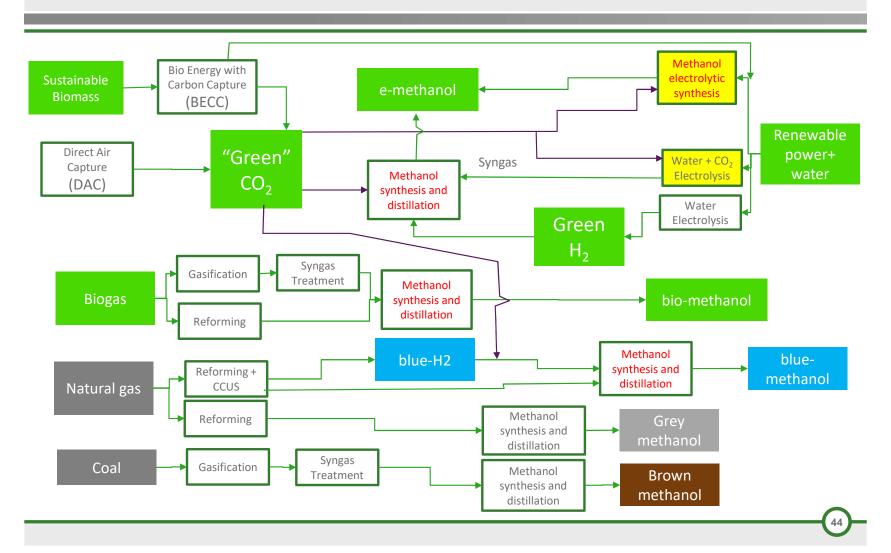




- Generally corrosive to copper, copper alloys, nickel and plastics
- <u>Carbamates:</u> need to remove traces of carbon oxides to avoid formation of ammonium carbamate and corrosion of downstream equipment
- Scaling: Tube failure due to scaling and under-deposit microbial corrosion in cooling water side of heat exchangers: eliminate low-velocity areas and CW treatment program
- Nitriding and H₂ embrittlement: HT/HP in ammonia-synthesis converter and nitriding (pipes and catalyst support grids) and hydrogen embrittlement can occur
- Stress Corrosion Cracking: SCC of carbon steel equipment used for storage and transport of anhydrous liquid ammonia
- <u>H₂ production/ Primary reformer</u>: Carburization, oxidation, overheating, stress corrosion cracking (SCC), sulfidation and thermal cycling of reformer tubes.
- Metal dusting: Metal dusting in the secondary reformer outlet sections. Carburizing reactions and C diffusion into the Fe-Cr-Ni alloy causing local mechanical fracturing of surface layers, pitting and failure
- Corrosion Loops Identification, Risk Assessment & Management (CRAS), FMECA, Risk Based Inspection (e.g. via MES software) and Reliability Centred Maintenance

Types of methanol





Methanol hazards

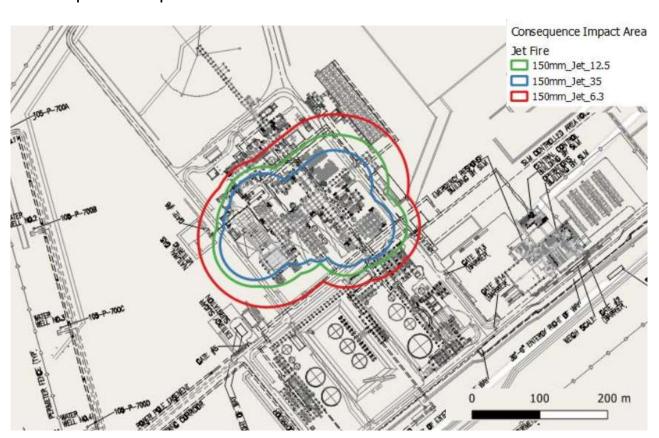


- Low flashpoint (11 $^{\circ}$ C), relatively low ignition energy (0.14 mJ compared with 0.28 mJ of methane)
- Heavier than air vapours and relatively low toxicity (IDLH 6000 ppm) but vapours are invisible and odour threshold is close to IDLH and health effects are delayed. Hence gas detection is important gas mapping should be considered along with CFD dispersions in congested areas
- Methanol fires are difficult to see (little emission in visible spectra)
- Water can be used as fire suppressant
- Risk dominated by events associated with syngas (due to H₂ and CO) and natural gas inventories
- Thermal radiation hazards (and in particular jet fires) represented the highest risks
- Inventory with highest contribution to LSIR on analysed plant was the natural gas desulphurisation, KO drum, pre-heating circuit and lines to fuel and to boiler (11.8t)
- The process area contributed 79% to the overall LSIR (31% JF, 16% EX, 15% Toxic, 5% PF)
- The storage area jet fire contributed 13% to LSIR (with PF 4%). This low PF contribution is due to methanol low burning rate and low released energy
- Overpressures calculated by CFD simulations and ignited at 4 locations. Max overpressure
 1.9 bar within plant area
- Distance between production and storage (vs. extra sectionalisation)

Jet fires



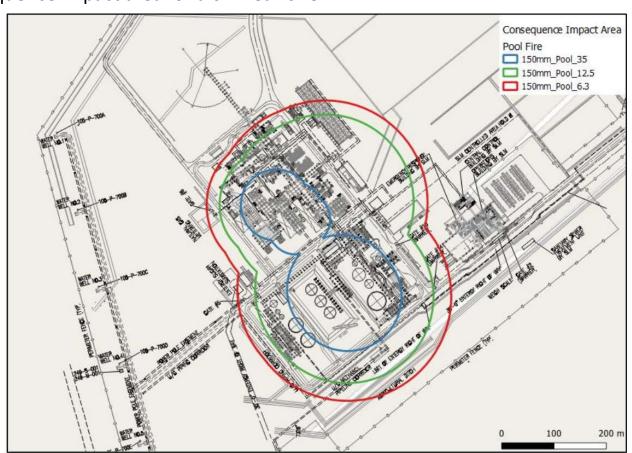
Consequence impact area for a 6 in leak size



Pool fires

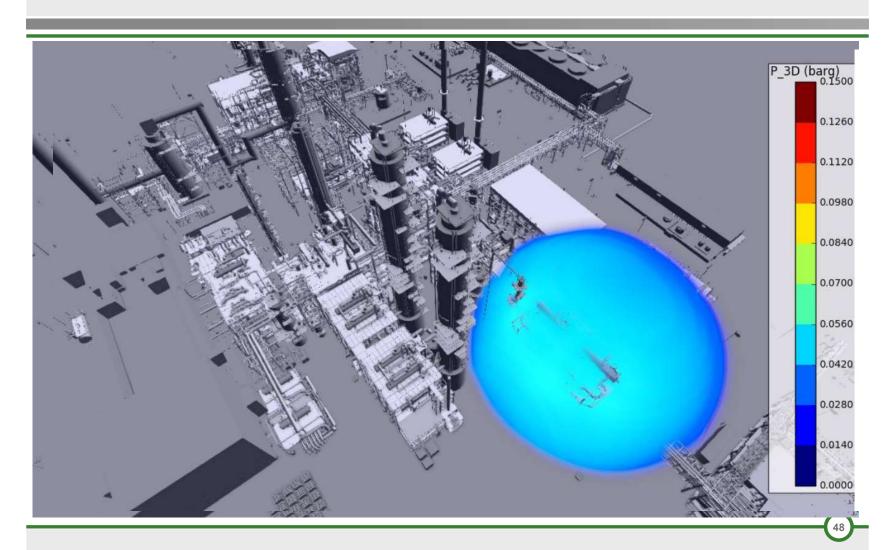


Consequence impact area for a 6 in leak size



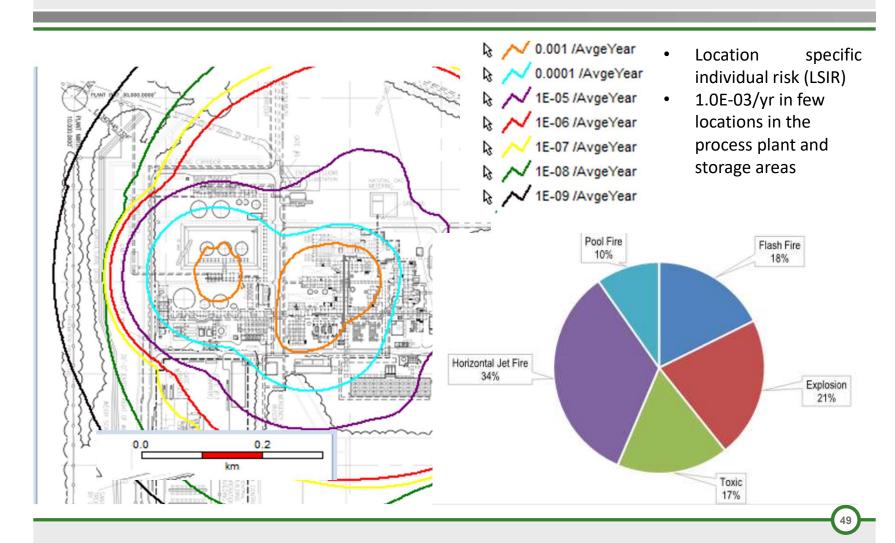
Explosion in methanol production plant





Methanol risks





Methanol - Other considerations



- Relatively low loading/offloading and transportation risks due to relatively benign flammability
- Incomplete combustion can lead to formaldehyde and formic acid pollutants
- Carbonic acid attack
- Formic acid causing corrosion of columns and trays
- Can be corrosive to some metals including Cu, Zn, Ti and some of their alloys. Al alloys not generally suitable due to methanol conductivity and galvanic corrosion (unless methanol vapour pressure is kept low, e.g. in tank roof due to blanketing)
- Effect on elastomers for sealing applications (valve, flange, pump and compressors seals).
 Swelling, chemical attack or explosive decompression (ED). High and low T limits
- Carbon steel, or 300 series austenitic stainless steels such as ASTM 304, 304L, 316, or 316L
 are preferable choices
- Techno economic considerations such as cost and weight are important but should be accompanied by adequate RBI and an RCM

LOHC



Carriers	PDBT - DBT		DNEC	- NEC	MCH - TOL	
Properties	-9 H ₂ -9 H ₂		- 6 H ₂		-3 H ₂ →	
Carrier Property	Perhydro- dibenzyl- toluene	Dibenzyl- toluene	Dodecahydro–9- ethylcarbazole C14H25N	9-Ethyl- 9H - Carbazole C14H13N	Methyl- cyclohexan e CH ₃ C ₆ H ₁₁	Toluene C ₆ H ₅ CH ₃
MW (g/mol)	290.5	272.4	207.4	195.3	98.2	92.1
Melting point (°C)	NA	-34/-39	NA	69	-126	-95
Flash point (°C)	NA	190	NA	186	-3	6
Boiling point (°C)	NA	390-398	270	280	101	111
Hydrogenation (HYD)/ De- hydrogenation (DEHYD)	DEHYD 1 bar/ 320°C	HYD 30-50 bar/ 150°C	DEHYD 1 bar/ 220 °C	HYD 70 bar/ 150 °C	DEHYD 3 bar - 350°C	HYD 10-50 bar/ 50-100 °C

⁻ Generally, toxicity assessment is more common for dehydrogenation counterparts than hydrogenated molecules

LOHC



	PDBT - DBT		NEC - DNEC		MCH - TOL	
	0,	9 H ₂	-6 H		-3 H ₂	
Carrier Property	Perhydro- dibenzyl-toluene	2,3-Dibenzyl- toluene	Dodecahydro-9- ethylcarbazole	9-Ethyl- Carbazole	Methyl- cyclohexane	Toluene
IDLH (ppm)					1200	500
Inhalation		Avoid breathing mist, gas or vapours		May cause respiratory tract irritation	May be fatal if enters airways	Exposure to high concentrations can lead to coma and death
Toxicity		LD50 Oral – Rat > 2000 mg/kg		LD50 Oral – Rat > 5000 mg/kg	LD50 oral rat 1280mg/kg	LD50 Oral –rat: 7530 mg/kg
Carcinogenicity		Not listed in IARC, OSHA and NTP		Not listed by ACGIH, IARC, NTP, or CA Prop 65		There is no evidence suggesting carcinogenicity of toluene in experimental animals
Ecotoxicity		Very toxic to aquatic life with long lasting effects		Toxic to aquatic life with long lasting Effects	Very toxic to aquatic life with long lasting effects Not readily	Expected to be harmful to aquatic organism But it is biodegradable

Alternatives



Alternative	Toxicity	Fires	Expl.	Synthesis	Conversion/ Liquefaction	Storage and Transport	Reconversion/ vaporisation
Liquid H ₂	N/A	High risk		N/A		High risk	Medium/ High risk
Ammonia	High risk	Low risk	Low risk	High risk	High risk	Medium/ High risk	Medium risk
Methanol	Low risk	Medium risk	Medium risk	High risk	N/A	Low risk	Medium risk
LOHC	Medium risk	Medium risk	Very low risk	N/A	Medium risk	Low risk	Medium risk

Questions?



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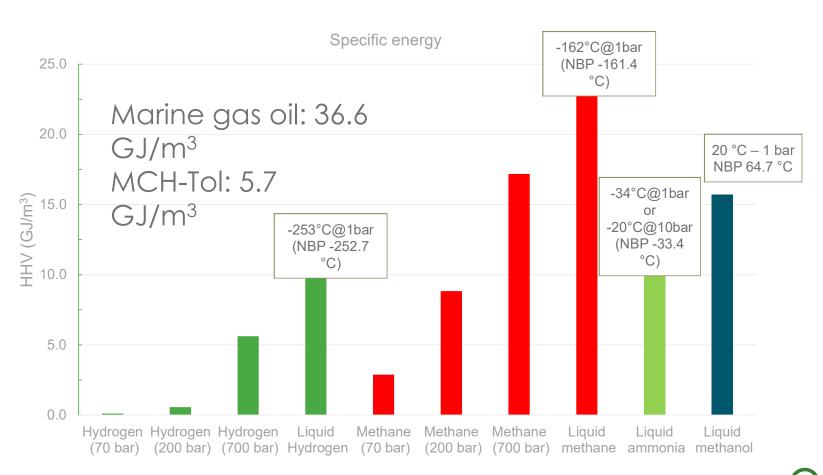
Flammability



Property	CH ₄	H ₂	CH ₃ OH	NH ₃	Toluene
Laminar burning velocity (m/s)	0.38	3.51	0.36	0.07	0.36
Min ignition energy (mJ)	0.28	0.011	0.14	8.0	0.24
AIT (°C)	586	499-577	439	657	535
Adiabatic flame T (°C)	1950	2210	1637	1577	2071
Flash point (°C)	Gas	Gas	11	132	4
Flammability limits (%)	5-15	4-73	6.7-36	15-28	1.2-7.1
IDLH (ppm)	Not toxic	Not toxic	6000	500	500

Fuel comparison



























Time for questions