

# Ammonia as a Marine Fuel: Safety

Ammonia Energy Conference - Niels de Vries

13 November 2019

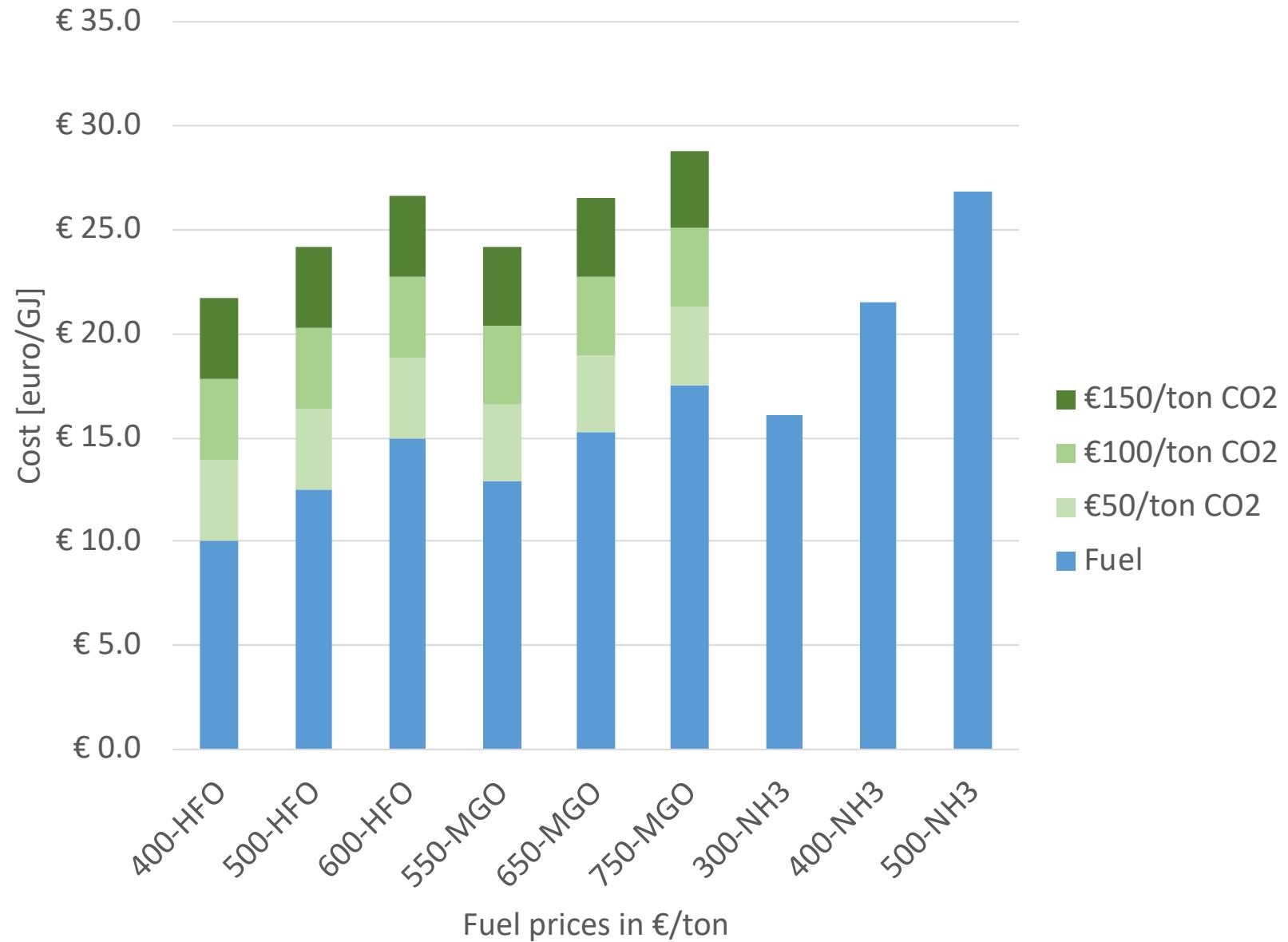


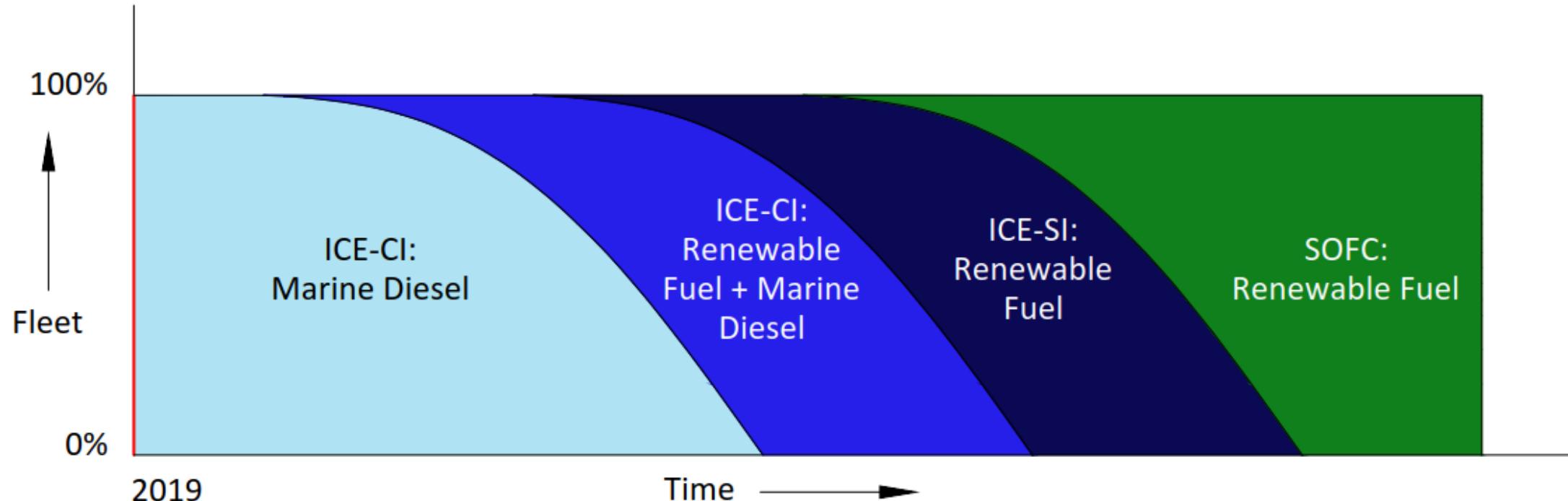
## Renewable Fuel Options: Potential of Ammonia

Fuel type:	Energy density LHV [MJ/kg]	Volumetric energy density LHV [GJ/m <sup>3</sup> ] ↓	Renewable synthetic production cost [MJ/MJ]	Storage pressure [bar]	Storage temperature [°C]
Marine Gas Oil (reference)	42.7	36.6	Not applicable	1	20
Liquid Methane	50.0	23.4	2.3	1	-162
Ethanol	26.7	21.1	3.6	1	20
Methanol	19.9	15.8	2.6	1	20
Liquid Ammonia	<b>18.6</b>	<b>12.7</b>	<b>1.8</b>	<b>1 or 10</b>	<b>-34 or 20</b>
Liquid Hydrogen	120.0	8.5	1.8	1	-253
Compressed Hydrogen	120.0	4.7	1.7	700	20

- Ammonia balanced solution
  - Volumetric energy density
  - Renewable synthetic production cost

## Fuel Pricing





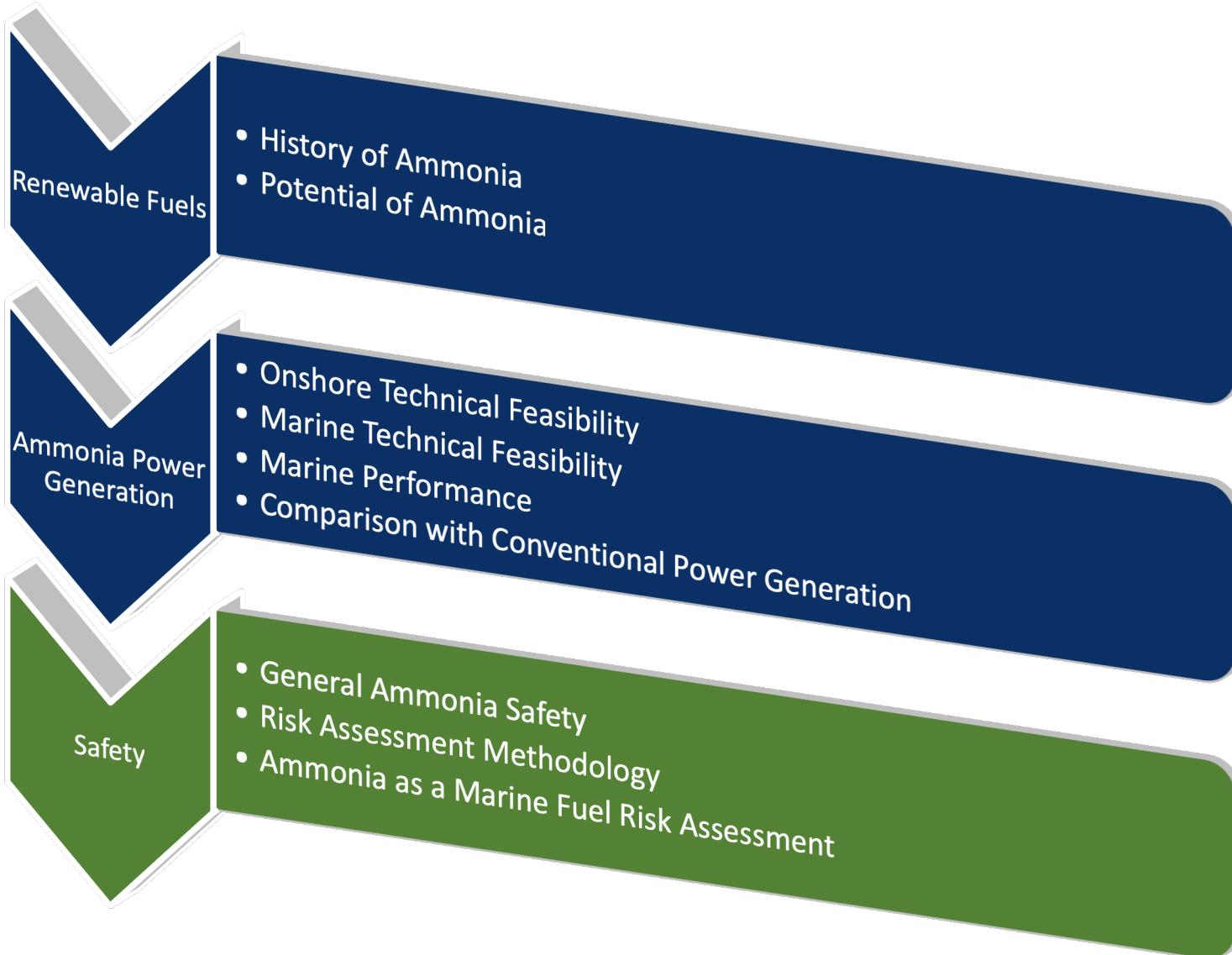
Renewable Fuel options:  
Hydrogen, Ammonia, Methanol  
and Others

ICE: Internal Combustion Engine  
Cl: Compression Ignition  
SI: Spark Ignition  
SOFC: Solid Oxide Fuel Cell

SCR: Selective Catalytic Reduction  
Exhaust gas after treatment, capable  
of reducing NOx more than 95%

Reduction of Harmful Emissions				
CO2	>80%	100%	100%	100%
NOx	0% (Apply SCR)	0% (Apply SCR)	100%	100%
SOx	>80%	100%	100%	100%
PM	>80%	100%	100%	100%

# Agenda



## What is Safety?



## What is Safety?



# Safety (Rules and Regulations)

## Natural Gas

- Bulk transport
  - IBC Code - International Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk, Amended by Resolution MEPC.225(64)
  - 1983/2014 IGC Code - International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk
- Fuel
- 2005:
  - IGF Code - International Code of Safety for Ships Using Gases or Other Low-Flashpoint Fuels First draft initiated
- 2017:
  - IGF Code Adopted

Fully developed for natural gas only

## Ammonia

- Bulk transport
  - IBC Code - International Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk, Amended by Resolution MEPC.225(64)
  - 1983/2014 IGC Code - International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk
- Fuel
- Future:
  - ?

# General Ammonia Safety

- CNG: Compressed Natural Gas
- LNG: Liquefied Natural Gas
- ULSFO: Ultra Low Sulphur Fuel Oil (0.1%)
- Globally Harmonized System of Classification and Labelling of Chemicals (GHS)

Hazard statements	Hazard category	Ammonia [79]	CNG [80]	LNG [81]	Diesel [82]	ULSFO [83]
H220 Extremely flammable gas	1A		X	X		
H221 Flammable gas	2	X				
H226 Flammable liquid and vapour	3				X	
H227 Combustible liquid	4					X
H280 Contains gas under pressure; may explode if heated	Compressed gas Liquefied gas (b)	X	X*			
H281 Contains refrigerated gas; may cause cryogenic burn or injury	Refrigerated liquefied gas			X		
H304 May be fatal if swallowed and enters airways	1				X	
H313 May be harmful in contact with skin	5				X	
H314 Causes severe skin burns and eye damage	1B	X				
H315 Causes skin irritation	2				X	
H331 Toxic if inhaled	3	X				
H332 Harmful if inhaled	4				X	X
H350 May cause cancer	1B				X	
H351 Suspected of causing cancer	2				X	
H361 Suspected of damaging fertility or the unborn child	2				X	
H373 May cause damage to organs through prolonged or repeated exposure	2				X	X
H410 Very toxic to aquatic life with long lasting effects	1	X				X
H411 Toxic to aquatic life with long lasting effects	2				X	

Table 7-1: Hazard statements comparison of ammonia with other fuels

# General Ammonia Safety

- Risk levels:
  - Flammability
    - Flammable gas
    - A narrow flammability limit: 15-28%, with a high lower limit compared to other fuels
    - A high absolute minimum ignition energy compared to other fuels
    - A high auto ignition temperature: 651 °C
- Toxicity
  - AEGL 3: Life-threatening health effects or death
- Environmental impact
  - Very toxic to aquatic life with long lasting effects

(ppm)	10 min	30 min	60 min	4 hr	8 hr
AEGL 1	30	30	30	30	30
AEGL 2	220	220	160	110	110
AEGL 3	2,700	1,600	1,100	550	390

Table 7-4: Acute Exposure Guideline Levels (AEGL): Ammonia

## Risk Assessment Methodology

- Identification, where the risk is identified
- Analysis, where the risk is quantified
- Assessment, where the risk is prioritized/ranked
- Mitigation, where the risk is eliminated, reduced or prevented

# Risk Assessment Methodology

- Assessment based on IGF Code No. 146

Multiple fatalities	Catastrophic damage	E						
*Single fatality	Major damage	D						
Major injury	Localised damage	C						
Minor injury	Minor damage	B						
Zero injury	Zero damage	A						
People	Assets/ Environment		1	2	3	4	5	
Severity ↑		Chance	Remote	Extremely Unlikely	Very Unlikely	Unlikely	Likely	
Likelihood →		Chance per year	$<10^{-6}/y$	$\geq 10^{-6}/y$ $<10^{-5}/y$	$\geq 10^{-5}/y$ $<10^{-4}/y$	$\geq 10^{-4}/y$ $<10^{-3}/y$	$\geq 10^{-3}/y$	
		Chance in Vessel Lifetime	$<1$ in 40,000	$\geq 1$ in 40,000 $<1$ in 4,000 $<1$ in 400	$\geq 1$ in 4,000 $<1$ in 400	$\geq 1$ in 400 $<1$ in 40	$\geq 1$ in 40	

Table 9-1: Risk matrix, People, Assets and Environment combined

# Risk Assessment Methodology

- Work flow example

Reference	Failure Mode	Cause	Effect	Detection	Original Risk Ranking
1-3-01	Ammonia leakage	Various	Engine room exposed with gaseous ammonia	None	E5

Table 9-2: Part I: Risk assessment work flow methodology example: Identification, Analysis and Assessment

Reference	Mitigation	Overall Assessment	Final Risk Ranking
1-3-01	<ol style="list-style-type: none"> <li>1. Reduce exposed length ammonia piping length in engine room</li> <li>2. Apply double walled vented piping in engine room</li> <li>3. Add ammonia detectors in engine room and within double walled vented piping</li> <li>4. Add main isolation valves</li> </ol>	<p>Chances reduced by exposed length reduction. Impact reduced by application of double walled piping in engine room. Impact further reduced by adding ammonia detectors and main isolation valves which close when an ammonia leakage occurs. Ammonia piping outside of engine room to be reviewed separately.</p>	C2

Table 9-3: Part II: Risk assessment work flow methodology example: Mitigation

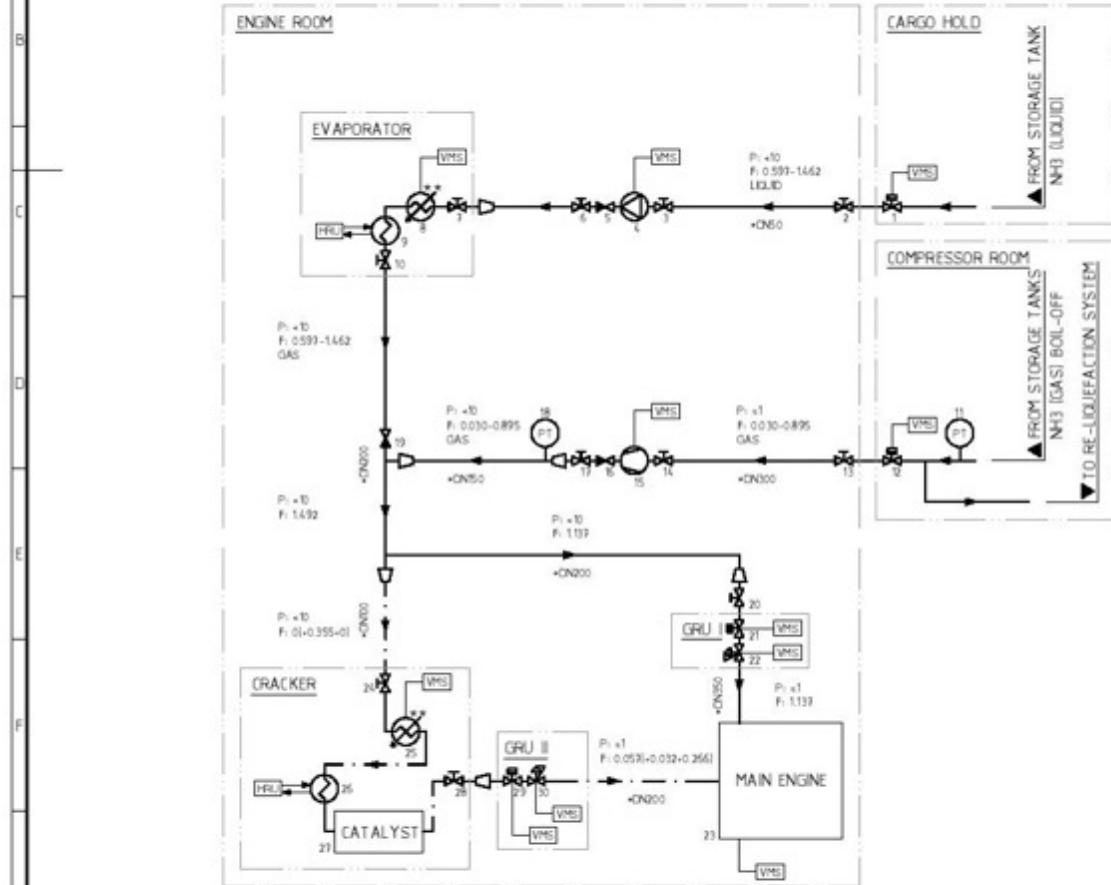
# Ammonia as Marine Fuel Risk Assessment

- Risk assessment 1 (based on technical basis NH3 fuel system diagram, zero safety measures, functional only)
- Reflection risk assessment 1
- Risk assessment 2

# Ammonia as Marine Fuel Risk Assessment

Main scope and assumptions:

- Zero leakage in normal operational conditions
- Main engine assumed to be inherently safe considering fuel injection
- Fuel label: Ammonia & hydrogen



SYMBOLS	
	HAND OPERATED VALVE
	NON RETURN VALVE
	REDUCER
	COMPRESSOR
	HEAT EXCHANGER
	REMOTE OPERATED VALVE
	PRESSURE REGULATING VALVE
	PRESSURE TRANSMITTER
	CENTRIFUGAL PUMP
	HEATER

## LEGEND

— NH<sub>3</sub> FUEL  
 — H<sub>2</sub>-NH<sub>3</sub>-NO<sub>x</sub> FUEL

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**NOTES**

PIPE INDICATION  
P: PRESSURE bar  
F: FLOW kg/s  
STATE OF MATTER (GAS, UNLESS NOTED OTHERWISE)

HRU: EXHAUST GAS HEAT RECOVERY UNIT  
GRU: GAS REGULATING UNIT  
VMS: VESSEL MANAGEMENT SYSTEM (POWER SUPPLY AND CONTROL)

### • PROVISIONAL DIMENSIONS

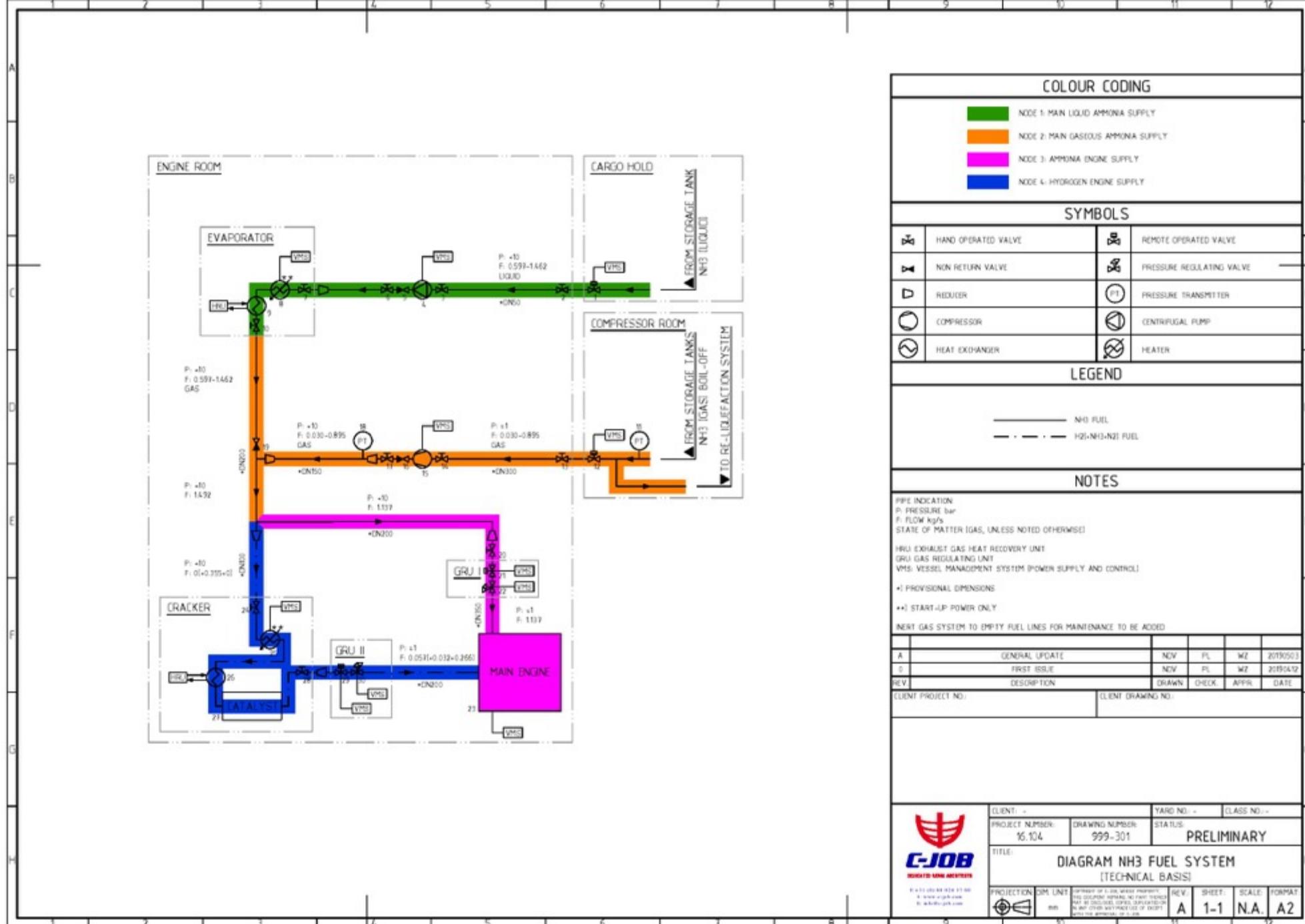
••) START-UP POWER ONLY

INERT GAS SYSTEM TO EMPTY FUEL LINES FOR MAINTENANCE TO BE ADDED

A	GENERAL UPDATE	NOV	PL	WZ	20190503
B	FIRST ISSUE	NOV	PL	WZ	20190412
REV	DESCRIPTION	DRAWN	CHECK	APPR	DATE
	CLIENT PROJECT NO.:	CLIENT DRAWING NO.:			



CLIENT: -	YARD NO.: -	CLASS NO.: -
PROJECT NUMBER: 16.10.4	DRAWING NUMBER: 999-301	STATUS: PRELIMINARY
TITLE: DIAGRAM NH3 FUEL SYSTEM [TECHNICAL BASIS]		



# Ammonia as Marine Fuel Risk Assessment

Highlighting most important risks:

- Space (and environment) exposure with liquid and/or gaseous ammonia
- Space (and environment) exposure with gaseous hydrogen
- Increase in temperature and pressure within system
- Unable to supply fuel

E	2	4	9	10	
D		3	4	9	
C				1	
B			4	5	
A			2	8	
	1	2	3	4	5

Table 10-2: Original risk rating results risk assessment 1

# Ammonia as Marine Fuel Risk Assessment

Mitigations and consequences similar as natural gas fuel system:

Highlights:

- Redundancy
- Ammonia and hydrogen detection
- Ventilation
- Pressure relieve system
- Remote operated isolation valves
- Route piping with sufficient distance from shell
- Locate piping in separate unmanned space
- Double-walled piping

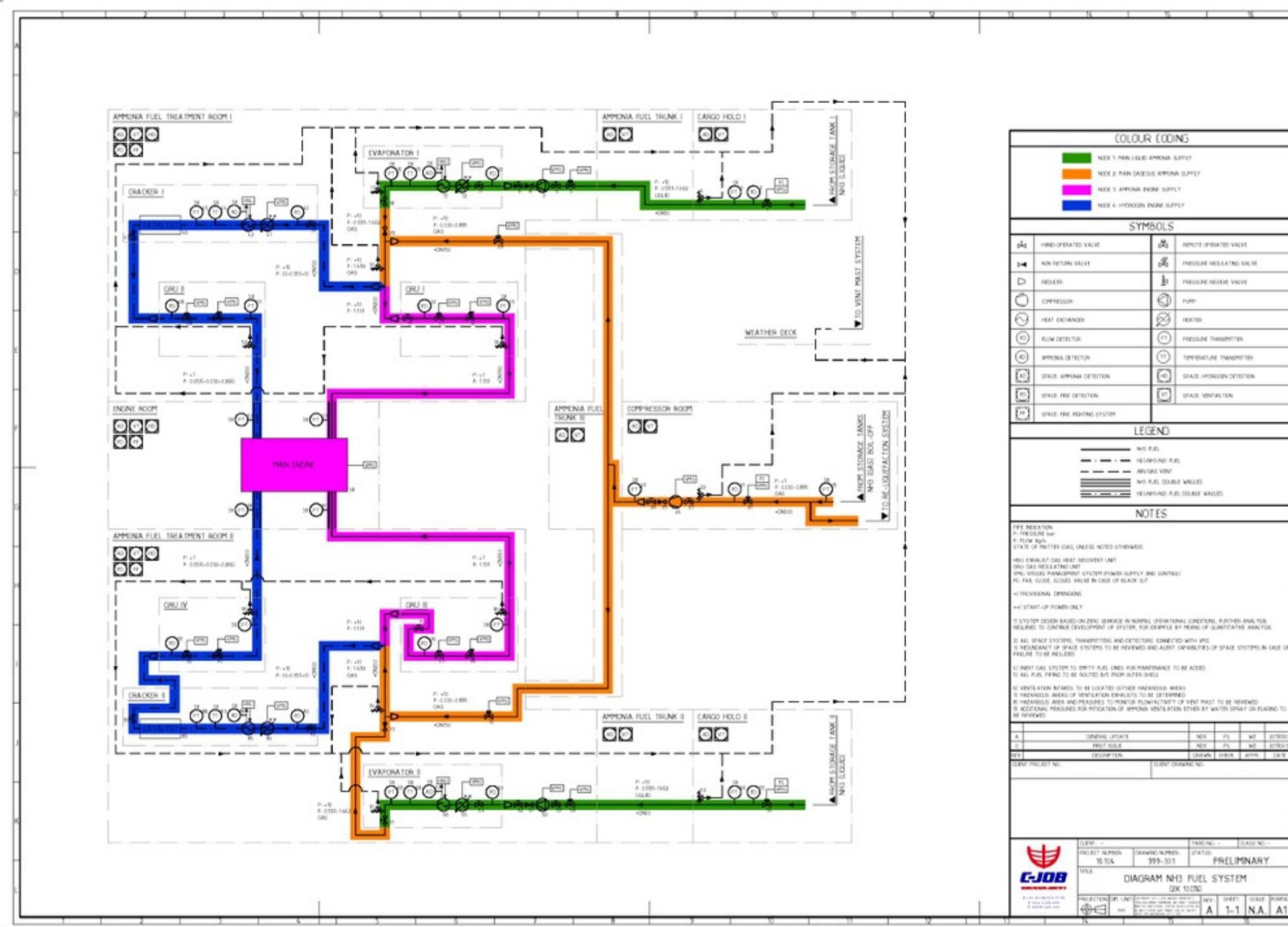
E	2	4	9	10	
D		3	4	9	
C				1	
B			4	5	
A		2	8		
	1	2	3	4	5

Table 10-2: Original risk rating results risk assessment 1

E		1			
D	9	1			
C		12		2	
B				2	
A		3	10	21	
	1	2	3	4	5

Table 10-3: Final risk rating results risk assessment 1





## Ammonia as Marine Fuel Risk Assessment

Redundancy -> 2x 100%

Requirement: maintain adequate ship speed and manoeuvrability

Convert -> 2x 50%

50% power results in roughly 80% maximum ship speed

# Ammonia as Marine Fuel Risk Assessment

## Risk assessment 2

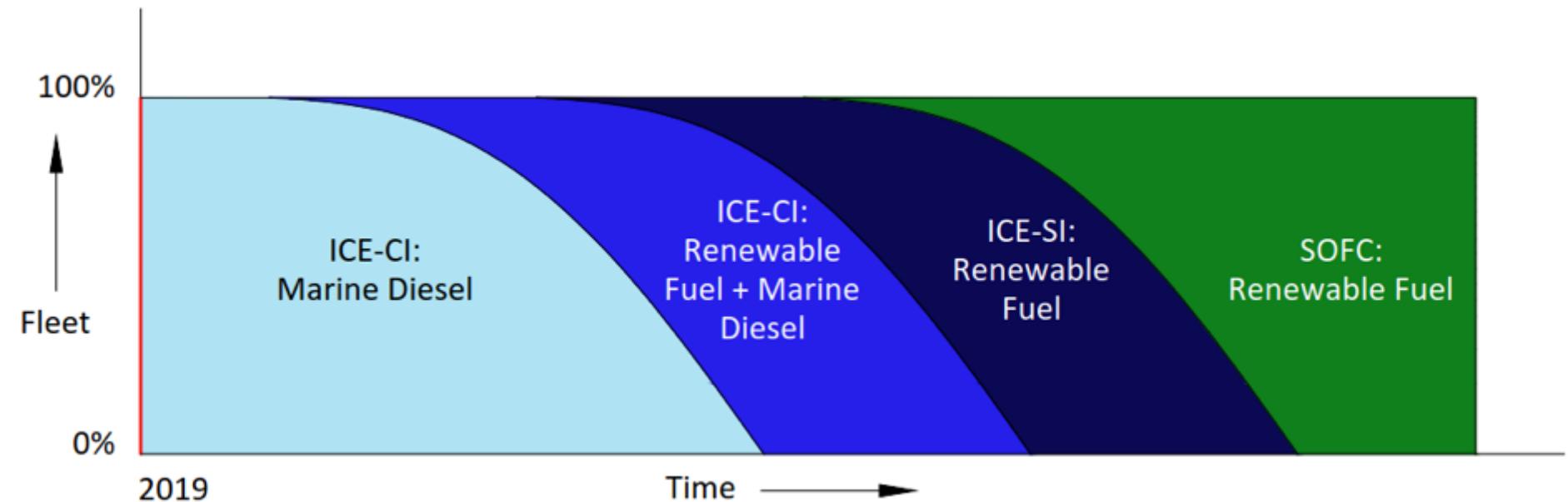
E		1			
D	9	1			
C		12		2	
B				2	
A		3	10	21	
	1	2	3	4	5

Table 10-3: Final risk rating results risk assessment 1

E		1			
D	11	1			
C		16		2	
B				2	
A		3	12	33	
	1	2	3	4	5

Table 10-4: Risk rating results risk assessment 2

## Outlook



Further research:

- ICE Ammonia + Hydrogen
- ICE Ammonia + Diesel
- Fuel cell application, especially the SOFC and vessels which already have fuel-electric configurations
- Other vessel types, besides ammonia carrier, to address fuel storage
- Further study safety, class involvement HAZID

## Ammonia + Diesel

- Storage Space
- Fuel Treatment Room
- Gas Regulating Unit Room
- Engine Room

## More information

- <https://cjob.nl/the-next-step-in-c-jobs-ammonia-research/>
- <https://repository.tudelft.nl/islandora/object/uuid:be8cbe0a-28ec-4bd9-8ad0-648de04649b8?collection=education>





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## Back-up Slides



## General Ammonia Safety

- Existing safety measures
  - Leakages in enclosed spaces (Ventilation)
  - Leakages in open spaces (Water spray)
  - Overpressure in storage tanks (Flaring)

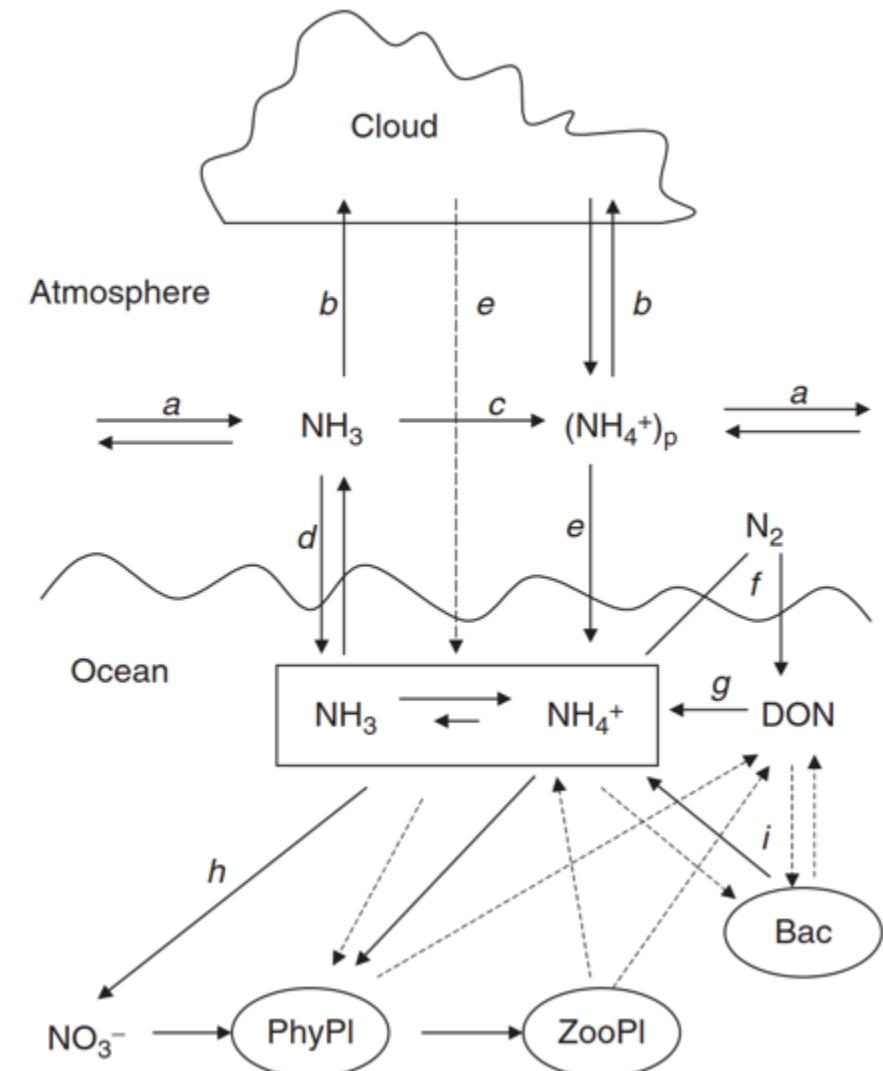


# General Ammonia Safety

- Ammonia in the Nitrogen Cycle

pH Water	mol Ammonia NH <sub>3</sub>	mol Ammonium NH <sub>4</sub> <sup>+</sup>	mol NH <sub>3</sub> /NH <sub>4</sub> <sup>+</sup>
7.25	1%	99%	1:100
8.25	9%	91%	1:10
9.25	50%	50%	1:1

Table 7-3: Fraction of chemical species of ammonia present with change in pH (at 25°C)



D. G. Capone, D.A. Bronk, M. R. Mulholland and E. J. Carpenter, "Chapter 2: Gaseous Nitrogen Compounds (NO, N<sub>2</sub>O, N<sub>2</sub>, NH<sub>3</sub>) in the Ocean - Ammonia & Outlook," in *Nitrogen in the Marine Environment (2nd edition)*, Burlington, Elsevier, 2008, pp. 75 - 84.