Safe and Effective Application of Ammonia as a Marine Fuel NCE: Ammonia in the Maritime Sector - Niels de Vries



MARINE NH3

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Renewable Fuels Motivation

- Reduction of greenhouse gas (GHG) emissions
- Circular economy

IMO Goals

- IMO: reducing overall carbon intensity of the cargo transported per kilometer by at least:
 - 40% by 2030
 - 70% by 2050

(compared to 2008)

- IMO: reduce total annual GHG emissions by at least 50% by 2050 (compared to 2008)
 - Pursuing efforts towards phasing them out entirely



INTERNATIONAL MARITIME ORGANIZATION



History of Ammonia

- 100 years of experience transporting & handling
 - Fertilizer industry
 - Global production > 180 million tonnes
 - Bulk transport (ships/tankers up to 60,000 tonnes DWT)
 - Cooling systems
 - DeNOx (Ammonia in form of Urea)



History of Ammonia as Fuel

• Transportation methods













Renewable Fuel Options: Potential of Ammonia

Fuel type:	Energy density LHV [MJ/kg]	Volumetric energy density LHV [GJ/m3] ↓	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	18.6	12.7	1.8	1 or 10	-34 or 20
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

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Ammonia Properties

- Ammonia
 - Flammable and highly toxic gas
 - Auto-ignition temperature: 651 °C
 - Flammability limits: 15-28% (vol)
 - Low flame speed
 - High heat of vaporization
- Ammonia Hydrogen Mixtures
 - Improve combustion properties



Ammonia Power Generation Options



Ammonia Power Generation: Selection Onshore Technically Feasible Options





Ammonia Power Generation: Marine Technically Feasible

• Ship type: Ammonia carrier

Efficiency dominant performance indicator



Ammonia Power Generation: Selection Marine Technically Feasible Options







- Internal Combustion Engine: Harmful emissions
 - NOx (Guideline)

Ammonia		Diesel (IMO Tier	Diesel (IMO Tier II)			
Large engine Low speed	?	Large engine	Low speed High speed	14 g/kWh 8 g/kWh		
Small engine High speed	+/-8 g/kWh	Small engine	High speed	8 g/kWh	-	



• Internal Combustion Engine: Harmful emissions (NOx)

Reasons for higher NOx: -More Nitrogen in fuel (NH3) Reasons for lower NOx:

-Lower exhaust gas temperature compared to diesel
-More homogenous air fuel mixture compared to diesel
-No 'diesel dilemma' reducing peak temperatures*
-Selective Non-Catalytic Reduction due to fuel slip could aid NOx reduction (unconfirmed)

Reference:

Selective Catalytic Reduction (NOx reduction) applied for diesel engines:

Ammonia in form of Urea:

 $(\mathrm{NH}_2)_2\mathrm{CO}~+~\mathrm{H}_2\mathrm{O}~\longrightarrow~2~\mathrm{NH}_3~+~\mathrm{CO}_2$

Actual process:

 $4 \ NO \ + \ 4 \ NH_3 \ + \ O_2 \ \longrightarrow \ 4 \ N_2 \ + \ 6 \ H_2O$



- Internal Combustion Engine: Harmful emissions
 - NOx (Guideline)

Ammonia		Diesel (IMO Tier	11)			
Large engine Low speed	+/-14 g/kWh	Large engine	Low speed High speed	14 g/kWh 8 g/kWh		
Small engine High speed	+/-8 g/kWh	Small engine	High speed	8 g/kWh	_	

- <u>To be further investigated</u>
- Results will show to what extend SCR (NOx reduction) is required









Option	*Power density		*Power density		Harmful emissions	***Loa	d respo	nse
	[kW/ton] [kW/m3]		[kW/ton] [kW/m3]		Heavy weather	Port	[%Pmax/s]	
ICE	+/-38	+/-29	**+/-14 g/kWh NOx &	V	V	+/-0.800		
			100ppm ammonia slip					
PEMFC	+/-256	+/-99	None	V	V	>16.000		
AFC	+/-8	+/-6	None	V	V	>16.000		
SOFC	+/-17	+/-8	None	Х	Х	+/-0.003		

Table 5-18: Comparison of options, Part 1

*Power density is a guideline based on simplified measurements of the engine or fuel cell only. Other equipment such as support systems and electrical systems are excluded.

**Emissions of main engine, apply SCR to reduce NOx as much as possible.

***Load response:

V: System has sufficient capability to cope with conditions

X: System insufficiently capable, additional measures to be taken, part of problem could be solved with batteries, which are already installed for start-up power %Pmax/s is a guideline only.



Option	*Part load	Marine environment	System efficiency	Total cost of ownership (ΔTCO)
ICE	V	No issues	49.4%	€689,496,925
PEMFC	V	Air treatment required: filtration	44.5%	€795,923,500
AFC	V	Air treatment required: CO ₂ scrubbing	44.8%	€807,876,500
SOFC	V	No issues	53.9%	€744,443,475

Table 5-19: Comparison of options, Part 2

*Part load

V: System has sufficient capability to supply minimum power in port conditions



Ammonia Power Generation: Selection Marine Performance Option



Ammonia Performance Comparison with Conventional Power Generation

Ammonia Performance Comparison with Conventional Power Generation

Option	*Power	density	Harmful emissions	***Load response	
	[kW/ton]	[kW/m3]		Heavy weather	Port
ICE (NH ₃)	+/-38	+/-29	**+/-14 g/kWh NOx	V	V
			100ppm ammonia slip		
Conventional	+/-35	+/-32	561 g/kWh CO ₂	V	V
			1 g/kWh SOx & PM		
			**14 g/kWh NOx		

Table 6-5: Comparison with Conventional option, Part 1

*Power density is a guideline based on simplified measurements of the engine. Other equipment such as support systems and electrical systems are excluded.

**Emissions of main engine, apply SCR to reduce NOx as much as possible.

***Load response:

V: System has sufficient capability to cope with conditions

Option	*Part load	Marine environment	System efficiency	Total cost of ownership (ΔTCO)
ICE (NH ₃)	V	No issues	49.4%	€689,496,925
Conventional	V	No issues	47.3%	€212,988,650

Table 6-6: Comparison with Conventional option, Part 2

*Part load

V: System has sufficient capability to supply minimum power in port conditions

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Fuel Pricing

SCR: Selective Catalytic Reduction Exhaust gas after treatment, capable of reducing NOx more than 95% **MARINE NH3**

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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 <u>First draft initiated</u>
- 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:
 - ?

MARINE NH3	Hazard statements	Hazard category	Ammonia [79]	CNG [80]	LNG [81]	Diesel [82]	ULSFO [83]
General Ammonia Salety	H220 Extremely flammable gas	1A		Х	Х		
	H221 Flammable gas	2	Х				
	H226 Flammable liquid and vapour	3				Х	
CNG: Compressed Natural Gas	H227 Combustible liquid	4					Х
ING: Liquefied Natural Gas	H280 Contains gas under pressure; may explode	Compressed gas		Х			
	if heated	Liquefied gas (b)	Χ*				
• ULSFO: Ultra Low Sulphur Fuel Oil (0.1%)	H281 Contains refrigerated gas; may cause	Refrigerated			Х		
	cryogenic burn or injury	liquefied gas					
	H304 May be fatal if swallowed and enters	1				Х	
Globally Harmonized System of Classification and Labelling of Chamicals (CHS)	airways						
	H313 May be harmful in contact with skin	5				Х	
	H314 Causes severe skin burns and eye damage	1B	Х				
	H315 Causes skin irritation	2				Х	
	H331 Toxic if inhaled	3	Х				
	H332 Harmful if inhaled	4				Х	Х
	H350 May cause cancer	1B					Х
	H351 Suspected of causing cancer	2				Х	
	H361 Suspected of damaging fertility or the	2					Х
	unborn child						
	H373 May cause damage to organs through	2				Х	Х
	prolonged or repeated exposure						
	H410 Very toxic to aquatic life with long lasting	1	Х				Х
	effects						
	H411 Toxic to aquatic life with long lasting effects	2				Х	

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

(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

- Environmental impact
 - Very toxic to aquatic life with long lasting effects

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	Catastrophic	E					
fatalities	damage						
*Single	Major	D					
fatality	damage						
Major	Localised	С					
injury	damage						
Minor	Minor	В					
injury	damage						
Zero	Zero	А					
injury	damage						
People	Assets/		1	2	3	4	5
People	Assets/ Environment		1	2	3	4	5
People	Assets/ Environment	Chance	1 Remote	2 Extremely	3 Very	4 Unlikely	5 Likely
People	Assets/ Environment erity 个	Chance	1 Remote	2 Extremely Unlikely	3 Very Unlikely	4 Unlikely	5 Likely
People Seve	Assets/ Environment erity 个	Chance Chance	1 Remote <10 ⁻⁶ /у	2 Extremely Unlikely ≥10 ⁻⁶ /y	3 Very Unlikely ≥10⁻⁵/y	4 Unlikely ≥10 ⁻⁴ /γ	5 Likely ≥10 ⁻³ /y
People Seve	Assets/ Environment erity 个	Chance Chance per year	1 Remote <10 ⁻⁶ /γ	2 Extremely Unlikely ≥10 ⁻⁶ /y <10 ⁻⁵ /y	3 Very Unlikely ≥10 ⁻⁵ /y <10 ⁻⁴ /y	4 Unlikely ≥10 ⁻⁴ /γ <10 ⁻³ /γ	5 Likely ≥10 ⁻³ /y
People Seve Likeli	Assets/ Environment erity ↑ hood →	Chance Chance per year Chance	1 Remote <10 ⁻⁶ /у <1 in	2 Extremely Unlikely ≥10 ⁻⁶ /y <10 ⁻⁵ /y ≥1 in	3 Very Unlikely ≥10 ⁻⁵ /y <10 ⁻⁴ /y ≥1 in	4 Unlikely ≥10 ⁻⁴ /γ <10 ⁻³ /γ ≥1 in 400	5 Likely ≥10 ⁻³ /y ≥1 in 40
People Seve Likeli	Assets/ Environment erity ↑ hood →	Chance Chance per year Chance in	1 Remote <10 ⁻⁶ /у <1 in 40,000	2 Extremely Unlikely ≥10 ⁻⁶ /y <10 ⁻⁵ /y ≥1 in 40,000	3 Very Unlikely ≥10 ⁻⁵ /y <10 ⁻⁴ /y ≥1 in 4,000	4 Unlikely ≥10 ⁻⁴ /y <10 ⁻³ /y ≥1 in 400 <1 in 40	5 Likely ≥10 ⁻³ /y ≥1 in 40
People Seve Likeli	Assets/ Environment erity ↑ hood →	Chance Chance per year Chance in Vessel	1 Remote <10 ⁻⁶ /у <1 in 40,000	2 Extremely Unlikely ≥10 ⁻⁶ /y <10 ⁻⁵ /y ≥1 in 40,000 <1 in	3 Very Unlikely ≥10 ⁻⁵ /y <10 ⁻⁴ /y ≥1 in 4,000 <1 in 400	4 Unlikely ≥10 ⁻⁴ /y <10 ⁻³ /y ≥1 in 400 <1 in 40	5 Likely ≥10 ⁻³ /y ≥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	1. Reduce exposed length	Chances reduced by exposed length	C2
	ammonia piping length in engine	reduction. Impact reduced by application	
	room	of double walled piping in engine room.	
	Apply double walled vented	Impact further reduced by adding	
	piping in engine room	ammonia detectors and main isolation	
	Add ammonia detectors in	valves which close when an ammonia	
	engine room and within double	leakage occurs. Ammonia piping outside	
	walled vented piping	of engine room to be reviewed	
	Add main isolation valves	separately.	

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

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

Main scope and assumptions:

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

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

Ε	2	4	9	10	
D		3	4	9	
С				1	
В			4	5	
Α			2	8	
	1	2	3	4	5

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

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

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

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

Redundancy -> 2x 100%

Requirement: maintain adequate ship speed and manoeuvrability

Convert -> 2x 50%

50% power results in roughly 80% maximum ship speed

Risk assessment 2

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

Е		1			
D	11	1			
С		16		2	
В		6		2	
Α		3	12	33	
	1	2	3	4	5

Table 10-4: Risk rating results risk assessment 2

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MARINE NH3

- 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

More information

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

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