JORNADA

EL POTENCIAL DEL AMONIACO COMO COMBUSTIBLE MARINO

23 de marzo de 2022 – Instituto de la Ingeniería de España (Madrid)

Aspectos básicos de seguridad, diseño y normativos en el uso de amoniaco como combustible marino

Manuel Sánchez Macías.
Lloyd´s Register

Fundación Ingeniero Jorge Juan

COMISIÓN DE TRANSICIÓN ENERGÉTICA DE LA
ASOCIACIÓN DE INGENIEROS NAVALES Y OCEÁNICOS DE ESPAÑA

ASOCIACIÓN DE INGENIEROS NAVALES Y OCEÁNICOS DE ESPAÑA

Ammonia and its grades

- Ammonia is a compound of nitrogen and hydrogen with the formula NH_3
  - Anhydrous ammonia: colorless gas and liquid depending on pressure and temperature
  - Ammonia hydroxide solution (NH_4OH): solubility of ammonia is strongly affected by solution temperature

- Grades of anhydrous ammonia
  - Premium grade "Metallurgical" – 99.995% purity
  - Refrigeration Grade "R-Grade" – 99.98% purity
  - Commercial grade "C-Grade" – 99.5% purity
  - Fuel grade posed "F-Grade" – 99.5% purity by Ammonia Energy Association (*right table*)

	Ammonia	Methane
Boiling Point	–33.3°C	-161.5 °C
Vapour pressure (45°C)	18 bar	345 bar
Critical point	133°C	-82.5°C
Heat of vaporisation	1369.5 kJ/kg	510.83 kJ/kg
Superheat limit temp. (SLT) (approx.)	70 °C	-105.55 °C
Flammability range (LEL-UEL)	15% - 28%	5.3% - 17%
Minimum ignition energy	8 mJ	0.27 mJ

F-Grade - base

Specification Parameter	Units	Limit	Test Method
NH3 (anhydrous ammonia)	% (w/w)	99.5 minimum	Evaporative Residue
H20 (water) minimum %	% (w/w)	0.2 minimum	CGA G-2.2
Oil maximum %	ppm	5 maximum	FTIR Analysis
Appearance	n/a	Clear, Colorless liquid or gas	Visual

Ref: ammonia energy association

Consequences – unique and common to ammonia and natural gas

Initiating hazardous events		Ammonia	Natural gas
Pressure related	Liquid-to-gas expansion	✓ (greater)	✓
	Vacuum by absorption	✓	
Material related	Brittle fracture	✓	✓ (much greater)
	Material compatibility	✓	
	Stress Corrosion Cracking	✓	

Consequences		Ammonia	Natural gas
Fire related	Flash Fire	✓	✓ (much greater)
	Jet fire	✓	✓ (much greater)
	Pool fire	✓	✓ (much greater)
Explosion related	BLEVE	✓	✓
	Vapour Cloud Explosion	✓	✓ (much greater)
	RPT		✓
Exposure related	Asphyxiation	✓	✓
	Blast overpressure	✓	✓ (much greater)
	Cryogenic/cold burns	✓	✓ (much greater)
	Toxicity	✓ (significant)	

Initiating hazardous events (NH_3 specific)

- *Vacuum by absorption*

Ammonia is fully miscible with water by the process of absorption. This initiates a vacuum hazard if the volume is enclosed, or partially enclosed, as the vessel containing ammonia vapour would dissolve, and in doing so, form a vacuum.

  - Ammonia solution is created due to absorption, where the process affects volumes rather than just the surface, which is described as adsorption;
  - Ammonia absorption is temperature dependent, the higher the temperature the lower the maximum absorption. In addition, absorption is exothermic, meaning that the process releases heat to the solution; and,
  - Vessels have collapsed when ammonia vapor from the head space dissolved in water within the vessel.

- *Material compatibility*

  - Ammonia is readily reactive with other materials and substances. Ammonia significantly contributes to the corrosion of copper, zinc, copper-based alloys, high tensile steels if totally anhydrous, i.e. stress corrosion cracking. It is compatible with aluminum, steel, and stainless steels;
  - Carbon dioxide, water, and anhydrous ammonia form ammonium carbonate and could form ammonium bicarbonate
  - Ammonia is miscible with water, alcohol, ether, and other organic solvents, whereas it is not with most mineral-based lubricating oils;
  - And for elastomers and sealants, the compatibility varies and is associated to a temperature range.

- *Stress Corrosion Cracking*

SCC initiates cracking and hence threatens the integrity of the containment system. SCC has been found in ammonia storage tanks and process equipment in contact with ammonia. It can occur due to refrigerated liquid ammonia, compressed liquified ammonia, and ammonia solution. Stress-corrosion cracking is a fracture, or cracking, phenomenon caused by the combined action of tensile stress, a susceptible alloy, and a corrosive environment.

  - Carbon steel is susceptible to SCC in anhydrous ammonia
  - Ammonia solutions may cause SCC in some copper alloys due to the pH (NH3 ~11)

Exposure related – Toxicity

- *Description*
  - Ammonia is toxic to both humans and marine organisms, as a liquid, vapour, gas, or in solution;
  - Toxicity is **load dependent** where the level of harm is affected by ammonia **concentration**, exposure **duration**, and the **route of exposure;**
  - It is generally recognised that detection of ammonia by **human smell** is approximately **5 – 25ppm** depending upon personal sensitivity. Importantly, the human detection value is substantially below the threshold of irreversible damage;
  - For the US EPA Acute Exposure Guideline Levels (AEGL), **irreversible damage** is caused **above 30ppm** over a **time-weighted-average (TWA) of eight hours.**
- *Ammonia compared to natural gas*
  - NH3 is toxic whereas NG is relatively non-toxic and both gases are colourless
- *Barriers and controls*
  - Systems containing ammonia are to be considered as Class I systems irrespective of the operational pressure and temperature;
  - The elimination and mitigation measures to reduce ammonia leakage include fully welded construction of piping, components and equipment; a reduction in flanged connections; secondary barrier; concentrated ventilation of areas of known permeation and installation of additional highly sensitive ammonia detectors .
  - Instrumented detection limits are suggested by LR. Developed with recognition of other industry standards, although these are not specific to ships and the use of ammonia as fuel.

Inhalation Exposure		Signs and symptoms
mg/m^3	ppm	
35	50	Irritation to eyes, nose and throat (2 hours' exposure)
70	100	Rapid eye and respiratory tract irritation
174	250	Tolerable by most people (30–60 minutes' exposure)
488	700	Immediately irritating to eyes and throat
>1,045	>1,500	Pulmonary oedema, coughing, laryngospasm
1,740–3,134	2,500–4,500	Fatal (30 minutes' exposure)
3,480–6,965	5,000–10,000	Rapidly fatal due to airway obstruction, may also cause skin damage

Values in mg/m^3 are approximate calculations from ppm, where mg/m^3 = ppm x gram molecular weight/24.45 (molar volume of air at standard temperature and pressure.

Summary of toxic effects following acute exposure to ammonia by inhalation, reproduced from UK Public Health England, Ammonia, Toxicological Overview. PHE publications gateway number: 2014790, August 2015

	10 min	30 min	60 min	4 hr	8hr
AEGL 1	30ppm	30ppm	30ppm	30ppm	30ppm
AEGL 2	220ppm	220ppm	160ppm	110ppm	110ppm
AEGL 3	2700ppm	1600ppm	1100ppm	550ppm	390ppm

AEGL 1 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic nonsensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure

AEGL 2 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape

AEGL 3 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening adverse health effects or death

Acute Exposure Guideline Levels (AEGL) reproduced from EPA US Environmental Protection Agency, Ammonia Results – AEGL, Program, Acute Exposure Guideline Levels, 2007

Regulatory views

Rules and Regulations for the Construction and Classification of Ships for the Carriage of Liquefied Gases in Bulk

The consumption of toxic cargoes as fuel shall not be permitted.

IGC Code, 16.9.2 (not verbatim)

Rules and Regulations for the Classification of Ships using Gases or other Low-flashpoint Fuels

… an inherently safer design is to be sought in preference to operational or procedural controls…
LR 4.1-01

MARPOL International Convention for the Prevention of Pollution from Ships - Annex VI

Fuel oil for combustion purposes shall not be harmful to personnel

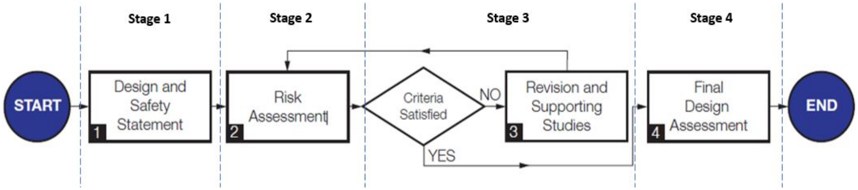
MARPOL Annex VI, 18.3.2 (not verbatim)

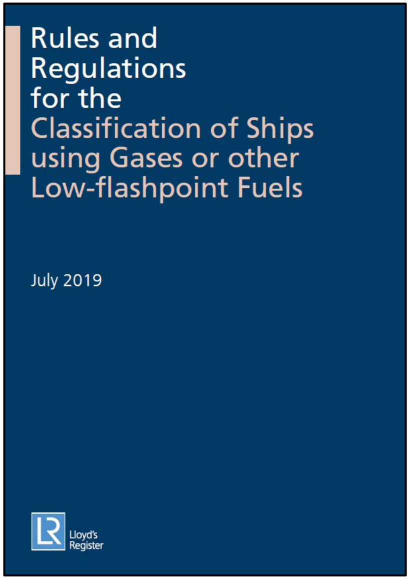
Rules, Regulations, Codes and Standards

- **Gas carriers (where permitted)…** using their cargoes as fuel and comply with the requirements of the IGC Code for gas as a cargo (SOLAS, Chapter II-1, Part G, Regulation 56, 4 & 5)
- **Other than gas carriers…** ships using low-flashpoint fuels shall comply with the requirements of the IGF Code. (SOLAS, Chapter II-1, Part G, Regulation 56 & 57)
- Ammonia as fuel for ships is not yet part of the IMO work programme
- ***Likely pathway forward***… Interim Guidelines for both IGC and IGF Code with amendments to MARPOL Annex VI and NTC2008
- ***IMO SOLAS Chapter II-1, Part F, Regulation 55 Alternative Design and Arrangements***
- ***IMO MSC.1/Circular.1455 Guidelines for the Approval of Alternatives and Equivalents as Provided for in Various IMO Instruments***
- ***IMO MSC.1/Circular.1212 Guidelines on Alternative Design and Arrangements for SOLAS Chapters II-1 and III***

Other than Gas carriers – *LR Rules and Regulations for Classification of Ships using Gases or other Low-flashpoint Fuels*

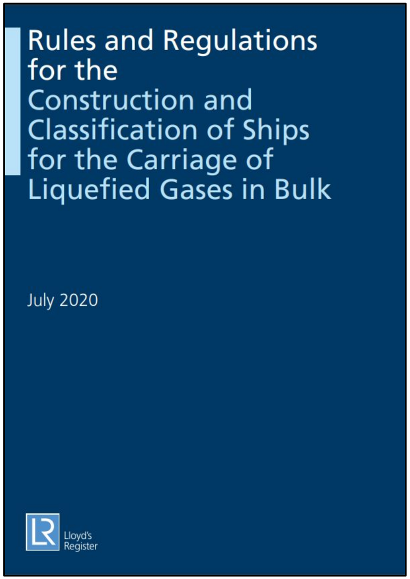
- Developed based on methane (LNG) as fuel (Part A, 2.3 Alternative design – Such fuels, appliances and arrangements can be used provided that these meet the intent of the goal and functional requirements concerned and provide an equivalent level of safety of the relevant chapters.)
- Part A and Part D applies to other gaseous and other low flash point fuels e.g. ammonia;
- Safety and Environmental, Part A, Chapter 3, Goal and Functional Requirements
- Risk based approach





Rules and Regulations for the Construction and Classification of Ships for the Carriage of Liquefied Gases in Bulk

- ✔ Developed based on methane (LNG) as fuel (16.1 General – Except as provided for in 16.9, methane (LNG) is the only cargo whose vapour or boil-off gas may be utilized in machinery space of category A.)
- ✔ The use of cargoes identified as toxic products shall not be permitted.
- ✔ The IGC Code provides insights into some potential safeguard. However, requirements regarding these safeguards need to be critically reviewed by all participating stakeholders.
- ✔ Chapter 11.3 Water-spray system.
- ✔ Chapter 17.2.1 Materials of construction.
- ✔ Chapter 17.12 Ammonia



Inherently Safer Design

- *What is a hazard…*

  A hazard is an inherent characteristic of a material or its condition of use that has the potential to cause harm.

- *Inherently safer design strategies…*

  The essence of the inherently safer approach to system design is the avoidance of hazards rather than their control by added-on protective equipment.

  - *Reduce consequence*: the quantity of fuel that is stored and present within equipment and pipework should be minimised;
  - *Reduce likelihood*: the number of equipment items, instruments and connections should be minimised to limit the number of potential leak sources; and,
  - *Protect life*: persons onboard (particularly passengers) should be separated as far as possible from ammonia sources.

Reduce consequence

e.g. reducing the inventory, reduce pressure

Reduce likelihood

e.g. welded connections rather than flanged

Protect life

e.g. separation distances such as physical, water curtains…

Hazardous area classification

How to address toxicity? What criteria?

Goal (Lloyd's Register, 2020)

3.1 *The goal of this Code is to provide for safe and environmentally-friendly design, construction and operation of ships and in particular their installations of systems for propulsion machinery, auxiliary power generation machinery and/or other purpose machinery using gas or low-flashpoint fuel as fuel.*

Functional Requirements (Lloyd's Register, 2020)

3.2.2 The probability and consequences of fuel-related hazards shall be limited to a minimum through arrangement and system design, such as ventilation, detection and safety actions. In the event of gas leakage or failure of the risk reducing measures, necessary safety actions shall be initiated;

3.2.4 Hazardous areas shall be restricted, as far as practicable, to minimize the potential risks that might affect the safety of the ship, persons on board, and equipment.

3.2.5 Equipment installed in hazardous areas shall be minimized to that required for operational purposes and shall be suitably and appropriately certified. 3.2.12 Fuel containment system and machinery spaces containing source that might release gas into the space shall be arranged and located such that a fire or explosion in either will not lead to an unacceptable loss of power or render equipment in other compartments inoperable; and,

3.2.8 Sources of ignition in hazardous areas shall be minimized to reduce the probability of explosions.

- For ammonia fuel systems the hazardous area classification should be identified in the risk-assessment during RBC-2.
- IEC 60079-10-1 is intended to be applied where there may be a flammability hazard due to the presence of flammable gas or vapour, mixed with air and does not apply to toxicity or catastrophic failures or rare malfunctions which are beyond the concept of abnormality dealt with in the standard
- Hazardous area classification study should consider all machinery and equipment which could represent a source of release of flammable/explosive and toxic gas, as applicable in: normal operation, start-up, normal shutdown, non-use, and emergency shutdown of the fuel-gas system; and, equipment intended for recovery from unintended releases of gas (e.g. venting systems).
- This could include spaces containing: the fuel bunkering system (e.g. Bunkering Station); Fuel Storage Hold Space, Tank Connection Space; and fuel supply to consumers; machinery spaces shall be gas safe where the arrangements are such that the spaces are considered gas safe under all conditions, i.e. inherently gas safe.

Fire fighting

- Ammonia vapour will ignite between 15% to 28% by volume or if exposed to temperature exceeding 651degC;
- Ships shall comply with the requirements of regulation II-2/10.2 of the SOLAS Convention and the FSS Code, as applicable;
- Extinguishing ammonia fires is effective with dry chemical, carbon dioxide and for larger fires water spray or alcohol-resistant foam;
- On detection of a fire, the fuel supply system should be shutdown so as not to fuel the fire further, or to create additional vapour release;
- The release condition is important as the pooling ammonia and heavy ammonia vapours could occur. Ammonia pooling should not be agitated by the application of extinguishing medium as this would further exacerbate the vaporization rate;
- Unignited vapours in confined and semi-confined spaces could explode if exposed to an ignition source or a hot surface.

Personal Protection Equipment

Rules and Regulations for the Classification of Ships, Part 6, Chapter 3 Refrigerated Cargo Installations, 2.4 :

- *Where the charge is greater than 50 kg, emergency body shower and eye wash facilities shall be installed locally outside the compartment. The water for the shower is to be thermostatically controlled so as to avoid low temperature shock.*

Other safety and personal protection equipment could include:

- Protection clothing
- Respiratory protection
- Protective goggles
- Eye washer (5% boric acid solution)

14.4 Personal protection requirements for individual products

14.4.1 Requirements of this section shall apply to ships carrying products for which those paragraphs are listed in column "i" in the table of chapter 19.

14.4.2 Suitable respiratory and eye protection for emergency escape purposes shall be provided for every person on board, subject to the following:

.1 filter-type respiratory protection is unacceptable;

.2 self-contained breathing apparatus shall have at least a duration of service of 15 min; and

.3 emergency escape respiratory protection shall not be used for firefighting or cargo-handling purposes and shall be marked to that effect.

14.4.3 One or more suitably marked decontamination showers and eyewash stations shall be available on deck, taking into account the size and layout of the ship. The showers and eyewashes shall be operable in all ambient conditions.

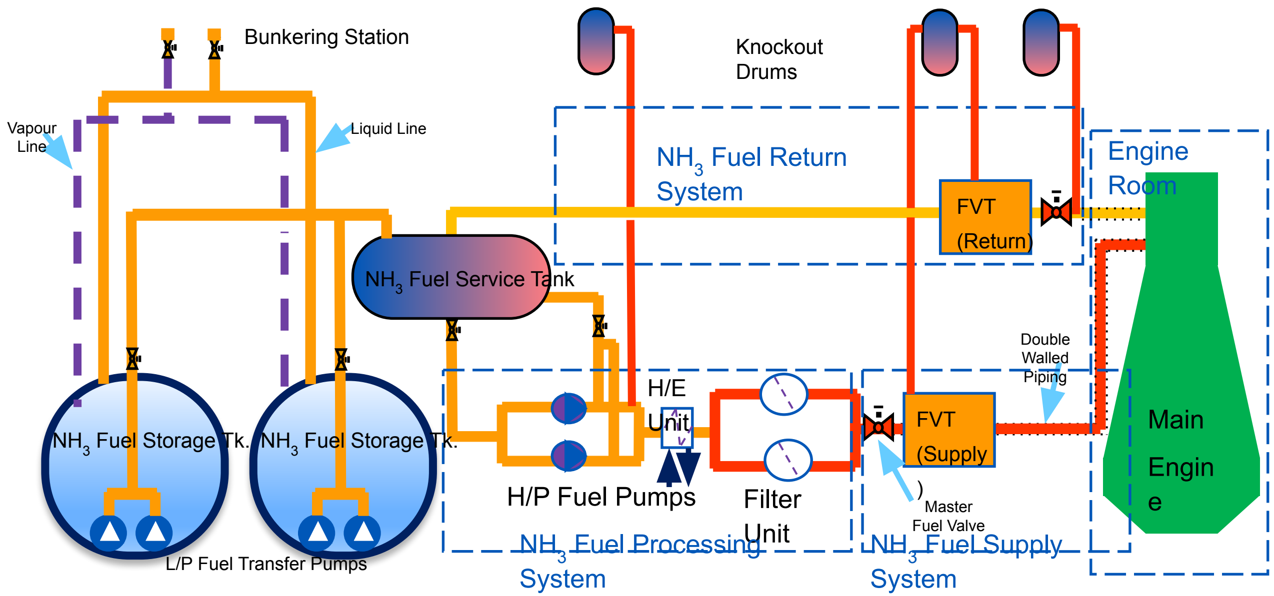
14.4.4 The protective clothing required under 14.3.2.2 shall be gastight.

REF - Rules for Gas Ships

Introduction to LPG (Ammonia) Carriers

- *Fully refrigerated LPG gas carriers…*
  - Full refrigerated LPG Carriers vary in size from 30,000m^3 to 100,000m^3. This vessel size with containment pressures at or slightly above atmospheric pressure; an on board reliquefication plant would maintain the cargo thermodynamics. The IMO Type A tank is likely.
- *Semi-pressurised liquefied LPG gas carriers…*
  - Semi-pressurised LPG Carrier are in the 2,000-20,000 m^3 size range. This vessel size is generally arranged with spherical, bi-lobe or cylindrical type. The design and arrangement is likely to have reliquefication plant and deck-mounted cargo heaters to accommodate cargo flexibility. These carriers, incorporating tanks either cylindrical (Type C) or bi-lobe in shape, are able to load or discharge gas cargoes at both refrigerated and pressurised storage facilities.
- *Fully pressurised liquefied gas carriers…*
  - Fully pressurized LPG Carriers in the 600 to 3,000 m^3 range. This vessel size is generally arranged with two or three pressure containment vessels operating at ambient temperature. The IMO Type C tank is likely.

IMO Tank Type C – NH3 Fuel Containment and Fuel Supply to Consumers



Challenges of ammonia as a fuel

	Bunkering	Containment	LFSS & FGSS
Current Status	▪ NH3 loading and unloading in terminals for NH3 carrier is available ▪ IGF Code bunkering in ports – no acceptable standard ▪ No developed procedures for NH3 fueled ships	▪ Technologies applied to LNG and LPG as fuel and gas carriers	▪ Technologies applied to LPG as fuel and LNG as fuel
Addressing & overcoming the challenges	✔ Develop bunkering procedure with bunker supplier ✔ Consider Ammonia vapour handling during bunkering ✔ Handling of leaked ammonia during bunkering and structure protection (Low temperature)	✔ Existing technology can be applicable (IGC and IGF Code) ✔ Consider to develop environment control (e.g. inerting, dry air) of hold spaces for ammonia as fuel ✔ Consider large leakage from Type A tank	✔ Develop LFSS (Liquefied Fuel) for ammonia as fuel ✔ Develop FGSS (Fuel Gas) for internal combustion engine and fuel cell

Challenges of ammonia as a fuel

	Consumers	Regulatory	Safety
Current Status	▪ No proven technologies at marine full scale yet.	▪ IGC Code is applicable for cargo systems only ▪ No Rules for ammonia as fuel ▪ No international methodology for the hazardous area classification for toxicity	▪ The toxicity of ammonia vapour & resultant health & safety risks may be a barrier for uptake of NH_3 as a fuel ▪ Corrosivity of ammonia to materials
Addressing & overcoming the challenges	✔ Fuel cells & internal combustion engines are being developed & should be demonstrated within 3-5 years. ✔ MAN plans for their ME-LGI ammonia engine to be available in 2024. ✔ Wartsila four-stroke full-scale testing underway	✔ Establish the first projects based on the IGC Code (for gas carrier) or the IGF code for alternative design ✔ Development of NH3 Ready and Classification Society Rules for ammonia as fuel is underway ✔ Discuss with Flag Administrations	✔ Develop venting and ventilation system through gas dispersion analysis ✔ Develop toxic safety level (Gas detection) ✔ Develop NH3 engine safety concept (probability of leakage, purging, ESD etc.) ✔ Develop the way to prevent gas release into atmosphere (e.g. NH3 scrubber, water screen)

Ammonia as fuel: R&D projects

- Passenger ship (Feasibility study)
- Containership 15K TEU (Membrane – Mark III)
- Containership 23kTEU (IMO Type B)
- Product/Chemical Carrier (IMO Type C)
- Newcastlemax bulkcarrier (IMO Type C)
- Aframax Tanker (IMO Type C)
- Collaboration with the *UK MCA*
- Korean Research Institute of Ships and Ocean Engineering (KRISOE), Ammonia fuelled ammonia carrier (VLGC)
- Environmental Defence Fund

Manuel Sánchez Macías
Senior Specialist, Madrid Technical Support Office
Lloyd's Register EMEA

C/ Princesa, 29,
Madrid. Spain

Working together
for a safer world

¡MUCHAS GRACIAS!

ANFITRIÓN

ASOCIACIÓN DE INGENIEROS NAVALES Y OCEÁNICOS DE ESPAÑA

ASOCIACIÓN DE INGENIEROS
NAVALES Y OCEÁNICOS DE ESPAÑA

www.ingenierosnavales.com

ORGANIZADOR

Fundación
Ingeniero Jorge Juan

Lloyd's Register

DNV

Navantia

ACS

GrupoFertiberia