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No. : 2021-ETC-01 Date : 2021.01.31

## **Subject: Report on Ammonia-Fueled Ships**

As the IMO decided to reduce GHG emissions from ships by 2050, compared to 2008, and reduce carbon intensity of international shipping by 40% by 2030 compared to 2008 there is strong increase in demand for alternative fuel. In particular, ammonia is attracting worldwide interest as a potential carbon-free fuel for marine sector.

Please be informed that "Technical information for Ammonia-Fueled Ships" to use for establishing the direction of safety regulations of ammonia-fueled ships by studying the characteristics of ammonia necessary to use ammonia as marine fuel and to support KR surveyor, shipyards and ship owner.

## Attachment

: Report on Ammonia-Fueled Ships (Korean/English)---each 1 copy. (The end)

(Distributions: KR surveyors, Ship owners, Other relevant parties)

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(서식번호: FI-03-04) (20.06.2018)



# Report on Ammonia-Fueled Ships



January 2021 KR

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## 1 Research Background and Purpose

## 1.1 Research Background

Increasing greenhouse gas (GHG) emission, one of the causes of global warming, has resulted in abnormal climate phenomena such as heatwaves and floods. People have recognized that eco-friendliness is essential for the sustainable growth of humankind. Accordingly, research on converting fossil fuels to eco-friendly alternatives is ongoing in all industrial sectors.

The Kyoto Protocol and the Paris Agreement as part of the United Nations Framework Convention on Climate Change (UNFCCC) specifically delegated the International Maritime Organization (IMO) to address all matters for achieving GHG reduction targets in the marine transportation sector. Subsequently, IMO strengthened the PM, SOx, and NOx emission regulation and specified the GHG emission reduction target. It decide to halve GHG emission from ships by 2050, compared to 2008, and reduce carbon intensity of international shipping by 40% by 2030 compared to 2008. (See Figure 1)

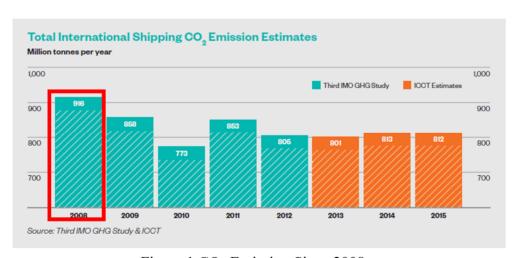


Figure 1 CO<sub>2</sub> Emission Since 2008

However, since CO<sub>2</sub> emission is expected to be 3,000 Mt or more if GHG is emitted in the current trend (Business as Usual (BAU) scenario), it is necessary to reduce it by 85 %. (See Figure 2).

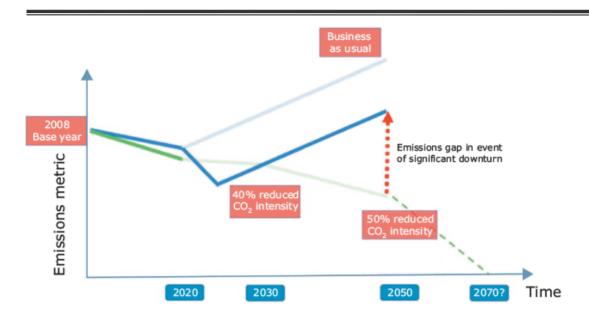


Figure 2 IMO's Long-Term CO<sub>2</sub> Reduction Plan (Source: MEPC 72/7/3)

IMO's carbon reduction target of 40 % by 2030 is attainable through the currently enforced technological measures such as increasing ship size and improving propulsion system and navigational efficiency increase such as low-speed operation as shown in the following table and Figure 3. These two measures alone, however, have limitations since there is no significant change after 2030.

|           | Technological (Design Viewpoint)  Measures | Navigational Measures | Total |
|-----------|--|-----------------------|-------|
| 2008-2015 | 7 %  | 25 %                  | 30 %  |
| 2015-2030 | 11 %                                       | 5 %                   | 15 %  |
| 2008-2030 | 17 %                                       | 28 %                  | 40 %  |

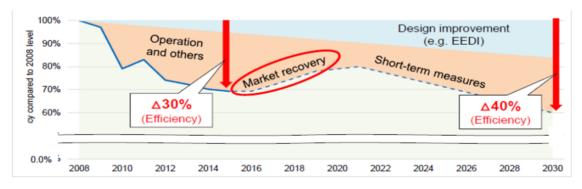


Figure 3 CO<sub>2</sub> Reduction Rate Through Technological and Navigational Efficiency Improvement (Source: MEPC 72/7/3)

## 1.2 Research Goal

## 1.2.1 Purpose

• The purpose of this study is to investigate the feasibility of whether ammonia can be used as fuel for ships and to establish the direction for regulation of ammonia-fueled ships by identifying the ammonia characteristics to be considered in ship structures and facilities.

#### 1.2.2 Goal

- The restrictions of using ammonia as a fuel for ships are as follows:
  - Although the IGC Code has been amended to allow cargo other than natural gas to be used as ship fuel provided that it can guarantee the same safety level, Paragraph 16.9.2 prohibits cargo classified as toxic from being used as fuel. Therefore, it is necessary to review the clause.
  - The IGF Code specifies the detailed requirements of the LNG only, and the recent IMO Sub-Committee on Carriage of Cargoes and Containers (CCC) meeting completed the tentative guidelines on the detailed regulation of methyl/ethyl alcohol. Although it is developing detailed requirements for fuel cell, low flash point diesel, and LPG, there is no plan to develop detailed requirements for ammonia.
  - From a safety viewpoint, ammonia is toxic and corrosive. Therefore, it is necessary to establish the standard for securing safety in consideration of the ammonia characteristics to use ammonia as a fuel for ships.
  - Ammonia has characteristics of being difficult to ignite and having a slow combustion speed due to a very slow flame speed compared to other fuels. On the other hand, ammonia causes a rapid explosion when it is mixed with fuel such as petroleum, chlorine gas, or urea gas, or when it reacts with heavy metals such as gold and mercury. Since unburned ammonia emissions are much lighter than air, they rise rapidly in dry air. At sea, however, they quickly react with the humidity in the air, remaining close to the ship's surface, which may cause hull corrosion. Therefore, it is a factor to be considered. Moreover, since ammonia is a cause for ultrafine dust, it is necessary to establish the requirements for emission restrictions.

- O Despite the aforementioned difficulties, its cost, safety, cost, safety, availability, and pollutant reduction must be considered comprehensively for the continued use of ammonia. The following detailed goals were set to use ammonia as a marine fuel by considering existing ammonia production methods and future green ammonia production, experience in land use and sea transportation, ammonia supply chain and process, and considerations for application as fuel on-board:
- Analysis of availability and pollutant reduction by investigating properties of ammonia, existing fields using ammonia, and a comparison with other carbon-free fuels
  - \* Industrial fields using ammonia
  - \* Properties of ammonia
  - \* A feasibility study by comparing with other carbon-free fuels such as hydrogen, methanol, a biofuel
- Study on safety of ammonia-fueled ship structure and facility
  - \* Review of the analysis of risk factors of ammonia-fueled ship structure and facility
  - \* IGC Code requirement analysis and identification for revision to apply
  - \* IGF Code requirement analysis and identification of additional requirements to apply
  - We intend to identify the development direction for safety regulation of ammoniafueled ships based on the detailed goals.

## 2 Production and Use of Ammonia

#### 2.1 **Ammonia Production Process**

#### 2.1.1 Traditional Ammonia Production Process

As shown in Figure 5, the current Haber-Bosch ammonia production process uses natural gas or coal for high-pressure (~200 bar) and high-temperature (300–400 °C) reaction. The process produces and separates hydrogen through natural gas reformation or coal gasification and synthesizes ammonia through heated hydrogen and nitrogen reaction as follows:

$$N_2+3H_3->2NH_3$$
 ( $\Delta H = -92.4 \text{ kJmol}^{-1}$ )

Although the process is suitable for high pressure since the volume decreases after the reaction and advantageous for low temperature as it is a heated reaction, the reaction temperature is generally 300-400 °C because of catalyst activity. Iron catalysts or ruthenium-based catalysts are most widely used commercially. Many studies are ongoing to reduce the reaction pressure and save energy use since this method uses very high energy, but there is a limitation because of low yield of ammonia. The current method is analyzed to generate about 1–2 % of global CO<sub>2</sub> emissions.

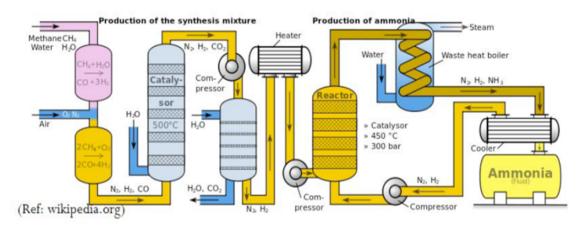


Figure 4 Haber-Bosch Ammonia Production Process

#### 2.1.2 Green Ammonia Production

The green ammonia synthesis emitting no carbon is essential for ultimate ecofriendliness. Green ammonia is produced through the electrical synthesis of hydrogen produced through electrolysis of water and nitrogen separated from the air. It uses renewable energy for the process. The electrochemical ammonia synthesis produces ammonia using water and air in the atmosphere. It is a fundamental technology that can replace the conventional Haber-Bosch process if renewable energy electricity in the future becomes significantly cheaper than today. Producing and storing electrochemical ammonia through renewable energy can minimize the surplus power loss to secure economic efficiency and stability of renewable energy electricity prices.

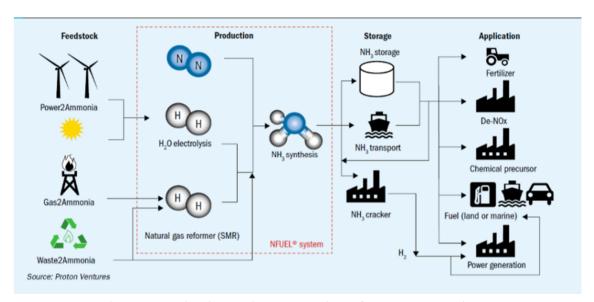


Figure 5 Production and Consumption of Green Ammonia

(Source: Nitrogen+Syngas, Sustainable ammonia for food and power by Trevor Brown)

#### 2.2 Use of Ammonia

More than 120 ports are already handling ammonia products for import and export, and some even have storage facilities. Such an infrastructure can be an important resource to secure the ammonia's availability as fuel. A wide range of sectors use ammonia, and the handling procedures and safety education have been widely distributed. Therefore, using it for ships would not be a problem for people who have familiarized with it.

#### 2.2.1 Fertilizer

Ammonia is regarded as a substance as important as carbon compounds to chemical technical specialists since it is the driving force that has increased the marginal global population from 2 billion to 8 billion with the fertilizer synthesis and nitrogen process (Haber-Bosch process). Fertilizers are classified into nitrogen fertilizers, phosphate fertilizers, potassium fertilizers, and complex fertilizers according to the production method. Ammonia accounts for more than 30% of nitrogen fertilizer.

#### 2.2.2 Industrial Fuel

High-purity ammonia has a purity of 99.9995 (5N5) or higher and is produced by additionally refining produced or imported raw material gas with a purity of 99.8 %. NH<sub>3</sub> refined into high purity (blue ammonia) or ultra-high purity (white ammonia) has a completely different value from low-purity materials. Firstly, high-purity NH<sub>3</sub> is treated as a special gas, not ammonia as a simple raw material gas.

High-purity ammonia is mainly used as compound semiconductors such as gallium arsenide (GaAs), silicon germanium (SiGe), indium phosphorus (InP), and silicon carbide (SiC), as well as the light emitting diode (LED) and liquid crystal display (LCD) panel markets. Moreover, new demands have emerged recently in the solar cell industry along with the development of the photovoltaic industry.

Semiconductors and LCD panels have developed notably that it is no exaggeration to say that these two fields have led the ammonia market expansion in recent years. Its application has expanded to ultraviolet light emitting diode (UV-LED), which is emerging as next-generation lighting due to a high luminance and low manufacturing cost, as well as sterilization, wastewater treatment, deodorization, medical use, skin disease treatment, counterfeit detection, and environmental sensors. The demand for ultra-high purity ammonia (white ammonia with more than 99.99999 % purity) is expected to continue to increase.

## 2.2.3 Refrigerant

Ammonia, along with Freon gas, is used as a refrigerant that has saved humankind from heatwaves. In 1832, M. Faraday established the ammonia vapor-compression theory, and the French scientist F. Carre received a patent for ammonia absorption chiller in 1859. Ammonia is still widely used in large industrial refrigeration units and ships (Sec 12, Ch. 6, Pt 5 and Ch. 1, Pt. 9 the Rules for the Classification of Steel Ships).

Since ammonia is easy to liquefy, it is often used with hydrogen fluorocarbon (HFC)<sup>1</sup> to design general-purpose compressors. Its latent heat of vaporization is second to water and is superior to other refrigerants. As a result, its refrigeration capacity per enclosed unit volume in a system is extremely high. Moreover, the critical temperature is also high at 132.4 °C, and the refrigerant evaporation temperature can range widely from 0 to 60 °C in a refrigeration cycle. In general, materials with a lower molecular weight have a higher thermal conductivity rate. The thermal conductivity rate of ammonia, which has an extremely small molecular weight, enabling the heat exchanger to be miniaturized.

## 2.2.4 Automobile Fuel Additive

Ammonia can be converted into urea solution to reduce NOx in the exhaust gas. Moreover, it reacts with haloalkyl, such as alkyl chloride (RCI), to form an amine mixture in the form of diethylamine and hexamine, which are used as engine oil or a fuel additive for corrosion prevention and curing.

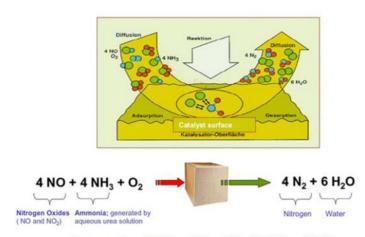
## 2.2.5 Selective Catalytic Reduction (SCR) Catalyst

Methods of controlling NOx using a catalyst include a method of directly decomposing NOx (without using a reducing agent) and the catalytic reduction method using a reducing agent. The catalytic reduction method that decomposes NOx on a catalyst decomposes NOx into nitrogen and hydrogen without reducing agents. Therefore, it is economically advantageous since it requires less maintenance cost and requires no means to supply the reducing agent. However, it shows an excellent catalytic activity only at high temperature (600 °C or higher), and the hydrogen and carbon dioxide in the exhaust gas inhibit NOx decomposition, resulting in low removal

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<sup>&</sup>lt;sup>1</sup> HFC, a substitute for Freon gas, does not destroy the ozone layer because it does not contain chlorine in its molecule. However, it is classified as a GHG.

efficiency. On the other hand, the SCR process using ammonia can remove more than 90 % of NOx emitted by a fixed source. It has been commercialized as the optimal NOx control technology from the price competitiveness and stability aspect. Refer to the "Guidance for Exhaust Gas Emission Abatement System" by the Korean Register (KR).



Fast reaction: 2NH<sub>3</sub> + NO + NO<sub>2</sub> → 2N<sub>2</sub> + 3H<sub>2</sub>O

Figure 6 NOx Removal Reaction

## 2.2.6 Ammonia Engine Development

Considering ammonia as a fuel is not a brand new concept. There is a record of the ammonia-fuel bus in the 19th century, and an ammonia, coal, and gas hybrid engine were developed in Brussels in the 1940s to maintain public transportation in the middle of the war. However, the engine was developed to overcome the shortage of oil rather than to meet the environmental requirement. It was no longer needed after the war since natural gas and oil were available in abundance at lower prices.

#### 2.3 Carbon-Neutral Fuels Compared With Ammonia

The currently available carbon-neutral fuels that can be produced and consumed with zero carbon emission include biofuel, hydrogen, and methanol.

## 2.3.1 Biofuel

Biodiesel is the carbon-neutral fuel that is the most superior from the storage and transport aspect. It is because it has almost the same properties and energy density as existing fossil fuels. Therefore, its advantage is that the fuel system and tank used in existing ships can be used as it is.

Biogas also has the advantage that it can be used in LNG-fueled ships since it is mostly comprised of methane gas.

Ethanol produced from corn and methanol produced from synthetic gas generated by organic waste are also eco-friendly, but they have a low energy density.

Fuels like biodiesel and biogas obtained from biomass have a unit process that requires massive facility investment and can cause competition with food when used in excess. While the first-generation materials used food, the second-generation materials can use livestock manure, food waste, and agricultural/fishery waste. However, these wastes are incidentally produced by other industries, and it is difficult to increase production by assuming that they will be stably available at all times.

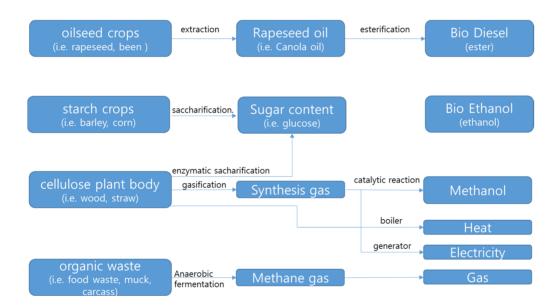


Figure 7 Biofuel Production [First and Second Generations]

Microalgae, which are recognized as the third-generation biomass in the future following grains (first generation) and wood (second generation), are characterized by biological recovery of carbon dioxide in the atmosphere because they perform photosynthesis. Since it can efficiently convet carbon into biomass, biofuels made from microalgae are called "green gold." Recent analyses have reported that microalgaebased biofuels can meet the world's energy demand, but it will take time before mass production becomes possible due to the need to develop efficient microalgae containing high lipid.

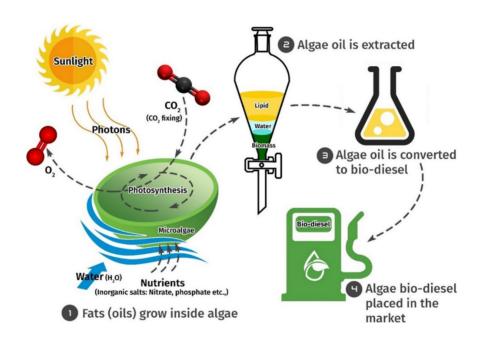


Figure 8 Biofuel Production [Third Generation] (© 2020 Elsevier B.V)

## 2.3.2 Hydrogen

Hydrogen has the advantage of being immediately producible through water electrolysis using renewable energy. The produced hydrogen, however, must be liquefied at -253 °C to store it in large quantities. Therefore, large energy is consumed for the storage and transport process. Liquefying hydrogen requires energy equivalent to about 30 % of the calorific value, and the amount of energy loss due to boil-off gas (BOG) generated during storage and transportation increases even more.

#### 2.3.3 Methanol

Methanol can be produced using biomass or synthesized through the reaction of carbon dioxide or carbon monoxide with hydrogen produced by water electrolysis using renewable energy. Although it can be regarded as very eco-friendly in that it can use the captured carbon dioxide in the long term, carbon dioxide capture technology has been inadequate until now, and hydrogen is also produced using fossil fuels. Moreover, methanol is inefficient to be used as a fuel since its energy density is low.

# 3 Economic Efficiency of Ammonia

The following figure shows ammonia production costs according to the existing route through steam reforming of natural gas, carbon capture and storage, electrolysis of water followed by the Haber-Bosch synthesis, and electrochemical ammonia production (direct electrochemical nitrogen reduction). These costs are the costs per energy unit based on the low calorific value which did not reflect the different efficiency according to the fuel and ship propulsion system.

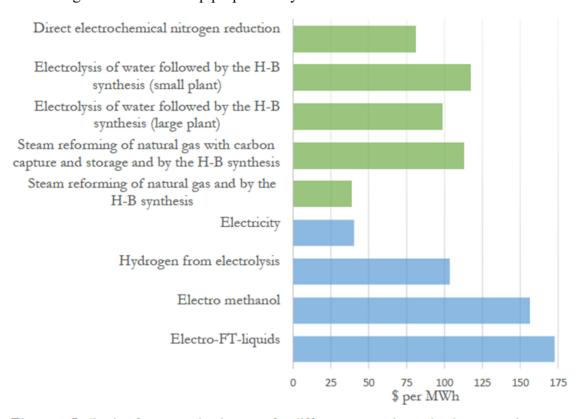


Figure 8. Indicative future production cost for different ammonia production routes in 2040 based on Hochman, et al. (2019) and compared with the cost for electricity, hydrogen and selected electrofuels production routes in 2030 based on Brynolf, et al. (2018). An electricity price of \$40.2/MWh and a natural gas price of \$14/MWh is assumed in the assessments.

Figure 9 Electrochemical Ammonia Product Cost

The production cost of green ammonia to be used as a marine fuel to achieve zerocarbon is estimated by summing up the capital investment cost, the fixed operating cost, and the cost of energy used as raw material. The following figure shows the expected break-even selling price for green ammonia.

Small plants are expected to emerge beginning in 2025 to produce green ammonia at the cost of USD 650-850 per tonne. The green ammonia cost is expected to drop to USD 400-600 as larger plants will be constructed in 2030 and then to further drop to USD 275-450 in 2040. It is an analysis that the higher the price competitiveness as more ammonia used,

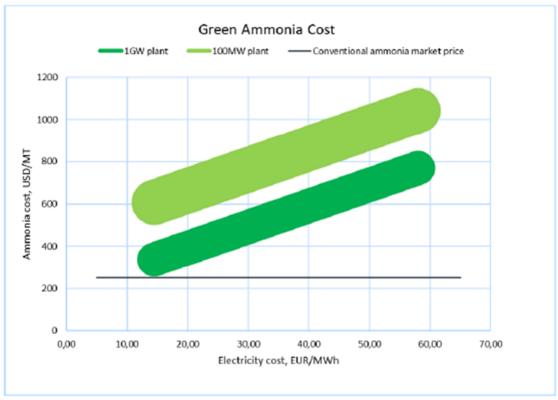


Figure 10 Costs of Green Ammonia Production Using Renewable Energy

# 4 Properties of Ammonia

## 4.1 Physical Properties of Ammonia

- O Since ammonia's vapor pressure at 37.8 °C is 1.46 MPa, the gas is relatively easy to liquefy<sup>2</sup>. Like LPG, ammonia can be liquefied by applying a certain pressure event at room temperature.
- Table 1 summarizes the general ammonia properties as well as those of other carbonneutral fuels for comparison.

| Property   | Ammonia   | Hydrogen  | Methanol | Methane (LNG) | Propane (LPG) |
|--|-----------|-----------|----------|---------------|---------------|
| Flash point (°C)   |           | -150      | 11       | -188          | -105          |
| Autoignition temperature (°C)  | 651       | 535       | 464      | 595           | 459           |
| Ignition energy (mJ)   | 8         | 0.011     | 0.14     | 0.28          | 0.25          |
| Basic burning rate (cm/s)  | 12        | 312       | 56       | 40            | 46            |
| Flammable concentration range in the air (%)                               | 15-28     | 4-75      | 5.5-44   | 5-15          | 2.2-9.5       |
| Boiling point at atmospheric pressure (°C)                                 | -33.5     | -253      | 64.7     | -161          | -42           |
| Critical temperature (°C)  | 132.4     | -239.9    | 239      | -82.95        | 96            |
| Critical pressure (saturated vapor pressure at critical temperature) (MPa) | 11.28     | 1.297     | 8.1      | 4.6           | 4.26          |
| Static pressure/static specific heat ratio k (Cp/Cv)                       | 1.312     | 1.405     | 1.233    | 1.31          | 1.13          |
| Vapor pressure at 45 °C  | 1.78      | -         | 0.045    | -             | 1.5           |
| Liquid/vapor volume ratio  | 850 times | 800 times | -        | 600 times     | 300           |

Table 1 Physical Properties of Ammonia

• Since ammonia gas is colorless and has a strong odor, it has the advantage of being immediately detected when there is leakage. It has good ventilation because it is lighter than air, it is easy to control leaked ammonia because it tends to concentrate on the ceiling or high places, and it can be used as marine fuel because it has little explosive

<sup>&</sup>lt;sup>2</sup>The IGF Code defines fluid, having absolute vapor pressure higher than 0.28 MPa at 37.8 °C, as gas.

property.

• Ammonia bonded with another substance in the air must be not discharged as it is since it creates the main component of ultrafine dust, as shown in Figure 12. The Korean Ministry of Environment has set the ammonia emission standard, as shown in Table 2.

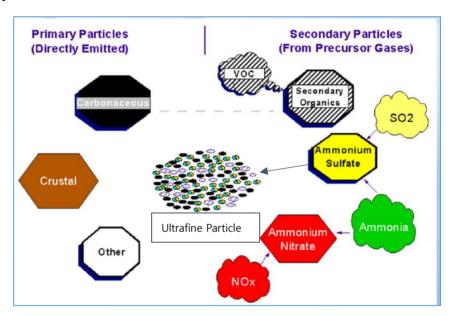


Figure 11 Ultrafine Dust Generation and Ammonia (Source: PECHAN)

| Туре     |                                    | Emission Allowance Standard |  |  |
|----------|------------------------------------|-----------------------------|--|--|
|          | Dust (mg/S m³)                     | 5–50                        |  |  |
|          | Zinc and its compounds (mg/S m³)   | 4                           |  |  |
|          | Carbon monoxide (ppm)              | 50–300                      |  |  |
| Gen      | Ammonia (ppm)                      | 12–30                       |  |  |
| eral (10 | Nitrogen oxide (ppm)               | 10–250                      |  |  |
| Тур      | Sulfur oxide (ppm)                 | 10–250                      |  |  |
| es)      | Hydrogen sulfide (ppm)             | 2–5                         |  |  |
|          | Carbon disulfide (ppm)             | 10                          |  |  |
|          | Hydrocarbon (ppm)                  | 40–200                      |  |  |
|          | Copper and its compounds (mg/S m³) | 4                           |  |  |

Table 2 Atmospheric Pollutant Emission Allowance Standard (Source: Ministry of Environment)

- O Vaporization occurs not only on the surface but also inside the liquid when the temperature of the liquid is increased or the pressure applied to the gas is decreased. Vaporization that takes place inside the liquid is called boiling, and the boiling point at which ammonia begins to vaporize is -33.5 °C at atmospheric pressure.
- If an ammonia tank is installed on an exposed deck, the container is heated by radiant heat. When the ammonia container is heated, the ammonia's temperature rises, causing the volume to expand and the pressure in the container to rise.
- If the tank is filled with liquid so that the liquid comes into contact with the safety valve designed to discharge gas, the safety valve may not function properly, causing the pressure in the container to continue to rise, and at worst, to rupture the container. Therefore, the maximum filling limit must be set for each container to prevent from this.
- Ammonia can easily liquefy at high pressure and vaporize at atmospheric temperature. If the tank is ruptured under pressure, most pressurized ammonia is released as vapors or fine aerosols and diffuses into the atmosphere. If a large amount of ammonia is released, ammonia gas generated from a liquid reacts with air to generate mixed gas, which is heavier than air and may cause hull corrosion when deposited on the surface of the ship.

## 4.2 Fuel Properties of Ammonia

- Liquefied ammonia has a relatively low volume energy density (see Table 2) and requires about 4.1 times as much tank volume as conventional fossil fuels. The storage performance of future energy is a very important factor in ships with a relatively severe space constraint, and liquefied ammonia can be stored in a pressurized tank or lowtemperature tank. Ammonia can be stored in a pressurized tank at about 1 MPa and lowtemperature tank at about -34 °C. Ammonia is weaker than biodiesel or methanol from the fuel storage and transportation aspect, but is superior to biogas or hydrogen from the storage aspect. As such, its transportation cost is lower than other carbon-neutral fuels, and transportation technology is already available.
  - The critical temperature is the upper limit temperature for the gas to be liquefied. In other words, the gas cannot be liquefied above the critical temperature, no matter how much pressure is applied. Since the critical temperature of LNG is -82.95 °C, it cannot be liquefied at room temperature and thus must be stored in a container at low temperature or a pressurized container at low temperature. On the other hand, ammonia with the critical temperature of 132 °C can be liquefied when pressurized at atmospheric temperature (25 °C) and thus can be conveniently stored.

O Combustion characteristics such as the calorific value, octane number, and flame speed shown in Table 3 must also be considered. The following table shows the characteristics of next-generation fuels. While the calorific value is very low compared to hydrogen, it is similar to methanol.

| Fuel                     | Ammonia               | Liquefied<br>Hydrogen | Hydrogen Gas | LNG     | MGO/<br>Diesel Oil | Methanol |
|--------------------------|-----------------------|-----------------------|--------------|---------|--------------------|----------|
| Storage condition        | Liquid                | Liquid                | Gas          | Liquid  | Liquid             | Liquid   |
| Storage temperature (°C) | 25                    | -253                  | 25           | -162    | 25                 | 25       |
| Storage pressure (kPa)   | 1000-1700             | 101-3600              | 25000        | 101-125 | 101                | 101      |
| Density (kg/m³)          | 603 (Liquid at 25 °C) | 71                    | 17.5         | 430-470 | 840                | 786      |
| Calorific value (MJ/kg)  | 18.6-18.8             | 120                   | 120          | 49      | 43                 | 19.7     |
| Octane number            | >130                  | >130                  | >130         | 120     | -                  | 109      |
| Flame speed              | 0.015                 | 3.5                   | 3.5          | 0.34    | -                  | 0.43     |

Table 3 Properties of Next-Generation Fuels

## 4.3 Comparison of Combustion Properties of Next-Generation Fuels

## 4.3.1 Importance of Combustion Properties

Understanding the fuel's combustion properties of fuel used by the ship is very important for assuring the ship safety from fire and explosion. When fuel is leaked due to an unsafe protective system condition or human error in handling, processing, or using the fuel, it can result in a fire or explosion if the leaked fuel mixes with air to form a gas mixture and there is an ignition source around it. Typical fire and explosion characteristics include flammable concentration range, flash point, autoignition temperature, ignition energy, and heat of combustion.

In general, an explosion occurs when combustible gas or vapor is mixed with air to form a large gaseous phase volume, and it comes into contact with an ignition source in a closed space state. It can occur in the engines and piping devices of a ship. When flammable gas or evaporated liquid is released into the atmosphere, the gas cloud formed from the leak is diluted or disappears into the atmosphere if the gas cloud is not within the explosive range or if the ignition source is insufficient.

The main variables affecting the gas explosion include the type of fuel and oxidizer, the concentration and size of the fuel in the vapor cloud, the intensity and location of the ignition source, the size, location, and shape of the explosion emission area, the location and size of the structural elements and facilities, the ignition delay, and the geometric conditions of the surroundings due to the closed system and open system. Consequently, it is not easy to predict the explosion phenomenon since the gas explosion is very sensitive to these factors.

Typical ways of preventing gas explosion include lowering the oxidizer or combustible gas concentration. Ways to prevent loss include an explosion suppression technology that detects and prevents early development of pressure that can result in explosion, deflagration pressure containment technology that designs the container and accessories to withstand the pressure generated by deflagration inside the container, and the equipment to extinguish sparks that can be an ignition source of the explosion. Moreover, the facility design must consider factors such as the effectiveness of the prevention method, the facility's reliability, and the risk to human life.

Fire and explosion characteristics of fuel used in ships can be obtained through Material Safety Data Sheet (MSDS) provided by the Korea Occupational Safety and Health Agency (KOSHA). In addition, the lower/upper limits of the explosion, flash point, autoignition temperature, and heat of combustion can be obtained through the Fire and Explosion Parameters in the Properties in the Environmental, Safety and Health Database of the American Institute of Chemical Engineers (AIChE)'s Design Institute for Physical Property Data (DIPPR). However, it requires much research and consideration to extract accurate fire and explosion characteristics data through testing under various conditions.

#### 4.3.2 Ammonia

Since ammonia is gas, it is not appropriate to measure its flash point by a closed bomb test, which generally measures a liquid fuel ignition point. Therefore, it is typically stated "Not applicable/None" in MSDS. The autoignition temperature is related to the temperature limit in the environment in which gas can be leaked by exhaust gas temperature. While the IGC Code limits the exhaust gas temperature to 535 °C, that for ammonia is 651 °C, which is higher than that for LNG. Therefore, there is no further consideration for the temperature limit.

Like hydrogen, ammonia does not contain carbon, but it has one more hydrogen than a hydrogen molecule and remains liquid when the pressure of about 1 MPa is applied at room temperature; thus, the existing ammonia and LPG infrastructure can be used as-is. As a fuel, ammonia's stability is known to be better than propane and similar to gasoline fuel.

The use of ammonia as vehicle fuel dates back to the 1930s, and studies for use as domestic fuel have also been conducted. Ammonia fuel has a calorific value of 18.6 MJ/kg, which is 0.44 times more calories per kg than gasoline. Despite that, it has not been widely used as fuel because of its disadvantages that the flame propagation speed is significantly lower than that of gasoline fuel. Furthermore, NOx can be generated depending on the fuel characteristics, and ammonia slip can occur according to engine control and can be discharged together with the exhaust gas.

## 4.3.3 Hydrogen

Hydrogen has emerged as a pollution-free energy source to replace fossil fuel since its combustion generates only water and no pollutant. Moreover, its heat of combustion is about three times higher than that of oil, making it a very efficient energy source. Therefore, it can also be used as the household energy source if its combustion can be controlled under an appropriate condition. However, it is very difficult to handle hydrogen since the material can melt metals, its storage and transport are very difficult, and its leakage can cause a huge explosion.

Hydrogen is mostly used by petrochemical or oil refining industries on land and is regulated as high-pressure gas according to the High-Pressure Gas Safety Control Act. Since a hydrogen-filled vehicle container's pressure can be up to 70 MPa, its leakage into the confined space can cause a major accident.

Hydrogen is the lightest of all elements. As a fuel, it is faster than currently used fuels, including LNG, LPG, and gasoline, and its buoyancy increases very quickly as well. Moreover, it is a colorless, odorless, and tasteless combustible gas at room temperature and has similar properties as LNG or LPG as a non-toxic gas. It can be said that its explosion risk can be higher than other fuels because of its wide explosive range; detonation risk is also regarded to be high since it correlates with an explosion risk. In the case of an open area, however, unlike closed area, it has been reported to have a similar risk as other fuels. Since its minimum ignition energy is lower than conventional fuels, hydrogen has a higher explosion risk as it requires less energy for the explosion. Moreover, the flame speed is 6 to 7 times faster than that of LNG or LPG.

#### 4.3.4 Methanol

Methanol, also called methyl alcohol, has a very low flash point of 11 °C, at which the methanol and air mixers are present on surfaces that can be ignited by an ignition flame or small sparks. When it is diffused in the form of a flam on a surface, the surface temperature increases to the boiling point, and the evaporation rate or the combustion rate also increases accordingly.

#### 4.3.5 Ethanol

Ethanol, also called ethyl alcohol, has a flash point of 13 °C and an autoignition temperature of 363 °C, which is lower than methanol. It is easy to burn and can explode when ignited in a vapor form. It is necessary to control acetaldehyde and other products generated during combustion which are harmful to the human body.

#### 4.4 Risk of Ammonia

## 4.4.1 General

- The risk of ammonia as a fuel is different from the properties and risk of conventional fuels like HFO and MDO and liquefied gas fuels like LNG and LPG. Therefore, it is more rational to identify risks of using it as fuel for ships by identifying risks of transporting it as cargo according to the IGC Code and risks of using it as a refrigerant or catalyst rather than identifying additional risks compared to conventional fuels.
- It is important to understand the risk factors among general properties of ammonia to study the ammonia-fueled ships' structural and facility safety.

### 4.4.2 Toxicity

Ammonia liquid strongly irritates the mucous membrane and, if inhaled, causes laryngeal spasm, laryngitis, bronchitis, etc. If not treated promptly, it can be toxic to cause asphyxial death. Since ammonia is alkaline and irritates living tissues, it may damage the eyes, liver, kidneys, or lungs if the body is exposed to it for a long time. It can cause a burning sensation and turns the skin red if it comes into contact with the skin. If the skin is exposed to it for a long time, it can cause sore oozes or other damages to the skin tissue. It can cause hair loss if it comes into contact with the scalp. Drinking it can cause pain in the mouth and throat and can lead to stomach pain, nausea, and a state of despondency. It can lead to the following symptoms according to the concentration. The actual symptoms may differ depending on the person.

| Concentratio<br>n (ppm)  | Symptom   |  |  |
|--|---|--|--|
| 5  | It has a characteristic smell.  |  |  |
| 6-20   | It causes eye irritation or the problem in the respiratory system.                      |  |  |
| 40-200   | It causes headaches, nausea, loss of appetite, and airway, nose, and throat irritation. |  |  |
| 400  | It irritates the neck.  |  |  |
| 700  | It can damage the eyes.   |  |  |
| 1700 It causes coughing and trouble breathing. It causes momentary to breathing. |   |  |  |
| 2500-4500  | Even brief exposure can be fatal.   |  |  |
| 5000 or higher   | It can lead to death due to respiratory arrest.   |  |  |

Since ammonia is a toxic gas, most countries control it by establishing the allowable concentration limit in workplaces or daily life. The allowable concentration is classified into the short-term exposure limit (STEL) for the case of 15-minute contact and the timeweight-average (TWA) concentration for an 8-hour work period. For ammonia, STEL is 35 ppm, and TWA is 25 ppm. It is managed according to the Occupational Safety and Health Act, and in the United States, the allowable concentration is managed by the regulation of the Occupational Safety and Health Administration (OSHA).

#### 4.4.3 Corrosion and Material Selection

Gas carriers transport gases by liquefying them with the temperature or pressure control. Therefore, it is necessary to manufacture a gas tank to withstand the pressure with steel that does not break even at low temperatures. An ammonia carrier is built in a similar specification as LPG carriers, and the tanks in the carrier are manufactured with steel to withstand the boiling points (-42 °C for LPG and -33 °C for ammonia) and pressure at the same time. If a tank is stressed by gas pressure, the affected metal structure is deteriorated to be corroded. As a result, cracks can occur which may cause gas leakage. It is important to prevent the deterioration of strength and toughness after the post-weld heat treatment (PWHT) to remove the stress generated after welding the steel material for tank manufacturing.

Ammonia vapor in contact with moisture can corrode copper, zinc and its alloys, as well as rubber and plastics. Heavy metals such as silver, gold, mercury, and thallium must be handled with care since they can form explosive compounds.

## 4.4.4 Gas Vapor Pressure

When the ammonia liquid vaporizes, its volume expands more than 850 times, causing a pressure increase in the closed facility. The design tank pressure is inevitably increased if an ammonia fuel tank applies the independent tank type C, and the tank pressure is controlled only by pressure.

## 4.4.5 Fire and Explosion Risk

Although ammonia's fire risk is low, it increases if flammable material like oil is present. Ammonia can generate an explosive compound if it is in contact with a strong oxidizer like chlorine and hypochlorite bleach.

#### 4.4.6 Odor

Ammonia has a very strong, unique odor, and its odor threshold is 5–50 ppm in the air. It is no longer used as a refrigerant in refrigerators as it did in the past because of an irritating order. Conversely, the strong odor makes it easy to detect its leakage.

# **5 Safety Features of Ammonia Handling Facilities**

#### 5.1 General

- Ammonia has been used on land for various purposes by industries. The regulations on safe ammonia handling include the "High-Pressure Gas Safety Control Act," "Rules on Occupational Safety and Health Standard," and "Toxic Chemicals Control Act."
- Land facilities cannot be directly applied to ships, considering differences in ship structure and arrangement. Therefore, we reviewed the appropriateness and replacement requirements for application to ships after understanding the purpose of on-land safety standards.

## 5.2 Marine Transport of Ammonia

Millions of tonnes of ammonia are distributed worldwide through liquefied gas carriers equipped with low-temperature pressure or low-temperature tank subject to Ch 5, Pt 7 of the Rules for the Classification of Steel Ships (IGC Code). As described above, ammonia is generally consumed for agricultural or industrial purposes. Although it can be directly delivered to consumers, it is often unloaded to dedicated ammonia storage at ports.



Figure 12 Gas Carrier

## 5.2.1 Low-Temperature Transportation

According to the existing hull strength analysis method, the independent tank type A usually applied to low-temperature transport of ammonia refers to a tank designed according to the accredited standard. The design vapor must be less than 0.07 MPa if the tank is mainly constructed in a flat structure. A complete secondary barrier must be installed, and low-temperature steel that can withstand -45 through -50 °C is typically used if the cargo temperature is less than -10 °C at atmospheric pressure.

## 5.2.2 Pressurized Transportation

The independent tank type C is used for pressurized ammonia transportation; it is the simplest format. The design pressure is usually 1.75 MPa, which is equivalent to the propane saturation pressure. It has a volume limitation and is costly because it is heavy. Since it is a high-pressure application, there is no need to consider the re-liquefaction facility.

## 5.2.3 Semi-Pressurized, Semi-Low-Temperature Transportation

It is classified as the independent tank type C under the IGC Code. The design pressure of semi-pressurized transportation is 0.5–0.7 MPa. Since the design pressure is low compared to pressurized tanks, the thinner steel that can withstand -10 °C is used.

#### 5.3 Ammonia Above-Ground Storage Facility

The ports must have the bunkering facility to service conventional ships that do not transport ammonia but use ammonia fuel. About 120 ports worldwide have the storage facilities to import and export ammonia, and they can be used for bunkering.

The challenge to overcome for ammonia bunkering is a large ammonia discharge. Although LNG and LPG are also classified as GHG, they are not particularly harmful unless they contact the human body; they have no color or odor. However, ammonia has a strong odor and causes ultrafine dust when it is released into the air; it can be a new pollution source in ports unless special measures are implemented. Therefore, the ports must seek additional measures to prevent major leakage during bunkering by referring to the above-ground storage facilities' safety measures.



Figure 13 Ammonia Storage Tank < Source: Proton Ventures>

## 5.3.1 Technical Guidelines on Anhydrous Ammonia Storage

The KOSHA has issued the "Technical Guidelines on the Storage of Anhydrous Ammonia" that establishes requirements for the toxic anhydrous ammonia storage to prevent serious industrial accidents caused by ammonia leakage. The guidelines are applied to the design, inspection, location selection, and installation of facilities that store liquid anhydrous ammonia. Anhydrous ammonia refers to anhydrous ammonia gas or liquid and excludes ammonia dissolved in water.

#### **5.3.2 Safety Measures in the Guidelines**

- Storage facilities
  - The storage tank capacity is in the range of 500 to 3,000 tonnes when stored in an old container at a non-low-temperature in consideration of economy and safety. A large capacity of 5,000 tonnes or more, typically 20,000 to 35,000 tonnes, is used for low-temperature storage.
  - Storage facilities are laid out with consideration to the wind direction to minimize the effect of ammonia leakage.
  - The storage facilities must be installed in a place where operators can easily access them for operation inspection and maintenance.
  - They must be installed far enough from other process facilities to minimize potential damage from external impact or leakage of explosion and fire corrosive

materials.

- All storage tank nozzles must be flange type and must be installed on the manhole cover or on the top of the storage tank.
- Materials of ammonia storage facilities
  - The design tensile strength of the steel plate must not exceed the maximum allowable value.
  - Copper and copper alloy materials must not be used.
  - It is necessary to conduct a 100 % non-destructive test of welded joints of storage facilities.
  - 100 % magnetic particle inspection must be conducted before the internal welding part's operation and the areas where temporary attachments were installed.
  - The welded area where the nozzle is attached to the main body must be subjected to ultrasonic inspection.
  - The acoustic emission test must be carried out during the storage tank test period.
  - After the successful non-destructive inspection, PWHT must be performed on the weld joint.

## • artificial barricade<sup>3</sup>

- Artificial barricade to prevent leakage must be installed around the storage tank, and the effective capacity of the oil fence must be calculated according to the KOSHA Guide, "Technical Guidelines for artificial barricade Installation."
- The material for the artificial barricade and its inner bottom must be able to prevent liquid ammonia penetration, and the cross-section area must be minimized to suppress the vaporization of leaked ammonia.
- Installation of the facility to collect liquid ammonia leaked into the oil fence or transport it to another area must be considered in preparing the emergency situation of liquid ammonia leakage.
- Drainage facilities must be installed to prevent the accumulation of rainwater inside the oil fence.

<sup>&</sup>lt;sup>3</sup>An oil fence is a wall made of concrete or others when installing storage tanks. It prevents leakage out of the facility due to earthquake damage, etc.



## Pipeline

- The pipeline must be installed on the ground considering the mechanical damage, corrosion, and fire.
- All pipes must have the indication that they are processing ammonia.
- The edge of the storage tank's liquid ammonia inlet pipe must be higher than the maximum liquid level of the storage facility to prevent backflow of liquid ammonia due to the inlet pipe's rupture, etc. If the edge of the liquid ammonia inlet pipe is to be lower than the storage facility's liquid level, a hole must be made in the upper section of the liquid ammonia inlet pipe inside the storage facility to prevent backflow.
- An emergency shut-off valve with a remote control must be installed in the liquid ammonia discharge pipe to prevent ammonia leakage due to pipe rupture.
- The number of joints must be minimized. Welded joints are preferable when connecting pipes, and flange joints must be used only for connection with devices such as storage containers.
- Thermal expansion safety valves must be installed in the pipeline for liquid ammonia.
- The material used for piping must not cause brittle fracture even at temperatures below 0 °C.
- Valves must generally be a flange type, and the carbon steel welded valves must pass the impact test.

## Ammonia transport

- The pump's discharge-side pipe must be installed to circulate the minimum flow line to the storage tank according to the pump and operation characteristics.
- The pumps must be interlocked to stop if the liquid level of the storage facility is low, or the pressure on the discharge side of the pump is low.
- The liquid outlet line from the tank to the pump must be kept as short as possible and sufficiently cooled.

## • Electrical equipment

- A ventilation facility must be installed in areas equipped with electrical facilities such as the ammonia compressor and building to discharge ammonia leakage into the atmosphere.
- Motors that expose copper to the outside must not be used.
- Field safety equipment
  - Anti-collision walls must be installed to prevent damage to pipes or ammonia handling equipment from external impact.
  - A cleansing facility must be located around the ammonia facility.
  - The following safety equipment must be provided at the site for immediate use:
    - (A) Gas masks used when people enter ammonia storage areas.
    - (B) Two sets of lifesaving breathing apparatus.
    - (C) Emergency and lifesaving protective clothing
    - (D) Plastic or rubber gloves and boots
    - (E) Safety goggles
    - (F) First-aid box

#### • Employee education

- Ammonia and liquefied gas characteristics
- Risk and result of ammonia liquid and gas leakage due to careless equipment handling
- Actions when ammonia is leaked
- Proper use of protective equipment, fire extinguishers, and gas masks

## • Operation

- Storage tank's oxygen content should be reduced to within 0.025 % of the capacity before injecting ammonia into the storage tank.
- In order to remove oxygen as much as possible while minimizing ammonia loss, internal air should be replaced with water first and again, water with nitrogen before injecting ammonia. The residual moisture must not exceed 100 ppm.
- Check the oxygen concentration in liquid ammonia at least once a month and confirm that it does not exceed 2.5 ppm by mass.

#### Shutdown

- When shutting down the ammonia storage facility for inspection, discharge the liquid ammonia as much as possible using a normal pump first and completely discharge the remaining liquid using a transport method by pressure difference.
- Draw in the air at the lowest point and release ammonia gas at the vessel's highest point.
- Although the risk of ignition is generally low, inject nitrogen instead of air into the container if any risk is expected.
- Do not perform the ammonia/air replacement in the event of lightning.

## 5.4 Ammonia as a Vehicle Fuel

Since pure ammonia has similar thermochemical properties as propane, the main component of LPG, it is possible to use it for internal combustion engines like an automobile engine. However, since ammonia has a high ignition point and a slow combustion rate, there is still a technical limitation to be used as fuel by itself. Therefore, the development has focused on engines that mix two fuels, such as gasoline-ammonia and natural gas-ammonia.

Korea has developed a car that uses ammonia as a fuel for the third time in the world and successfully tested it. It was remodeled to use a 7:3 mixture of ammonia and gasoline, resulting in a carbon dioxide emission ratio reduction from 13.5 % to 3.5 % or less compared to gasoline cars.

## 5.4.1 Ammonia Fuel Supply Pump

• The pump transfers liquid ammonia from a fuel tank to an engine. It is remodeled from the industrial ammonia pump.



Figure 14 Ammonia Fuel Supply Pump

## 5.4.2 Ammonia Fuel Pipe

• Ammonia reacts with rubbers, plastic, copper, etc. and is highly corrosive. The entire fuel pipeline is replaced with Teflon and stainless steel materials, and airtight agents such as rubber rings of fuel system parts are replaced with materials suitable for ammonia.

#### 5.4.3 Ammonia Emission Reduction

O Ammonia discharge is reduced by an oxidation catalyst installed at the rear end of the exhaust pipe to secure the cleanness of exhaust gas by blocking the discharge of unburned ammonia.



Figure 15 Ammonia Emission Reduction System

## 5.5 Comparison With Ship Safety Features

- The risk and safety features of using ammonia in above-ground storage tanks and automobiles mostly address the protection of the storage facilities and gas leakage as the IGF Code does. In this case, they consider especially the toxicity and corrosiveness.
- Comparison of the requirements specified by each code for on-land storage tanks and ship's cargo storage tanks shows the following differences:
- The installation environments of storage tanks on land and in ships differ in many factors, such as the space limitation, effect of wind in marine navigation, effect of fire and explosion, and structures around the gas facility (obstruction of the leaked gas dispersion). Therefore, the regulation on safety features required by ships may also differ.
- Requirements for fire protection on land and ships are different. Ships must ensure the separation of flame and fuel tank in a limited space and install cofferdams or A-60 class heat sink to protect tanks from a fire in high-fire hazard areas.
- For the double-walled storage tanks on land for low-temperature ammonia, the insulator must be filled between the inner and outer walls or installed outside the storage tank. Insulators must be non-reactive with ammonia and must not burn in a fire. When constructing the insulator outside the tank, the exterior of the insulator must be protected with the material not corroded by ammonia.

- Installation of the appropriate cleaning system is considered to prevent ammonia discharge from the discharge pipe and vent pipe of the on-land storage tank safety valve to the atmosphere.
- Comparing the requirements specified by each code for the fuel supplying systems in automobiles and ships shows the following differences:
- Automobiles do not require a sprinkler system for tank cooling. The sprinkler system for cooling prevents the temperature increase inside the tank by radiant heat when the tank is exposed to the outside. The automobile's fuel tank does not need the spray system since it is installed inside or below the automobile and thus is not significantly affected by radiant heat.
- Since automobile discharge leaked gas to the open space, they install ventilation pipes under the chassis to allow natural ventilation instead of forced ventilation. This is because the leaked gas is naturally discharged out of the automobile due to the pressure difference with the outdoor air as the automobile moves. Because of its structure, ships cannot install a ventilation duct under it and thus requires forced ventilation for effective ventilation.

# 6 Ammonia Fuel Cell and Internal Combustion Engine

## 6.1 General

Ammonia is used as an energy source in various forms. It is burned directly as the fuel of an internal combustion engine, used directly as a fuel for a fuel cell, or is used as a hydrogen energy carrier in a hydrogen fuel cell.

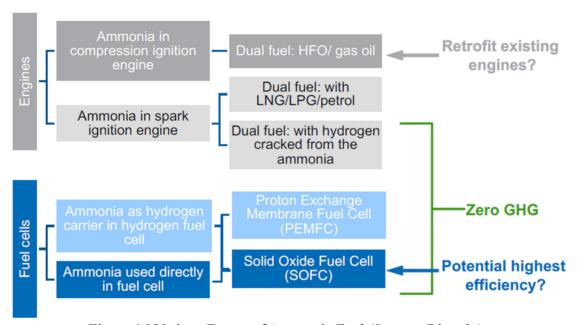


Figure 16 Various Forms of Ammonia Fuel (Source: Ricardo)

Although hydrogen is the ultimate eco-friendly energy source, there are many constraints in the current hydrogen energy supply industry. The main disadvantage is the difficulty of economical storage in large capacity and the long-distance transportation because of the small storage capacity per hydrogen volume. Although storing and transporting hydrogen in a liquid form is the most efficient in terms of energy conservation, the process of liquefying cost of hydrogen is increased in the process of liquefying and maintaining hydrogen is costly, resulting in price increase. Studies on hydrogen energy carriers that change hydrogen into other compound types to increase the storage capacity per volume and reduce the storage cost are ongoing to overcome it.

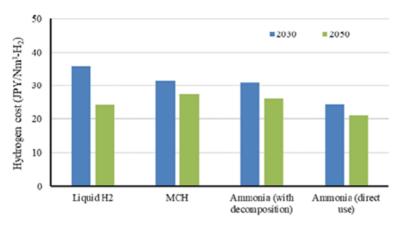


Figure 17 Comparison of Hydrogen Prices According to Production Method

## 6.2 Fuel Cell

Fuel cells that directly use ammonia as a fuel can be arranged in the form shown in the following figure.

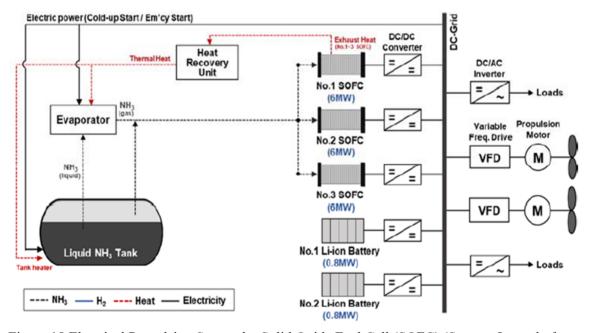


Figure 18 Electrical Propulsion System by Solid Oxide Fuel Cell (SOFC) (Source: Journal of Marine Science and Engineering; August 2020, 183-Strategy Planning Team, KR)

The direct ammonia fuel cell is based on the principle of generating power between the electrodes by directly supplying ammonia gas, which is a fuel for power generation, to an anode installed on one side of zirconia, which is an electrolyte, and air to the cathode on the opposite side. Ammonia fuel leaked from a pipe joint can cause pipe corrosion. It can be solved by developing a special glass to join the ammonia fuel without leakage. The direct ammonia fuel cell is confirmed to have a similar level of power generation characteristics compared to hydrogen fuel cells.

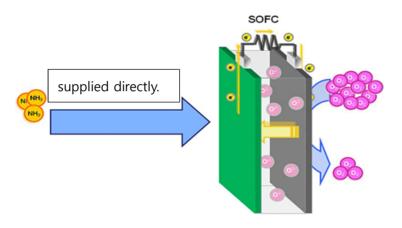


Figure 19 Principle of SOFC Fuel Cell < Source: Japan Science and Technology Agency (JST)>

# **6.3 Internal Combustion Engine**

It is necessary to analyze how ammonia is handled on ships and combusted in reciprocating engines. The industry is currently developing ammonia engines; MAN Energy Solution and Wärtsilä have the roadmaps to implement them by 2022 and 2023, respectively. Dual fuel technology is a proven solution for ammonia combustion. It offers an advantage of enabling gradual adoption of ammonia for ship fuel because of the possibility to use the mixture of alternative and conventional fuels. Moreover, the solutions adopted by commercialized LPG and LNG engines are the beginning point of the safety features and the fuel supply process for ammonia engines.

<sup>&</sup>lt;sup>4</sup> Shipping News Net (SNN) /July 7, 2020

## 6.3.1 Analysis of Engines and Fuel Supply System

### 6.3.2 General

- MAN Energy Solution and Wärtsilä are currently developing ammonia-fueled engines applicable to commercial ships.
- This section discusses the risks of ammonia engines installed in ships for navigation based on the currently available information.
- It focuses on whether the engines offer sufficient safety features in consideration of ammonia's characteristics.

## 6.3.3 MAN Energy Solution, ME-LGIA (2-Stroke Diesel Cycle Engine)

- Overview
- The ME-LGIA Engine ("Engine") has no installation reference. Its development is based on the ME-LGIP engine.
  - The design concept of MAN's 2-stroke ammonia-fueled engine is similar to that of existing engines based on liquid gas injection propane (ME-LGIP, LPG) and liquid gas injection methanol (ME-LGIM). The concept of the LGIM engine is based on that of the LGIP engine. The development of the LGIM engine addressed several problems related to ammonia: corrosion, toxicity, and low flammability.
- The Engine is a two-stroke diesel cycle engine using ammonia. Since ammonia has a low-autoignition temperature and a low-combustion rate, the ammonia engine uses MDO/HFO as the pilot oil.
- The fuel is supplied in a liquid state at 70 bar to up to the Engine connector, pressurized to 600–700 bar through the booster fuel injection valve, and injected into the cylinder. Therefore, the fuel supply system is configured at a relatively lower pressure than the ME-GI engine.

- The exothermic ammonia combustion that generates nitrogen and water can be explained in the following reaction:

$$4NH_3 + 3O2 \rightarrow 2N_2 + 6H_2O + Heat$$

- It is possible to reduce the NOx discharge with the exhaust gas post-processing technology and the SCR system. NH<sub>3</sub>, a reducing agent, is injected into the exhaust gas to generate only nitrogen and water as waste.

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$
  
 $6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$ 

- Since ammonia can corrode alloys with a 6 % or higher concentration of copper, copper alloy, nickel, and plastic, the fuel system using ammonia must avoid such substances. The sealing lining of an ammonia Engine is made of Teflon.
- Table 4 shows the ammonia properties required by the Engine.

Table 4 Physical Properties of Each Fuel Required by Engines

| Table 1   |        |                   |                      |                           |                           |        |                 |                            |    |  |
|---|--------|-------------------|----------------------|---------------------------|---------------------------|--------|-----------------|----------------------------|----|--|
| Energy storage type                                   | Supply | Energy<br>density | Required tank volume | Supply pressure           | Injection pressure        |        | _               | mission red<br>ared to HF( |    |  |
|   | MJ/kg  | MJ/L              | m <sup>3 *1</sup>    | bar                       | bar                       | %      | %               | %                          | %  |  |
| HFO   | 40.5   | 35                | 1,000                | 7-8                       | 950                       | SOx    | NO <sub>x</sub> | CO <sub>2</sub>            | PM |  |
| Liquefied natural gas (LNG -162°C)                    | 50     | 22                | 1,590                | 300 methane<br>380 ethane | 300 methane<br>380 ethane | 90-99  | 20-30<br>30-50  | 24<br>15                   | 90 |  |
| LPG (including Propane / Butane)                      | 42     | 26                | 1,346                | 50                        | 600-700                   | 90-100 | 10-15           | 13-18                      | 90 |  |
| Methanol  | 19.9   | 15                | 2,333                | 10                        | 500                       | 90-95  | 30-50           | 5                          | 90 |  |
| Ethanol   | 26     | 21                | 1,750                | 10                        | 500                       |        |                 |                            |    |  |
| Ammonia* (liquid -33°C)                               | 18.6   | 12.7              | 2,755                | 70                        | 600-700                   | 90-95  | Tier            | 95                         | 90 |  |
| Hydrogen (liquid -253°C)                              | 120    | 8.5               | 4,117                |                           |                           |        |                 |                            |    |  |
| Marine battery market leader,<br>Corvus, battery rack | 0.29   | 0.33              | 106,060              |                           |                           |        |                 |                            |    |  |
| Tesla model 3 battery Cell 2170 *2                    | 0.8    | 2.5               | 14,000               |                           |                           |        |                 |                            |    |  |

Table 1: Physical and chemical fuel properties related to combustion in two-stroke engines, where \*1 is based on a 1000 m³ HFO tank, the additional space required for insulation is not included in the table. All pressure values are for high-pressure injection and \*2 the values for the Tesla battery do not contain the energy/mass needed for cooling/safety/classification

- Fuel supply
- Figure 20 shows the schematic diagram of Engine fuel supply systems.

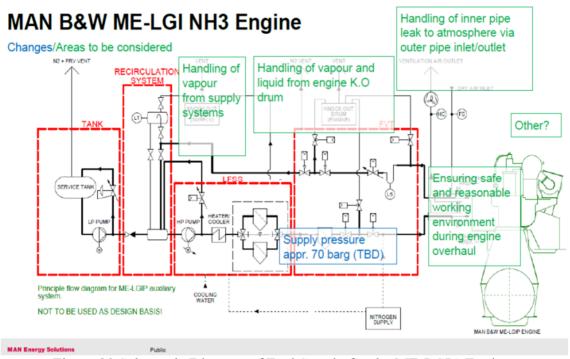


Figure 20 Schematic Diagram of Fuel Supply for the ME-LGIA Engine

- The ammonia fuel service tank is installed to separate the fuel/cargo tank from the pollution source.
- The liquid fuel supply system (LFSS) generally consists of the pump, compressor, heat exchanger, filter, and instruments. The carburetor is excluded since the liquid ammonia is used as fuel. A pump pressurizes ammonia to about 70 bar, and a heat exchanger heats it to the temperature range (25 °C–55 °C) required by the Engine.
- The fuel valve train (FVT) is a group of valves, such as double shut-off and discharge valves, vent valves, nitrogen supply valves, and pressure control valves, and various sensors, as shown in Figure 4–5. The IGF code specifies the valve group to shut off fuel effectively and discharging it in abnormal conditions.

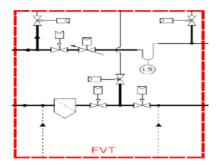


Figure 21 Schematic Diagram of Fuel Valve Train

## Safety features

- The safety features of the Engine are the same as those of a ME-GI engine. It applies the following specifications, most of which are required by the IGF Code:
  - \* Double shut-off and discharge valves: the valves installed in the fuel supply pipes block double valves and vents the pipes between them to separate the fuel supply pipes from the Engine to block the fuel supply.
  - \* Main fuel valves: the valves block the main supply pipe to prevent the fuel supply at the time of abnormal conditions, such as gas detection and ventilation failure.
  - \* Ventilation: the separate mechanical ventilation system with the capacity of ventilating 30 times per hour ventilates the enclosed gas pipe, including the space around the valves and flanges.
  - \* Nitrogen purging system: a nitrogen purging system is installed to discharge residual gas in the fuel pipeline and tanks. The fuel pipeline's purging is used to discharge residual fuel in the pipeline when the main fuel valve is closed, while the tank purging is used to make the tank free of gas for inspection and repair.
  - \* Double pipes: the fuel pipes in the enclosed area are enclosed by an outer pipe or duct to prevent gas from being discharged into the area even when gas is leaked from the fuel pipe. A gas detector and enforced ventilation are installed between the inner and outer pipes to detect and discharge leaked gas.

- Pressure relief valve (PRV) and leak gas detection devices to prevent explosion are installed in the same way as the LNG-fueled ME-GI engines' safety features.
- Additional considerations: while the Engine has no additional or different features from a ME-GI engine, it is necessary to review the following matters in consideration of the ammonia fuel characteristics:
- Fuel supplied in liquid state:
  - \* Discharge of liquid ammonia into a bleed pipe (connection to the vent mast not feasible)
  - \* Purging of liquid or gas with a high specific gravity during nitrogen purging (consideration of purging pressure and capacity)
- Ammonia being toxic and becoming the cause of atmospheric pollution when discharged as it is:
  - \* Since ammonia is toxic, it must never be leaked into the area where the crew may be around.
  - \* Ammonia is one of the causes of ultrafine dust. Therefore, it must never be released in more than a certain concentration into the atmosphere.

# 7 Analysis of IGC Code/IGF Code Requirements

#### 7.1 General

- The IGF Code has been applied to ships using fuel with a low flash point since January 1, 2017.
- A fuel with a low flash point refers to a liquid fuel having a flash point lower than gas or fuel oil permitted by SOLAS II-2, including LNG (gas fuel), methyl alcohol/ethyl alcohol (liquid fuel), LPG (gas or liquid fuel<sup>5</sup>), or ammonia.
- Although the IGF Code was developed for the use of fuels with a low flash point, the detailed specifications are currently applicable to LNG. The IMO has developed the detailed requirements for methyl alcohol/ethyl alcohol (to be issued as MSC Circular) and is currently developing detailed fuel cells and LPG requirements; yet it has no development plan for ammonia.
- IGC Code 16.9 does not allow the use of cargo identified as a toxic product.

## 7.2 IGC Code Requirements Applicable Due to Ammonia Properties

Although the entire IGC Code must be applied, the following requirements are specifically applied because of the anhydrous ammonia cargo's characteristics And the requirements may be used for the IGF Code revision.

### 7.3 IGF Code Requirements

- The concept of requirements in the IGF Code can be checked for the purpose of requirements applied to all gas and low flash point fuel and the ships' functional requirements. Functional requirement refers to the minimum functions required by ships from the safety, environmental, and performance aspects. They are the basis of the ship design safety concept. The detailed requirements for ammonia must be developed to meet the minimum functional requirements in consideration of the ammonia characteristics.
- The purpose and functional requirements of the IGF Code are described as follows:

<sup>&</sup>lt;sup>5</sup>LPG can be gas or liquid state depending on the engine since it becomes a liquid state if pressurized at room temperature.

| 1. To ensure the performance and safety reliability of the main and auxiliary engines 2. To minimize the risk of fuel hazards through ventilation, detection, and other safety measures 3. To prevent power loss with safety measures 4. To minimize the impact of danger zone on safety 5. To minimize equipment installation in the danger zone and install only approved, safe equipment 6. To prevent the unintended accumulation of gas 7. To prevent external damage to equipment 8. To minimize flame source in danger zones 9. To prevent ventilation from the fuel tank to the atmosphere and leakage from the fuel containment, supply, and receiving units 10. To design, manufacture, and install the pipe system, containment, and relief vale appropriately 11. To ensure safe and reliable operation of the engine and parts | Purpose       | It specifies the safe and eco-friendly design, building, and operation of ships equipped with propulsion engines and other engine parts using low flash point fuel.   |
|---|---------------|---|
| ments 11. To clistic safe and reliable operation of the eligine and parts 12. To secure redundancy to prepare for fire or explosion 13. To install the control, alarm, monitoring, and blocking systems for safe operation 14. To install the fixed gas detection system in the area vulnerable to gas leakage 15. To install the fire detection, fire extinguishing, and firefighting systems 16. To test operate and maintain/repair for the safety, availability, and reliability of the fuel systems 17. To generate the technical documents to confirm that the systems and components comply with the rules and standards 18. To take measures to ensure that a single failure does not deteriorate the safety and reliability of the system  | al<br>Require | <ol> <li>To minimize the risk of fuel hazards through ventilation, detection, and other safety measures</li> <li>To prevent power loss with safety measures</li> <li>To minimize the impact of danger zone on safety</li> <li>To minimize equipment installation in the danger zone and install only approved, safe equipment</li> <li>To prevent the unintended accumulation of gas</li> <li>To prevent external damage to equipment</li> <li>To minimize flame source in danger zones</li> <li>To prevent ventilation from the fuel tank to the atmosphere and leakage from the fuel containment, supply, and receiving units</li> <li>To design, manufacture, and install the pipe system, containment, and relief vale appropriately</li> <li>To ensure safe and reliable operation of the engine and parts</li> <li>To secure redundancy to prepare for fire or explosion</li> <li>To install the control, alarm, monitoring, and blocking systems for safe operation</li> <li>To install the fixed gas detection system in the area vulnerable to gas leakage</li> <li>To install the fire detection, fire extinguishing, and firefighting systems</li> <li>To test operate and maintain/repair for the safety, availability, and reliability of the fuel systems</li> <li>To generate the technical documents to confirm that the systems and components comply with the rules and standards</li> <li>To take measures to ensure that a single failure does not deteriorate the safety and reliability of the</li> </ol> |

- The detailed requirements for the LNG fuel to meet the above functional requirements can be summarized as follows:
  - 1. "10. Power Generation including propulsion and other gas consumers" of IGF Code specifies the detailed requirements related to ensuring the performance and safety reliability of the main and auxiliary engines. It specifies the requirements of the internal combustion engines, boilers, and gas turbines for each engine type.
    - \* The requirements related to the internal combustion engine include (1) the safety system to prevent explosion due to unburned gas in the exhaust gas (explosion relief devices), (2) the safety device against explosions caused by unintended gas leakage in the engine (explosion relief system), (3) monitoring of ignition failure or incomplete combustion and shutting off the gas supply, and (4) monitoring of gas leakage in the engine (gas detection system).
    - \* The requirements related to the boiler include (1) preventing fuel gas accumulation in the combustion chamber and flue, (2) shutting off the gas supply in case of abnormal ignition, and (3) purging unburned gas in the boiler

combustion chamber and gas supply pipe.

- \* The requirements related to the gas turbine include (1) the safety system against explosion caused by unburned gas in the exhaust gas (explosion relief system), (2) installation of the gas turbine in a separate airtight area according to the emergency shutdown principle, (3) redundant ventilation requirement (2 units with 100 % capacity), (4) monitoring of incomplete combustion (gas detection system) and shutting off the gas supply, and (5) monitoring of exhaust temperature and automatic shutdown system at the time of high temperature.
- 2. The detailed requirements related to "minimize the risk of fuel hazards through ventilation, detection, and other safety measures" are the ventilation and gas detection requirements of potential gas leaking areas. The requirements address the areas requiring ventilation, ventilation capacity, arrangement of the ventilation inlet and outlet, and installation of the airlocks. The detailed requirements are described as follows:
  - \* The process from supplying fuel to the engine is <manifold  $\rightarrow$  fuel tank  $\rightarrow$ connection of the fuel tank with the valves and fuel supply pipes (tank connection area) → fuel supply equipment such as the compressor and heat exchanger (fuel preparation room)  $\rightarrow$  gas valve unit  $\rightarrow$  engine>.
  - \* The parts with a high possibility of gas leakage include bunkering manifolds, flange connections between equipment, tanks and pipes, valves, tanks (excluding the independent tank type C since they are manufactured for no leakage), gas engines (excluding the engines manufactured with the concept of gas safety engine zone (double pipes)), damaged parts of fuel pipes (enclosing of the outer wall of the fuel pipe with pipe or duct in consideration of damage when the fuel pipe passes through an enclosed zone).
  - \* Therefore, a gas detection system and an exhaust type forced ventilation system must be installed to prevent the accumulation of leaked gas in the areas with a high possibility of leakage.
  - \* The areas with a high possibility of leakage include the tank connection area, the area with the gas fuel engine protected by the emergency shutdown, the fuel preparation room, and the double pipes and ducts that enclose the fuel supply location and the fuel pipe. Each area is required to install an exhaust ventilation system with a ventilation capacity of 30 times per hour (two minutes per ventilation based on a simple calculation using the capacity). The following safety

measures are required for leakage:

- \* Leakage behavior and safety measures in the fuel preparation room for LNG
  - ① Assuming that the liquefied gas is leaked through the fuel pipe, the liquid gas (-160 °C) is rapidly vaporized as it flows down to the floor.
  - ② Since LNG is heavier than air from the initial stage of vaporization to -100 °C, it settles to the floor and condenses the steam in the air to form a steam cloud that is visible to the naked eyes.
  - 3 As the temperature gradually increases, the volume ratio of gas to liquid expands 600 times, and the gas is dispersed as it rises upward. The concentration of the gas decreases, reaching 5 % to 15 % of the flammable atmosphere.
  - 4 Since the exhaust ventilation system is continuously operated in the fuel preparation room, the leaked gas is discharged to the open deck through the exhaust duct. Although the IGF Code does not specify the detailed requirements for ventilation arrangements, considering the fact that LNG accumulates at the top of the area as gas is dispersed, the inlet of the duct is placed at the top of the area.
  - ⑤ An alarm is activated at 20 % of lower explosive limit (LEL) when the gas detector detects a gas leak, and the tank valve is automatically shut off at 40 % of the LEL, stopping the fuel supply.
  - 6 While the IGF Code specifies the gas detector to be located in a place where gas can accumulate and at the ventilation outlet side, it also specifies the physical smoke test or gas dispersion analysis to find the best arrangement. Considering that LNG gas accumulates at the top of the area as it disperses, the detectors are installed at the top of the area and on the duct's inlet side.
- 3. A detailed requirement related to "prevent power loss with safety measures" is the fuel supply system's redundancy.
  - \* The propulsion engine and power generation engine in the engine area protected by the emergency shutdown are required to be installed separately in two zones, and the power is not lost even if the fuel supply to either zone is cut off.
  - \* The fuel supply system requires complete redundancy across the entire system from the tank to the engine. (The independent tank type C allows one tank but requires only the tank connection area to be separated.)
- 4. The detailed requirements related to "minimize the impact of danger zone on safety" specify the following requirements for the danger zone:
  - \* It defines the range of the danger zone and restricts the installation of electrical equipment in the danger zone.

- \* It specifies the minimum distance requirement between the ventilation opening in the danger zone and the opening in the non-danger zone to prevent the inflow of gas from the danger zone.
- \* Access between the danger and non-danger zones is regulated to be allowed through the airlock.
- \* It requires the installation of gas detection and exhaust enforced ventilation systems in the danger zone.
- \* It requires the safety functions, such as the alarm and shutting off the gas supply system when gas leakage in a danger zone is detected.
- 5. For the detailed requirement related to "minimize equipment installation in the danger zone and install only approved, safe equipment," IGF Code 14. Electrical installation requires compliance with IEC 60092-502 for the electrical equipment installed in a danger zone.
- 6. The detailed requirement related to "prevent the unintended accumulation of gas" specifies the requirements for leakage prevention, ventilation, gas detection, gasexposed unit arrangement, and opening of the non-danger zones.
  - \* The engine area's arrangement concept specifies the concept of arranging two types (gas safety engine area and engine area protected with the emergency shutdown system).
  - \* It specifies the fuel pipe area enclosed by double pipes to allow penetration of the fuel pipe.
  - \* It specifies the requirements for ventilation and gas detection mentioned in Requirement 2 above.
  - \* It specifies the structure and height requirement of the ventilation mast.
  - \* It specifies the minimum distance between the gas-leaked part and the opening in the non-danger zone.
- 7. The detailed requirement related to "prevent equipment from external damage" includes protecting the tank and the fuel pipe.
  - \* It specifies the fuel tank's minimum distance from the side and bottom of the ship to prevent damage to the fuel tank when the ship collides.
  - \* It specifies the fuel installed on open decks and ro-ro spaces to be protected with protective covers.

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- 8. The detailed requirement related to "minimize flame source in danger zones" is related to Requirement 5 above and restricts the use of mobile devices such as mobile phones, flashlights, and cameras that can be the ignition source in danger zones.
- 9. The detailed requirements related to "prevent ventilation from the fuel tank to the atmosphere and leakage from the fuel containment, supply, and receiving units" include the tank/pressure control inside the tank, secondary barrier, purging of the fuel and bunkering systems, and tank connecting area.
  - \* PRV is installed in the tank to prevent the fuel tank pressure from exceeding the design pressure due to the vaporization of the liquefied fuel during bunkering or navigation. The gas inside the tank is discharged into the atmosphere when the tank pressure reaches the PRV set pressure. IGF Code 6.9.1 prohibits the fuel gas emission to the atmosphere except in emergencies and requires the means to control the pressure and temperature inside the tank to prevent the PRV opening (re-liquefaction, combustion, pressure accumulation, or cooling).
  - \* The fuel containment facility must be equipped with a secondary barrier to prevent leakage from the fuel containment, supply, and receipt systems (except for independent tank type C).
  - \* The fuel pipes must be welded, and the fuel pipe passing through the enclosed area must be enclosed with a double pipe or duct.
  - \* Tank connections with a high probability of leakage must be enclosed in a separate space (tank connection zone) unless installed on an open deck.
- 10. The detailed requirement related to "design, manufacture, and install the pipe system, containment, and relief vale appropriately" includes the tank and pipe material selection and test, thickness calculation, stress analysis, prevention of excessive stress caused by heat expansion, and capacity and layout of relief valves.
- 11. The detailed requirement related to "ensure safe and reliable operation of the engine and parts" specifies the tank and system design requirement.
  - \* It specifies the requirements for the fuel tank's secondary barrier design load and structural analysis.
  - \* It specifies the requirements for the pipe design condition, thickness, assembly, and joint method.

- \* It specifies the requirements for the redundancy of fuel supply and the outer pipe design of the fuel supply pipe.
- \* It specifies the requirements for the gas leakage, incomplete combustion, and explosion prevention of the internal combustion engine, boiler and gas turbines.
- 12. The detailed requirement related to "secure redundancy to prepare for fire or explosion" includes the boundary between the fuel tank areas and the redundancy and boundary requirement of the engine area protected by the emergency shutdown system.
  - \* Two fuel tanks must be installed in an area separated by the A-60 class heat sink or cofferdam.
  - \* Two engines must be installed in the separated zones protected by the emergency shutdown system.
  - \* The Class A engine area and the high-risk fire area must be separated by the Class A-60 heat sink and cofferdams.
- 13. The detailed requirement related to "install the control, alarm, monitoring, and blocking systems for safe operation" specifies the safety system's operation for the fuel tank, fuel supply, gas/fire detection, and abnormal status.
  - \* It requires the installation of the system to prevent fuel tank flooding and the pressure monitoring system.
  - \* It specifies the alarm requirements for abnormal conditions during bunkering.
  - \* It specifies the requirements for the location of the gas detector installation and the detected concentration.
  - \* It specifies the requirements for the safety system that must be operated in abnormal conditions.
- 14. The detailed requirement related to "install the fixed gas detection system in the area vulnerable to gas leakage" is related to Requirements 2 and 4 above. It specifies the zones, quantity, and installation location of the fixed gas detection system.
- 15. The detailed requirement related to "install the fire detection, fire extinguishing, and firefighting systems" specifies the fire detectors' installation location, the firefighting structure, and the fire extinguishing system installation.
  - \* It specifies the heat dissipation structure requirement between the fuel

preparation room, the fuel storage area, the Class A engine area, and the high fire risk area.

- \* It specifies the requirements for a water spray system for tank cooling, a fire extinguishing system with dry chemical powder, and a fire detection system.
- 16. The detailed requirement related to "test operate and maintain/repair for the safety, availability, and reliability of the fuel systems" specifies the test and inspection of the safety system operation related to functions required by the fuel system.
- 17. Although the detailed requirement related to "generate the technical documents to confirm that the systems and components comply with the rules and standards" is not an IGF Code requirement, it is the KR requirement that specifies the drawing and data submittal.
- 18. The detailed requirement related to "take measures to ensure that a single failure does not deteriorate the safety and reliability of the system" specifies redundancy of the fuel supply and gas detection systems.
  - \* In a single fuel system, the fuel supply system must be arranged so that complete redundancy and separation are provided throughout all systems from the fuel tank to the fuel consumption system.
  - \* Double gas detection systems must be installed in the engine area protected by the emergency shutdown system, the area between the double pipes, the tank connection area, and the fuel preparation room.
  - \* Two engines must be installed in the separated zones protected by the emergency shutdown system.

## 7.3.2 Tentative Guidelines on Methyl/Ethyl Alcohol Fuel Ship

- The safety regulation added to the LNG detailed requirements in consideration of the methyl/ethyl alcohol fuel characteristics is described based on MSC.1/Circ.1621 Interim Guidelines for the Safety of ships Using Methyl/Ethyl Alcohol as Fuel.
  - 1. The detailed requirements related to the "fuel tank" are provided in "5. Ship design and arrangement" and "6. Fuel containment system." Since methyl/ethyl alcohol, unlike cryogenic LNG, exists in a stable liquid state at room temperature, the regulation for it is simpler than that for LNG.

- 2. The detailed requirements related to the "material and pipe design" are provided in "7. Material and general pipe design." Like the fuel tank, it does not consider the cryogenic temperatures and only considers the corrosion due to fuel.
- 3. The detailed requirements related to "bunkering" are provided in "8. Bunkering" and specify the following in consideration of the fuel characteristics.
  - \* They include emergency showers and eyewash stations to be installed near areas that can come into contact with fuel.
  - \* The ship's fuel hoses must be stored on an open deck or in a storage room with an independent mechanical exhaust ventilation system and ventilated at least six times per hour.
  - \* Means should be provided to drain the liquid from the bunkering piping after the completion of the bunkering.
- 4. The detailed requirements related to fire extinguishing are provided in "11. Fire safety" and require installing an alcohol-resistant fire extinguishing system at the fuel tank bottom, in the bunkering station, etc.

# 7.3.3 Detailed Requirements Requiring Correction and Supplementation for Ammonia **Application**

- As mentioned above, the detailed regulations of the IGF Code are based on LNG, but ammonia is considered to be more similar to methyl/ethyl alcohol than LNG in terms of toxicity and corrosiveness.
  - The most concerning factor among the ammonia's properties about human safety is toxicity. For the ammonia's toxicity, the requirements for personnel protection should be carefully reviewed with reference to the IGC Code and methyl alcohol fuel requirements.
  - Ammonia is corrosive. Ammonia vapor in contact with moisture can corrode copper, zinc and its alloys, as well as rubber and plastics. Moreover, heavy metals such as silver, gold, mercury, and thallium must be handled with care since they can form explosive compounds. The industry recommends 6 % or higher in consideration of corrosion when using nickel steel.
  - Since ammonia's autoignition temperature is very high at 651 °C and the lower flammable limit (LFL) in the air is significantly high at 15 %–28 %, there is a high risk of incomplete combustion. It means that the possibility of the ammonia slip is

high, and it is considered that there may be unintended emissions. Ammonia must be handled with special care since, if it is discharged as it is, it is corrosive when it encounters moisture in the sea or generates ultrafine dust by reacting with NOx.

- Ammonia is toxic and has a strong odor, so it is not free from complaints in the local community. Therefore, this should be considered when bunkering.
- When considering the aforementioned ammonia characteristics, the following detailed requirements do not apply directly to ammonia fuel unless additional requirements are applied.
- IGF Code requirements related to toxicity
  - 5.4.1 Layout of Engine Area
    - The layout concept of the engine area is the "gas safety engine area" and "engine area protected by emergency shut off." The "engine area protected by emergency shut off" is premised that the leaked gas must be effectively discharged when gas is leaked in the engine area. Although ammonia vapor is not heavy and is not difficult to ventilate, the leaked gas severely affects the human body. Therefore, it is necessary to exclude the "engine area protected by emergency shut off" in an engine area's layout concept.
- IGF Code requirements related to corrosion
  - 6.7.2 Ventilation Pipe of Fuel Tank's Pressure Relief Valve
    - Ammonia released from the fuel tank's pressure relief valve is discharged to the vent mast through the ventilation pipe. Since LNG gas is lighter than air, it is discharged into the atmosphere through the vent mast even without pressurization. Although ammonia can be discharged into the atmosphere in a dry state, it can get heavier when it reacts with moisture and settle down offshore; it can cause corrosion on the ship. Moreover, exposed ammonia can be a catalyst to generate ultrafine dust. Therefore, it is necessary to provide countermeasures to it.
- IGF Code requirements related to odor and toxicity
  - 8. Bunkering
    - Although the bunkering manifold is highly vulnerable to gas leakage, its requirement does not address matters related to gas leakage detection. In the case of LNG, the gas detector is less effective because the leaked liquefied gas vaporizes and diffuses to the upper section, and the leaked LNG condenses surrounding air and forms a vapor cloud that can be confirmed with the naked eyes. Although it is easy to identify ammonia leakage because of its peculiar smell, it may cause civil complaints even at

- a concentration that does not affect the human body if it is leaked from a port. Therefore, a regulation on emission is required even for bunkering. It is necessary to block ammonia emissions above a certain concentration that harms the human body.
- Ammonia has similar properties to LPG. The LPG transport system in an on-land LPG base uses a loading arm and has the gas detection and emergency shutdown systems for gas leakage. However, no emergency separation system<sup>6</sup> is installed. Therefore, while the requirements should cite the LPG transfer system requirements, installing an emergency separation system should be considered to protect the transfer system and manifold from excessive loads and prevent ammonia leakage.
- The risk of gas fuel is maximized in bunkering operations. Therefore, the requirements should consider the safety system for bunkering facilities and training on crew member safety during ammonia bunkering work.
- Since LNG is cryogenic, ammonia bunkering is likely to be less risky than LNG bunkering. Therefore, the requirements currently applied to LNG can be applied to ammonia, provided that those not applicable to ammonia (rollover, cryogenic requirements, etc.) are excluded, and those specifically needed for ammonia (safety measures for people in case of ammonia leakage) are added.

### 13. Ventilation

- Measures to vent ammonia include either diluting the concentration of ammonia to less than 10 ppm, collecting the ammonia, or extending the vent mast to a safe height. If an unpleasant odor is generated from the flue due to the ammonia combustion, the exhaust gas should be heated to increase the exhaust gas buoyancy.
- IGF Code requirements related to fuel storage temperature
  - 6.4 Storage of Liquefied Gas Fuel
    - The design temperature of the LNG fuel storage tank must be lower than -83 °C since the critical temperature of LNG is -83 °C. Therefore, the IGF Code only considers the cryogenic fuel temperature in the fuel tank (-55 °C or less).
    - Ammonia has a fuel temperature of -33 °C in atmospheric pressure and room temperature when a pressure tank is used. Therefore, extending the ammonia fuel tank's design temperature to higher than the temperature range specified in the IGF Code is necessary.

<sup>&</sup>lt;sup>6</sup>It is a device that safely separates the transfer system from the ship so that the load applied to the transfer system and manifold does not exceed the design load due to the ship's excessive motion. An emergency separation system is installed in the LNG transfer device.

- Applicable IGC Code requirements: 14. Protection of the human body

## 14.2. Protective gears

• Protective gears including eye protection in consideration of the characteristics of the transported cargo must be available to protect crew members engaged in cargo work.

## 14.3 Emergency equipment

- Stretchers must be stored in an accessible location to rescue the injured.
- Oxygen resuscitation device, etc.

# 14.4 Safety gear

- Three or more sets of safety gear in addition to the firefighter's equipment should be stored.
- 14.5 Personnel protection regulations for individual cargoes
  - Respiratory protection and safety glasses suitable for emergency escape should be available for all crew members.
  - Installation of decontamination shower and eye washer

- Applicable IGC Code requirements: 17.13 Ammonia
  - 1. Anhydrous ammonia can cause stress corrosion fracture in containers or manufacturing equipment made of carbon-manganese steel or nickel steel. It is necessary to follow the following countermeasures to minimize the risk of fractures.
  - 2. Cargo tanks, manufacturing pressure vessels, and cargo piping systems using carbon-manganese steel must be made of fine-grained steel with a minimum yield stress of 355 N mm or less and actual yield stress of 440 N mm or less. It must conform to one of the following structural or operational measures.
    - (1) It must use low-strength materials with a minimum tensile strength of 410 N mm or less.
    - (2) The cargo tank must be heat-treated to remove stress after welding.
    - (3) The temperature during transportation must be close to the product's boiling point of -33 °C, and in no case must exceed -20 °C.
    - (4) Ammonia must contain a moisture content of 0.1 % or more by mass, and the captain must have documents confirming it available.

- 3. If using carbon-manganese steel having higher yield stress than that used in Paragraph 2, the finished cargo tanks and pipe system must be heattreated to remove stress after welding.
- 4. If the process pressure vessel and pipe system in the condensation unit of the refrigeration system use the material specified in Paragraph 1, it must be heat-treated to remove stress after welding.
- 5. The welding rod's tensile and yield properties are the smallest actual values which must be greater than those of the tank or piping materials.
- 6. Nickel steel with a nickel content of more than 5 % and carbonmanganese steel that does not meet the requirements of Paragraphs 2 and 3 can easily cause ammonia stress corrosion fracture, thus must not be used as a container or pipe system for this product.
- 7. Nickel steel with a nickel content exceeding 5 % may be used, provided that the conveying temperature meets the specification of Subparagraph (3) of Paragraph 2.
- 8. It is recommended to maintain dissolved oxygen content of less than 2.5 ppm by mass to minimize the risk of ammonia stress corrosion fracture. The best method for it is to reduce the average O<sub>2</sub> composition to less than the value specified as a function of the transport temperature in the following table before putting the ammonia liquid into the tank.

| T (°C)        | O <sub>2</sub> (%, v/v) |
|---------------|-------------------------|
| -30 and below | 0.90                    |
| -20<br>-10    | 0.50<br>0.28            |
| 0             | 0.16                    |
| 10            | 0.10                    |
| 20            | 0.05                    |
| 30            | 0.03                    |

Oxygen percentages for intermediate temperatures may be obtained by direct interpolation.

## 7.3.4 Application of Risk Assessment of Ammonia Fuel

- The detailed requirements of the IGF Code specify only for LNG and methyl/ethyl alcohol. For other fuels, it specifies fulfilling the purpose and functional requirements of the IGF Code, securing the same safety level.
- The method for verifying the fulfillment of functional requirements and ensuring the same safety level is a risk assessment and risk-based approval. Therefore, it is necessary to identify all risk factors of ammonia fuel, perform a risk assessment, and prepare the risk-based approval. In this case, the approval criteria may differ since the risk assessment scope is wide, and the assessment results may be different for each project. Therefore, this study's final goal is to reduce the number of items required for risk assessment by creating reliable and consistent, detailed criteria.
- In the case of LNG fuel, the following items require a risk assessment:
- 5.10.5 Drip tray (Determining the drip tray capacity)
- 5.12.3 Airlock (Confirming that gas is not discharged into the gas safety areas even during the accident in the gas danger zone)
- 6.4.15.4.7 Accident design criteria (Determining the accident scenario according to the risk assessment)
- 8.3.1.1 Bunkering area (Risk assessment and enforced ventilation in case of enclosure or semi-enclosure)
- 13.4.1 Tank connecting area (Change of the ventilation capacity according to other explosion preventive measures)
- 15.8.1.10 Additional gas detection systems (Installation of the gas detector in the ventilation inlet of the accommodation area and engine room, if necessary)
- Attachment 4.4 Reduction of accident result classifications
- Attachment 6.8 Determination of additional accident scenarios
- For methyl/ethyl alcohol fuels, toxicity and corrosiveness must be considered in addition to LNG requirements.

- O Considering the ammonia characteristics, we suggest the following requirements of the risk assessment.
- Applying IGF Code 4.2 for ammonia fuel should include at least the following in the risk assessment scope:
  - \* The risk assessment of using ammonia fuel should be performed to identify possible hazards to the hull, ship equipment, and crew in consideration of the surface characteristics.
  - \* In relation to gas leakage, risk assessment of the following areas should be performed to ensure safety equivalent to that of LNG fuel against gas leakage. Ventilation and gas dispersion analyses may be required, depending on the result of the risk assessment.
    - Tank connection area, fuel preparation room, bunkering area, around vent mast, space between double pipes, gas valve unit enclosed area, and tank storage area (except for independent tank type C)

## 7.3.5 Crew Education

- The IGF Code (Part D 19) requires education on the STCW Convention and Code.
- o IMO Res. Requirements for the training and qualifications of captains, officers, and crew engaged in ships subject to the IGF Code were added to the STCW Convention (Regulation V/3) and the STCW Code (Section AV/3) in accordance with IMO Res. MSC.397(95).
- The requirements of STCW Convention's Regulation V/3 and STCW Code's Sections A-V/3 apply to all low flash point fuels subject to the IGF Code.
- O STCW Code's Section A-V/3 classifies the education level into basic training and advanced training. The crew responsible for safety missions must receive basic training, and the captain, marine engineer, and fuel handlers must receive advanced training. Moreover, all crew members aboard ships subject to the IGF Code must be trained to familiarize themselves with ships and equipment.
- IGF Code's "18. Operation" specifies the role of the person in charge of LNG bunkering work, safety system inspection, devices, inspection items before work, communication with the bunkering supplier, and actions taken during bunkering.

# **8** Conclusion

## 8.1 Ammonia Use and Related Regulatory Status

- Ammonia has been used as fertilizer, industrial raw material, refrigerant, etc. Since it is being transported via ships, regulations addressing the danger of ammonia have been prepared. However, there are risk factors with unproven safety for ammonia fuel, and this study has confirmed that regulations considering the structure and arrangement environment of the ship are necessary.
- It has been confirmed that it is not appropriate to apply the detailed requirements of the current IGC Code and IGF Code because ammonia as a marine fuel has risk factors different from conventional low flash point fuels, such as LNG or methyl/ethyl alcohol.

# 8.2 Revision of Rules for Application to Ammonia-Fueled Ships

- O It is clear that ammonia as a ship fuel presents additional risks when compared to conventional liquid fuels such as LNG, LPG, and methyl/ethyl alcohol. However, it is possible to lower these risks with additional safety measures considering the properties of ammonia. It is thus necessary to develop alternative and additional requirements to the existing IGC Code using Chapter 7.
- When applying the requirements to IGF Code developed using Chapter 7, it is necessary to perform a risk assessment of ammonia affected by the diversity of the ship structure, layout, and system to ensure safety.
- Since the IGC Code generally has safety regulations for ammonia, it is necessary to consider existing safety measures and identify the dangers in use as fuel to develop alternative or additional requirements for Chapter 16 of the IGC Code.

# Report on Ammonia-Fueled Ships

Published by

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