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Managing the Hazards of Ammonia in Seaports as a Potential Alternative Fuel for Green Shipping

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The article discusses the importance of safety management systems for seaports, especially in the context of the use of ammonia as a potential alternative fuel for the shipping industry. The article highlights the need for constant monitoring to detect non-conformities and reduce accidents, emphasizing the hazards of simultaneous operations (SIMOPs) and the lack of knowledge on the safety, security, and environmental risks associated with ammonia storage and loading in port operations. The paper focuses on the safety management system of the Port of Sillamäe in Estonia, which has the largest ammonia storage in Europe and three berths for ammonia loading to ships. The study suggests that only refrigerated ammonia should be used for bunkering ships to minimize accident risks. No major accidents or severe injuries have been reported among personnel handling ammonia since the beginning of operations at the port. The article also discusses the production of green ammonia from renewable energy sources to decarbonize ammonia production, while noting the need for high safety standards in its use as a hazardous chemical.

Keywords: safety management system, health and safety, major hazards, ammonia, decarbonization, maritime safety.

1. Introduction

Seaports (Ports) perform a central role in connecting maritime and land transport throughout the world. Along with the development of technology and industries, ports have also evolved into very complex systems that can simultaneously handle different types of cargo (e.g., containers, dry bulk cargo, liquid bulk cargo, general cargo, and roro cargo), which can also include very dangerous ones. The impact of their loading, storage, and unloading operations extends not only to the port area itself but also to the local community, which is usually located nearby. For this reason, the proper management system for safety, security, and environmental protection at ports is highly critical and requires constant monitoring so that non-conformities can be detected, and immediate corrective action taken. This responsible approach helps to reduce unreliability and, more importantly, reduce the number of accidents that pose a threat to persons, the environment, and port property. In addition, accidents and spills of chemically hazardous cargoes can seriously disrupt the operations of ports and, as a result, increase their operating costs.

The impact of shipping on the environment has also increased significantly in recent decades, and several actions based on the principles of sustainable development have been taken to reduce it. According to the International Maritime Organization (IMO), greenhouse gas (GHG) emissions must be reduced by 50% by the year 2050 compared with 2008 to ensure the implementation of the Paris Agreement on climate protection. This goal can be achieved by decarbonizing maritime shipping, which is why ship operators are looking for alternative „greener" fuels. A prospective candidate for this green fuel that meets the IMO goals is ammonia, which is sometimes called a future carbon-free oil (DNV, 2019). In order to meet the decarbonization goal, the maritime industry started to be prepared for using ammonia as a fuel (Fan et al., 2021).

Ammonia shows good handling, storage, and transportation advantages, and provides long sea passages without significant loss of cargo space at a reasonable price. Switching to ammonia as an alternative marine fuel represents an additional future option, but successful implementation of ammonia bunkering technology highly depends on the safety and efficiency of operations, which means the availability of trained personnel, working safety management systems, emergence preparedness for ammonia incidents, collective and personal protective equipment.

Traditionally, shipping has been considered a relatively hazardous industry, as marine crews are often subjected to prolonged hard labour, isolation, rigid organizational structures, high levels of mental stress, and physical fatigue, which can lead to accidents, injury, and hazardous chemical incidents. To meet tight sailing schedules and optimize costs, it is normal practice that loading and related operations (such as staff moving, other cargo loading/unloading, crew transfer, crane lifting operations, port operations, and oil bunkering) must be performed simultaneously, which is called simultaneous operations (SIMOPs). Over the past few years, several reviews and theoretical analyses have been published on the use of ammonia for shipping and energy production, especially for marine engines.

Aneziris et al. (2020) conducted systematic literature review on LNG at ports and identified several scientific gaps, emphasising the need to study and investigate safety and hazard zones in case of various LNG bunkering modes and storage capacities. McFarlane et al. (2020) also published a detailed roadmap for the ammonia economy. In these reviews and articles, the authors most often described technical problems, inventory routing problems, economic barriers, or regulations for future fuels to be used in the maritime industry (Gerlitz et al., 2022; Prause et al., 2022; Ayvalı et al., 2021). Reinhold et al. (2019) reviewed the occupational safety and health risks of green shipping for seafarers. A search of the literature revealed a lack of knowledge on the safety, security, and environmental risks associated with ammonia storage and loading (transfer) in port operations, which could be used to analyse future ammonia bunkering operations. In this light, the main objective of this paper is to highlight the management of ammonia hazards in seaports and to respond to the following question: Which are the main aspects of a safety management system and practice for ammonia storage and transfer?

The paper is structured as follows: Section 2 provides a literature review on ammonia as a alternative marine fuel; methods for ammonia transporting, storing, and transferring at the port; and aspects of major accident prevention policy and safety management systems. Section 3 describes the methodology used, Section 4 presents the results of the study and their discussion; and finally (Section 5) some conclusions.

2. Literature review

2.1.*Ammonia as an Alternative Marine Fuel*

Alternative or green fuels should lead to global reductions in GHG emissions. One of the strongest alternative fuel candidates is ammonia, which is an excellent carrier of hydrogen (17.6 wt%) and as cargo is also transported by the maritime sector. Ammonia (NH_3) is a colorless gas composed of nitrogen and hydrogen with a bitter-burning taste that liquefies at -33.3°C and freezes into white crystals at -77.7°C. This is one of the most widely produced inorganic chemicals, in 2019 about 240 million tons of NH_3 were produced, and by 2030 production is projected to increase to 300 million tons (Machaj et al., 2022). The main consumer of NH_3 is the production of fertilizers for agriculture (80%), as well as for the production of plastics, paints, pharmaceuticals, and explosives. The current production of NH_3 usually takes place by the Haber-Bosch process, which is based on the consumption of natural gas (methane CH_4) for the synthesis of NH_3 from nitrogen and hydrogen, which releases large amounts of GHG. In this case, NH_3 produced from methane (classified as brown ammonia) cannot be considered environmentally friendly (Prause et al., 2022). Therefore, the main efforts in NH_3 decarbonization are focused on the production of green ammonia from renewable energy sources (solar and wind power), usually by using electrolysis (see Fig. 1).

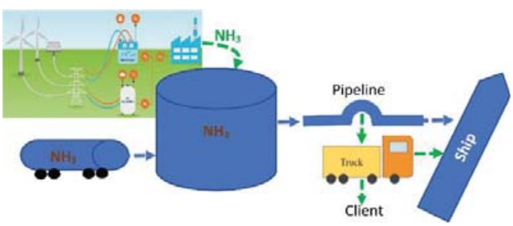

Fig. 1. Ammonia transporting, storing, and loading process at the Port of Sillamäe, Estonia. In green lines – planning green ammonia production and ammonia bunkering by truck-to-ship (TTS) (modified Olabi et al., 2023).

There are additional benefits of using NH_3 as alternative marine fuel: ammonia has a comparable energy density (22.5 MJ/kg) with some fuels containing carbon such as methanol (22.7 MJ/kg), ethanol (29.7 MJ/kg), brown coal (15 MJ/kg), anthracite (27 MJ/kg), but lower than other fuels such as natural gas (55 MJ/kg), diesel (45 MJ/kg) and hydrogen (142 MJ/kg) (Al-Aboosi et al., 2021). Easily liquefies when compressed to 0.8 MPa at 20°C or when cooled to 33°C at atmospheric pressure. It has a narrow flammability range so it can be stored safely. Due to ammonia's high-octane rating (120 compared to gasoline from 86 to 93), it can be used in internal combustion engines after minor modifications (Al-Aboosi et al., 2021). A well-established and reliable ammonia production, storage, and distribution infrastructure already exists. At the moment, more and more information is being received about the launch of new ammonia projects aimed at the production, transhipment, and use of blue and green ammonia.

However, NH_3 also has its drawbacks and hazards, namely its high toxicity to humans and marine organisms. Although ammonia can harm the aquatic environment, this is not a significant obstacle to its use as a fuel for several reasons: when liquid ammonia spills into the water, most of the ammonia evaporates, and the part that dissolves in the seawater will eventually turn into nutrient fertilizer (Machaj et al., 2022). But the use of such hazardous chemical as NH_3 requires high safety standards, which leads to complex design and construction procedures, as well as handling.

2.2. *Methods for ammonia transporting, storing, and transferring at the port*

Because NH_3 is such a valuable chemical, several methods are used to transport and store it. Compared to other gases (LPG, LNG), ammonia is easily liquefied at -33°C at atmospheric pressure (Appl M. Ammonia, 2012), so it is most conveniently transported by railway, road, sea, or pipeline. The choice of the optimal delivery method depends on the logistics capabilities and the remoteness of the production site from the delivery point. NH_3 is usually stored in the liquid phase from the start of its industrial production. Initially, pressurized vessels with a capacity of up to 2,000 tons were used for storage. Currently, isothermal storage tanks are used to store up to 45,000 tons of NH_3 at production sites and distribution sites (such as ports). Table 1 shows the amount of storage of ammonia in storage facilities that can be stored with small deviations in atmospheric pressure and temperature (Tawalbech et al., 2022). Storing ammonia in isothermal tanks (with a low temperature at -33°C) has two indisputable advantages: firstly, lower capital costs per unit volume, and secondly, storage at a pressure close to the atmospheric pressure is safer than storage in pressurized storage.

The main processes of NH_3 transfer in the port area are shown in Fig. 1 for distribution terminals where ammonia is stored in isothermal tanks. NH_3 is usually delivered to a port where the chemical is unloaded and stored. Then NH_3 is loaded onto a truck (TTS scheme) or directly onto a ship using fixed pipelines that are connected to the ship by a marine loading arm. The truck is used for the delivery of small consignments to customers, as well as for the possible bunkering of the ammonia-powered ships (via TTS). The volume of a ship's lot depends on the volume of the ship's tanks and can reach up to 30,000 m^3 in the shipping conditions of the Baltic Sea region.

Table 1. Pressure and temperature specifications of ammonia storage vessels, and their capacities.

Storage type	Typical pressure (bar)	Design temperature (°C)	Storage Capacity (t)
Pressure storage	16-18	Ambient	<270
Semi-refrigerated storage	3-5	0	450-2,700
Low-temperature storage	1.1-1.2	-33	4,500-45,000

2.3. *Aspects of major accident prevention policy, safety management system, and emergency preparedness*

According to the EU Seveso III Directive, the transport of dangerous substances and directly related intermediate temporary storage (in the case of ammonia 50 t and more) fall under the scope of those regulations and impose strong obligations on the ammonia site to implement a Major Accident Prevention Policy (MAPP), Safety Management System (SMS) and internal emergency response plan. MAPP must be adopted by the terminal senior management and designed to provide a high level of protection for human health and the environment. This policy specifies which major-accident risks to the health and safety of people, property and the environment require adequate preventive measures, which are included in the goals and general principles of the terminal. It must be stated that administration plays a key role in the functioning of SMS and is also responsible for the overall safety performance. It must delegate technical competence to specialists, provide adequate resources (e.g., technical, financial, and human) for the implementation of the MAPP, analyse performance and take measures to evaluate its effectiveness. In addition, prior to performance assessment, the strategic, tactical, and operational safety goals associated with MAPP must be determined, and the actual performance compared with the achievement of the goals must be assessed. MAPP must include top management commitment to continuous improvement of major accident hazard management and provide a high level of protection. Finally, the MAPP must be periodically reviewed by terminal management to verify actual progress toward strategic goals. Given the above, MAPP is a public declaration of top management commitment to the safe handling of chemicals, addressed to the stakeholders (such as employees, the public, and government agencies), usually published in mandatory documents (of SMS) and available on the website (Aneziris et al., 2021).

Following chemical legislation, every five years it is necessary to submit a safety report to the local authority (in the case of Estonia - Consumer Protection and Technical Regulatory Authority), which must contain a description of the implemented safety management system (SMS). The SMS is based on a continuous improvement cycle and must include 7 mandatory elements: 1. *organization and personnel* - this includes the distribution of the roles and responsibilities of personnel, involvement in ensuring the safety of employees and contractors, as well as activities to raise their awareness, safety communication; 2. *identification and evaluation of major hazards* - this includes procedures and tools for the systematic identification of major accident hazards under all possible modes of operation; 3. *operational control* - this includes procedures for operations and maintenance, as well as best practices for monitoring and managing operations; 4. *management of change* - this includes procedures for planning modifications and designing new installations, processes, or storage capacities; 5. *planning for emergencies* - this includes procedures for identifying emergencies, as well as testing and reviewing internal emergency response plans and conducting training of personnel under these plans; 6. *monitoring performance* - this includes procedures for assessing compliance with the established goals of MAPP and SMS, corrective actions, reporting of accidents and near misses, and their investigation and prevention measures; 7. *audit and review* - this includes procedures for periodic and systematic auditing of MAPP and SMS performance, as well as a documented review of the performance of MAPP and SMS by senior management (Aneziris et al., 2021).

3. Material and methods

The focus of this research is the Port of Sillamäe (Port) located in Estonia, which is unique by having the biggest ammonia storage in Europe (4 x 30 000 mt), three berths available for ammonia loading to ships, and development prospects for possible green ammonia production from renewable energy sources. The study uses both qualitative and quantitative approaches. We conducted semi-structured expert interviews with five experts in the field of safety, ammonia operations, and preparedness for accidents: head of ammonia terminal (Int. 1), head of operations (Int. 2), chief technologist (Int. 3), safety manager (Int. 4) and shift leader (Int. 5). All interviewed experts have worked with ammonia for at least 10 years. The purpose of these interviews was to obtain detailed information about the health and safety of terminal operators when working with ammonia, to identify potential hazards when transferring ammonia from a TTS scheme, and to understand the preparation context for emergency response. The interview questions were designed to explore safety management system shortages in ammonia operations, as well as to understand the following topics: 1. possible causes of accidents when transferring ammonia to a ship; 2. possible best practices in a safety management system and emergency preparedness to major accidents. The interviews were conducted by experienced university researchers. Interviews lasted about 60 minutes on average and were conducted in February and March 2023.

To assess the awareness about ammonia hazards by employees, the questionnaires were disseminated among workers. The questions included topics such as the knowledge of toxicity and health risks of ammonia, experienced health problems from ammonia exposure, possible incident and accidents nature with ammonia, health and safety practices with ammonia, etc. The questionnaire was anonymous and completed by 23 workers in March 2023.

4. Results and Discussion

The Port has been handling ammonia as cargo since 2009. During the interviews, it was reported by Int. 1 that: „there were no major accidents or severe injuries among personnel with ammonia since the beginning of operations in the port". Nevertheless, practical experience in incidents and near-misses has been accumulated. According to the respondents, so far, the most dangerous handling operation (with a high risk of leakage) is the unloading of railway tanks (from pressurized vessels, ammonia at ambient temperature with pressure up to 10-12 bar), when the operator is connecting the tank flanges with the loading arms. "According to risk analysis and operational practice, unloading operations at railway unloading area have a higher risk of accidents because of high pressure in ammonia railway tank cars and possible humane mistakes", said Int. 4. In the case of operator error, ammonia may leak with high pressure, which can generate a long release duration with a large gas cloud. Experts identified and discussed different human factors as the cause of situations, such as human error during the operation, deviation from the operating procedure, poor coordination or organization among operators, and poor experience. Managerial factors were also mentioned such as poor supervision, inadequate staff training, and inadequate operating and safety procedures (Int. 1, Int. 2, Int. 3, Int. 4, Int. 5). This is in a line with an exploratory HAZID study of 95 ammonia major accidents from 2005 to 2020 in various industries (such as agriculture, pharmaceuticals, fertilizers, etc.) showed that human factors account for 34% of the causes of accidents and management factors for 19% (Kahlouche et al., 2022).

In the case of an ammonia leak, it is highly critical that the operator is fully protected from ammonia exposure by personal protective equipment or PPE (wearing a full-face mask with filter, cold-resistant gloves, and protective clothing). To protect other operators, ammonia detectors are installed in the work area, which, in the event of an increase in ammonia concentration, automatically turn on water curtains that prevent the spread of the ammonia cloud beyond the leak. The water absorbs the ammonia and washes it off easily if it comes into contact with the skin or protective clothing. Emergency showers for washing off ammonia have been also installed in the immediate vicinity. The experience of transferring ammonia to a ship through the marine loading arm (as cargo) is noted by respondents as a moderate-risk procedure where risk factors have a minimal severity. Ammonia in pipelines is fully refrigerated (-32ºC) and the pressure does not exceed 5 bar. In the event of a leak, ammonia does not pose such a risk compared to a leak from a pressurized vessel. In the case of such operations, respondents (Int. 1, Int. 2, Int. 3, Int. 4) identified technical factors as the main causes of incidents - mechanical failure of equipment, failure of electrical equipment (including process automation), managerial factor – such as an inadequate system for planning repairs and maintenance, as well as external factors - such as weather conditions (storm, strong wind, high waves), and some external risks (security breaches by third parties or events on the ship, e.g., fire, explosion, sabotage). Kahlouche et al. (2022) determined in their study, that technical factors account for 40% of major ammonia accidents and are the most common causes of leaks, while external factors are rated as the least significant (7%) compared to other causes.

During interviews, respondents listed best practices in SMS and in emergency preparedness for spills to minimize the likelihood and consequences of hazardous events. „Since 2010, the terminal has implemented an integrated management system consisting of four different areas: quality, environment, occupational health and safety (OH&S), and industrial safety (by Seveso III). I am the responsible person for administration of IMS", said Int. 4. There are also different safety systems on industrial automation and control system levels. "Inside the terminal, pipelines, and berths, there is an ammonia leak monitoring system consisting of multiple ammonia sensors linked to a general automatic control system that automatically stops operations, closes valves, and turns on water curtains. It is our emergency shutdown system", said Int. 5. Another system for environmental monitoring has been installed at the border between the Port area and the local community (Sillamäe town), which, in case of exceeding the ammonia concentration, limits port operations or stop them until the causes are eliminated. An early warning system (alarm sirens) for a chemical accident has been installed on the territory of the port and the local community, and regular testing is carried out every quarter. The population of the community is familiar with the rules of action in case of hearing sirens and the danger of a major accident with ammonia. Every three years, joint training of the Port staff and the Rescue Board is held for exercising to eliminate the accident with ammonia according to different scenarios. To eliminate spills, leaks, and major accidents, the terminal has its own rescue team, consisting of trained personnel who know the process equipment and can work in hazmat suits with breathing apparatus.

Ammonia experts (Int. 1, Int. 2, Int. 3, Int. 4) were asked to discuss the risks associated with the use of ammonia as a green bunkering fuel by the TTS scheme (Fig. 1). And based on experience, possible accidents with ammonia during SIMOPs. According to the interviewed experts, two main scenarios can be considered – ship bunkering with fully refrigerated ammonia (loaded at the port and bunkering take place in the same port for up to 3 hours and the ammonia does not have much time to heat up) or pressurized ammonia (loaded at the port and, the truck transports to the place of bunkering, the ammonia may warm up to ambient temperature during this time). "The option with fully refrigerated ammonia is the most preferable because even in the case of a serious spill, the severity is low. It gives smaller gas clouds and shorter spill duration. If the bunkering operator and the ship's crew use personal protective equipment, then the risk to life and health is minimal. There is also a trained rescue team in the port who will quickly arrive and eliminate the leak," said Int. 3. In the second option, the likelihood of leakage increases, as well as the severity of the consequences. "In the event of a release of warm ammonia from a pressurized truck, it can pose a serious hazard not only to the bunkering operator, but also to the ship's crew, ship's passengers, and other persons within a dangerous zone of up to 1,500 m from the leak. It will also take a long time for the arrival of rescuers to eliminate the leak." Therefore, according to all interviewed experts, only fully refrigerated ammonia should be used for bunkering ships to minimize accident risks in the case of green shipment, and it is also necessary to conduct a detailed risk analysis (e.g., HAZOP) for such a bunkering scheme. Wu et al. (2015) conducted a quantitative risk analysis of the TTS bunkering scheme with the use of LNG and described such types of risks as LNG hose rupture, liquid and gas pipelines rupture, fuel tank master valve rupture, and low-temperature valve rupture, which are only technical factors.

The main document planning for emergencies (5th element of SMS) at the ammonia terminal is an internal emergency response plan (Response Plan). A response Plan is a written document, which consists of instructions, approved by the local authority (Estonian Rescue Board) and top management, that describes various emergency scenarios (incl. major accidents) and gives directions on how employees should respond in their workplaces in the event of an emergency. The Response Plan contains detailed instructions for crisis communication with authorities and the public, as well as ensuring the coordination of personnel with external rescue services and other agencies. The Response Plan is based on various scenarios of emergency incidents associated with ammonia handling operations identified during the major accident hazard assessment, as well as the possible consequences resulting from these emergencies. According to the Int. 4, "it includes a list of available resources for protection and liquidation of emergencies. Measures taken to reduce risks in the accident".

As it is known from the previous research, the toxicity has the greatest impact on the risks of ammonia bunkering compared with flammability (Fan et al., 2021). The workers in the current study demonstrated high awareness of the toxic properties of ammonia and OH&S of handling ammonia. All of them stated that they always distinguish the smell of ammonia from that of other chemicals and were aware that ammonia causes coughing and lung irritation as well as eye irritation. Seven workers also mentioned that there's a risk of blindness. According to literature (Padappayil and Borger, 2023), ammonia can cause severe damage to the cornea, lens and in the worst case, can lead to globe perforation. However, only 9 workers (39% of respondents) were aware that ammonia is flammable and therefore requires special attention to fire hazard; but almost all workers (95,6% of respondents) mentioned the environmental toxic properties of ammonia. A little more than half of the workers (56,5%) knew about the explosive properties of ammonia (in closed containers), at concentrations of 15-28%.

Ten workers have experienced health problems that they connect with chronic exposure to ammonia, but only one of them feels the health problems are frequent. The workers report such problems as skin burns caused by an accidental drop of ammonia; corneal burns, loss of vision if ammonia enters the eye and no protection was used; breathing difficulties if inhaled without protection; loss of sense of taste and smell for a short period of time from the result of deep inhalation of ammonia. The workers state that the employer has established clear rules about personal protective equipment and in practice, these rules are followed. All workers admitted that they use protective gloves, protective clothing, footwear with cold protection, and a face mask with filter type: K or ABEK. The majority of the workers (87,0%) wear also safety goggles. The workers emphasize that safety measures while working with ammonia are inevitable: if personal protective equipment is used correctly and precautions are meticulously followed, health and safety risks can be minimized.

When identifying the incidents caused by ammonia, 6 workers admitted that they have had situations where near-missed accidents have happened. These have included the contact of liquid ammonia with the operator's skin when opening the wagon valve; failure to comply with safety requirements and wear a face mask in required operations; inhalation of ammonia leaking from the equipment. These cases have been analysed in depth to find out the root causes of incidents followed by discussions with workers. According to Kahlouche et al. (2022), the most frequent consequence of major accidents with ammonia is the impact (leading to death or injury) on people (58%), of which on-site people account for 47% and off-site people 11%.

5. Conclusion.

In order to understand the important of chemical safety aspects of ammonia bunkering during SIMOPs, the current paper presents findings regarding the management of hazards for ammonia storage and transfer during SIMOPs. We can conclude that health and safety must be always prioritized while working with such chemicals which can cause a major hazard and legislative requirements connected with hazardous chemicals have to be punctually followed. Moreover, the paper sheds light on the aspects of ammonia bunkering during SIMOPs at the port, thereby helping to lay safety and knowledge transfer on the ammonia fuel to interested stakeholders that would potentially accelerate the development of safe and efficient ammonia bunkering on the way to green maritime shipping.

In conclusion, the handling of ammonia as cargo at the Port is a high-risk activity that requires strict safety measures to prevent incidents and protect workers and the environment. Although there have been no major accidents or severe injuries among personnel since the beginning of operations, practical experience in incidents and near-misses has been accumulated, particularly during the unloading of railway tanks with high-pressure ammonia. The respondents identified different human, managerial, technical, and external factors as the main causes of incidents. To minimize the likelihood and consequences of hazardous events, the terminal has implemented an integrated management system, multiple safety systems, an emergency response plan, and regular training of personnel and the local community. The use of fully refrigerated ammonia is preferable for bunkering ships to minimize accident risks. Overall, the terminal's commitment to safety and emergency preparedness is essential to ensure the safe handling of ammonia as a hazardous chemical.

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