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Health and Safety Workshop Report version 2, 2023

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2nd Symposium on Ammonia Energy

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Summary

This report summarises the discussions that took place at the workshop on "Ammonia as an Energy Vector – Health and Safety" during the 1st Symposium on Ammonia Energy hosted at Cardiff University from the 1st to the 3rd of September 2022. Furthermore, the document has been updated with discussions from the workshop on health and safety at the 2nd Symposium on Ammonia Energy hosted at the University of Orléans from the 11th to the 13th of July 2023. Several presenters from various companies and organizations participated in discussions at these two workshops, and all provided some insight into the most concerning issues when using ammonia as an energy vector. The workshop, co-led by the Health and Safety Executive (HSE) and Cardiff University, promised to examine some important questions that need to be answered via Research and Development (R&D) to tackle the unknowns of using ammonia in both the energy and transport sectors. The outcome of the workshop is this document, which will be put forward in the following health and safety workshops scheduled to take place in

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future sessions of the Symposia, with the aim of coordinating research efforts undertaken by industries, governmental bodies and academic institutions.

Introduction

Ammonia is both toxic and flammable and it is therefore important to carefully manage risks to health, safety and the environment related to potential loss of containment scenarios. Ammonia is usually stored and transported in liquid form at pressures above about 8 bar (at ambient temperature) or at temperatures below -33°C (at ambient pressure). Leaks of pressure-liquefied ammonia produce cold two-phase jets composed of ammonia aerosols and vapour. The resulting ammonia clouds are often heavier than air, due to the low temperatures and the presence of the aerosols. Releases of temperature-liquefied ammonia have also been observed to produce heavier-than-air clouds in some incidents. The dispersion of these dense toxic clouds can lead to significant hazard ranges.

Handling of ammonia presents some materials-related issues that need to be considered carefully. Appropriate materials should be selected and mitigations measures implemented, e.g., use of inert gas and the addition of a small quantity of water to anhydrous ammonia in cryogenic liquid ammonia storage tanks to prevent stress corrosion cracking[1]. It is also important to have appropriate inspection regimes.

These issues are recognized by the ammonia industry, who have a long track-record of operating ammonia production and distribution sites safely. However, the coming years are likely to see a significant growth in the use of ammonia as an energy vector and marine fuel. It is important to ensure that new entrants to the market are aware of the health, safety and environmental risks of ammonia, and that they manage these risks appropriately. Novel risks may also emerge due to the use of ammonia in new environments and/or for new applications. It is important that research is undertaken to ensure that these novel risks are identified and appropriately managed.

One of the active areas of research on ammonia currently is engine testing, where the primary aim is to develop internal combustion engines that can efficiently run on ammonia whilst producing low emissions of nitrous oxide and NOx. These nitrogen compounds have high global warming potential, so it is essential to minimise their emission rates for ammonia to become a genuine Net Zero fuel. They are also environmental pollutants, causing potential health effects, acid rain and atmospheric smog. Whilst engine research facilities are familiar with handling flammable fuels (primarily hydrocarbons), they mostly lack familiarity in handling ammonia. This is compounded with a lack of harmonised guidance on the safe design and operation of ammonia vessels and pipework systems. Whilst industrial gas companies

[1] Wright A. (2022) Cryogenic storage of anhydrous ammonia, IChemE Hazards 22 Symposium, Harrogate, UK, 18-20 October 2022, https://www.icheme.org/knowledge-networks/communities/special-interest-groups/safety-and-loss-prevention/resources/hazards-conference-archive/hazards-32/

(suppliers of ammonia) provide guidance for users, this appears to be inconsistent between different jurisdictions internationally.

Other areas where there are challenges for future use of ammonia as an energy vector and marine fuel relate to the use of ammonia in ports and on ships. Operators are familiar with the hazards of marine fuel oils and diesel, but the toxic risks both to humans and the environment from ammonia are very different. There is a need to develop new rules and standards for design and maintenance purposes. Production of ammonia will also need proper training requirements when using novel technologies, particularly for the reduction of leaks and potential exposure to personnel. Distribution and utilisation of ammonia will be only possible with adequate procedures, whilst engineering challenges such as co-firing, corrosion impacts, lubricant degradation, etc., becomes key aspects of deploying ammonia as a fuel.

Finally, aspects such as public perception, development of international standards, flexible approaches from companies to share guidelines and know-how, etc., will all be essential pieces of the complex puzzle needed for the use of ammonia as an energy vector. This manuscript presents some insights into these challenges and potential solutions that have been discussed in the health and safety workshops at the two symposia on ammonia energy. The compilation of discussion-outcomes was initially divided into four sections: production, storage, distribution and use of ammonia. Each contained the comments raised by the participants at the two meetings. Additional comments have been added in some cases to highlight the progress made on each point and the requirements for R&D. The latest update also includes a section on recent and ongoing safety-related research activities.

Production

A recurrent comment during the first workshop was that production, although not necessarily linked to ammonia for energy, needs to be made as inherently safe as possible, especially considering new methods of production using decentralized systems (i.e., renewable energy). Inherently safe designs could enable ammonia to find a new niche in decentralised energy generation and storage.

There is expertise on safely handling ammonia within the fertilizer and refrigeration industries, but much of the safety-related experience resides within companies and, to date, this information has not been shared widely with new entrants to the market. The Fertilizer Institute[2] and Ammonia Energy Association[3] share only limited information on safety-related topics. The main focus for safety-related discussions appears to be through the American Institute of Chemical Engineers (AIChE) annual safety symposia on ammonia plants and related facilities[4]. There are also organisations like the US-based Ammonia Safety Training

[2] https://www.tfi.org/
[3] https://www.ammoniaenergy.org/
[4] https://www.aiche.org/conferences/annual-safety-ammonia-plants-and-related-facilities-symposium

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Institute[5]. For other toxic substances, like chlorine, there is the Chlorine Institute, which produces many safety-related publications and runs various working groups and training courses. The equivalent institute does not currently exist for ammonia – but it would be useful for one to be developed to support the growing ammonia industry. Good sharing of knowledge and experience across the industry, government and research institutes is essential.

The state of Iowa, USA, has over a thousand facilities for farmers to fill their ammonia tanks for agricultural fertilizer applications. There is experience there that could be shared for new standards and regulations – a subject that needs to be brought forward during future events, conferences and projects.

Storage

It was noted that several field-scale experimental test series have been undertaken to understand the behaviour of pressure-liquefied ammonia releases (e.g., Desert Tortoise, FLADIS) but there is little or no data on releases of cold, refrigerated ammonia – which is the condition used for large-scale storage. Releases of refrigerated ammonia should in principle present a lower risk than pressure-liquefied ammonia, but incidents such as the tank overfill at Blair, Nebraska in 1970 demonstrated that temperature-liquefied releases could still give rise to large, heavier-than-air clouds. Comments raised in the discussions included: "Has this been a coincidence across those reports documenting health and safety events? Or is it that refrigerated ammonia has never caused major issues?".

It was noted that there are documented cases where people have been exposed to ammonia, sometimes where transfer connections to tanks were not properly made, leading to leaks and exposure, e.g., the Beach Park, Illinois incident in 2019.

An important issue that concerned potential users (including those participating in the workshop) was related to transfer operations and filling of cylinders. Potential future applications of ammonia could include it replacing LPG/propane as a fuel at sites that are not connected to the natural gas distribution network (or, in the future, the hydrogen distribution network). The level of training of operatives involved in filling ammonia tanks near occupied sites, and the use of appropriate risk assessment, were raised in the discussions. New systems need to be developed to reduce the risk of leaks. It is foreseen that these high-integrity designs will probably be developed, but they may incur an additional cost.

Regarding good practice guidance and standards, some good precedents can be seen in the fossil fuels industry. Standards have been under development for several decades for LPG and LNG. Sites currently handling ammonia have also developed standards and procedures, although these are often internal to the company and not widely shared. It was agreed that it would be useful for current ammonia producers/users to work with new entrants to the

[5] https://ammonia-safety.com/

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market, to share their expertise and develop new standards to ensure that new ammonia infrastructure is designed and operated safely. For the fossil fuel industry, trade organisations such as the Energy Institute and the Institute of Gas Engineers and Managers (IGEM) have helped to produce publications on good practice guidance. For the ammonia industry, it is less clear who is helping to coordinate similar efforts.

There have been some initial indications that lubricating oils have been contaminated with ammonia in engines operating on ammonia. The potential risks to health from exposure to contaminated oil, e.g., during engine maintenance, requires further R&D.

Similarly, the health and safety advice for research institutes and laboratories seems fragmented. Some limited guidance is available from organisations like the British Compressed Gas Association and European Industrial Gas Association. Advice seems to differ across different jurisdictions (worldwide). Ideally, we need one or more organisations to coordinate sharing of safety-related knowledge and guidance for ammonia, similar to the role played by the Chlorine Institute for chlorine. Unfortunately, the lack of such an organization creates frustration in the time it takes for each individual research institute to set up their own laboratories.

Finally, the potential uses of ammonia for aerospace applications were brought to the attention of the panel. Currently, the aerospace industry is focusing on hydrogen, but ammonia is a potential future option. A question was asked: “Would it be possible to design a system capable of controlling evaporation in case of a catastrophic event?” A point for future discussions, perhaps.

Distribution

Points raised regarding distribution were around the precedent of companies that have been already approached by ammonia producers. Ammonia is currently widely used in the fertiliser and chemical industries. It would be useful to benefit from the long experience of use in these industries. However, some new problems could arise with the use of ammonia as a fuel. Some of the challenges that need to be addressed, as distinct from the current use where specialists tend to handle ammonia, come when inexperienced people are handling the chemical. This is an important issue, since ammonia has now been seriously considered as a transportation fuel, particularly in the marine sector. Risk assessments followed by test and demonstration campaigns in marine transport are required, for what seems to be the most promising new market for the utilisation of ammonia.

Utilisation

Anhydrous ammonia has been identified as a potential long-term fuel that could enter the market relatively quickly and offer a zero, or a near-zero, carbon solution (on a tank-to-wake basis and in some cases on a well-to-wake basis), provided that it is not offset by harmful NOx generation.

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There is little recent marine experience when using ammonia as a fuel – and some of the key machinery technologies (such as engines) are under development. Extensive land-based experience with the production and use of ammonia for the petrochemical and fertiliser industries could help to inform its use as a marine fuel. Experience with the carriage of ammonia in liquefied-gas carriers – and the specific requirements for storage, distribution, personal protective equipment (PPE), etc., in the International Code of the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk (IGC Code) – provide some of the statutory requirements to guide its application on ammonia-fuelled ships.

However, toxicity challenges and related risks are significant and, while manageable, they will add complexity to ship designs (compared to those for conventional and other low-flashpoint fuels and gases) and will potentially limit the ships for which it is a suitable fuel. Ammonia ultimately may prove to be a more appropriate solution for deep-sea cargo ships rather than for passenger or inland waterway craft. It is also envisaged that long distance or heavy cargo will benefit from ammonia utilisation.

The use of ammonia as a marine fuel and energy vector is a rapidly evolving area, with new risk studies and infrastructure developments frequently in the news. These have recently included:

- Air Products announcing plans for green and blue ammonia production facilities associated with the NEOM project in Saudi Arabia and the Louisiana Clean Energy Complex in the USA
- The Port of Amsterdam risk study[6], which included analysis of bunkering ammonia
- The study of ammonia as a marine fuel by Nanyang Technological University and the Singapore Maritime Institute[7]
- The report by Lloyds Register and the Mærsk Mc-Kinney Møller Center for Zero Carbon Shipping on "Design and operation of ammonia-fuelled vessels based on multi-disciplinary risk analysis"[8]
- The new Yara Eyde ammonia-fuelled container ship[9]

Some key considerations for ammonia to be commercially used as a marine fuel and energy vector include:

- Ammonia bunkering and supply: from a technological and operational perspective, loading and unloading ammonia as a commodity at the terminal may have some

[6] https://sustainableworldports.org/wp-content/uploads/DNV-POA-Final-Report_External-safety-study-bunkering-of-alternative-marine-fuels-for-seagoing-vessels_Rev0_2021-04-19.pdf
[7] https://www.ammoniaenergy.org/articles/key-singaporean-safety-study-releases-report/
[8] https://www.lr.org/en/knowledge/research-reports/recommendations-for-design-and-operation-of-ammonia-fuelled-vessels-based-on-multi-disciplinary-risk-analysis/
[9] https://hydrogen-central.com/yara-the-worlds-first-ammonia-powered-container-ship/

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similarities to bunkering ammonia as a marine fuel. Where possible and appropriate, operators should learn from this experience.
- Safety considerations in ship and heavy-duty transport designs: one of the primary drivers of vessel design is the need to minimize the risk of exposure to crew in case of a leak. Design and layout must be treated with a high level of safety, from concept design through to material selection and operational measures. Relevant risk assessments are needed to prevent accidents. This would need to take into consideration the probability of leakage, gas detection systems, and certification along the supply chain. Research on these topics would be useful to inform standards, codes, guidelines and good practices.
- Handling ammonia onboard ships will require a new set of skills and safety procedures. Ammonia is toxic, corrosive and flammable. It also has potentially significant impacts on aquatic life. Airborne emissions also need to be minimized for environmental reasons, due to its role in atmospheric PM2.5 formation.

In the UK, operators of large-scale ammonia storage facilities will need to comply with the requirements of the Control of Major Accident Hazards (COMAH) regulations[10] (and in Europe, the Seveso directive[11]). Different requirements are placed on duty holders holding threshold quantities of ammonia above the COMAH lower tier threshold (50 tonnes) and upper tier threshold (200 tonnes). For new installations, there are also requirements under the Planning (Hazardous Substances) Regulations[12]. Namely, new sites handling 50 tonnes or more of ammonia will need to seek land-use planning consent. In terms of workplace exposure to ammonia, there are obligations under the Control of Substances Hazardous to Health (COSHH) regulations[13]. These include workplace exposure limits for ammonia of 25 ppm and 35 ppm, for 8 hour and 15 minute time-weighted average exposure periods, respectively[14]. There are also general provisions to consider under the Health and Safety at Work Act (1974)[15]. This list of regulations is not exhaustive and further information can be found in reviews such as the work of Fecke *et al*. (2016)[16].

An important topic that came up in discussions at both the 2022 and 2023 workshops at the Ammonia Energy Symposia was the use of ammonia in laboratories and other R&D facilities.

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[10] https://www.hse.gov.uk/comah/background/comah15.htm
[11] https://echa.europa.eu/regulations/clp/understanding-seveso
[12] https://www.gov.uk/guidance/hazardous-substances
[13] https://www.hse.gov.uk/coshh/basics/exposurelimits.htm
[14] https://www.hse.gov.uk/pubns/books/eh40.htm
[15] https://www.hse.gov.uk/legislation/hswa.htm
[16] Fecke *et al*. (2016) "Review of global regulations for anhydrous ammonia production, use, and storage", Institute of Chemical Engineers (IChemE) Hazards 26 Conference, Edinburgh, UK https://www.icheme.org/media/11771/hazards-26-paper-34-review-of-global-regulations-for-anhydrous-ammonia-production-use-and-storage.pdf

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Proper standards are needed for these facilities, taking into account relevant employment laws and regulations of the given country where the facilities are located.

Other important issues raised during the workshops were related to the heterogenous landscape of ammonia as a fertilizer, chemical, and now as a fuel. It was felt that some progress was needed in providing safety-related guidance for the final application. Some International Gas Codes currently prevent the utilisation of toxic substances as fuels, an issue that needs to be addressed with support from the industry.

It is likely that ammonia will have to be blended for use in combustion engines and a different pilot fuel will be needed to initiate stable combustion. Research in this area is taking place. There are still challenges ahead with the production of NOx and affordable cracking methods to produce hydrogen from ammonia (that will be blended with ammonia to optimise the combustion properties of the fuel). Corrosion in high-temperature components is critical, with seals, bearings, blades, etc., potentially being exposed to corrosive atmospheres. Research in this area is needed. Oils and ammonia can also react, hence the right lubricant needs to be employed to reduce risks. Similarly, there is a need for better materials that can withstand ammonia exposure at high temperatures over longer periods of time. There is a recurrent interest in smaller systems that can be deployed for small applications.

Safety concerns related to the use ammonia in test facilities have delayed progress on some of these topics, requiring further analyses to be conducted and interaction between interested parties to progress with this technology. There is a need for more ammonia engine demonstrators worldwide.

Fuel cells require high cleanliness in the fuel, so that materials and membranes are not corroded and/or poisoned. Although hydrogen fuel cells have existed for many years, using fuel cells with ammonia can pose a challenge in terms of its direct use as a fuel.

In terms of safety issues related to small leaks, ammonia does have the advantage of having a recognisable smell at low concentrations of around 5 ppm[17] (below harmful levels). Other toxic gases, such as carbon monoxide, are “silent” killers. Natural gas is odorized prior to distribution for end use, as a safety measure.

If ammonia is to become widely used as a fuel, in shipping for example, it is essential people handling ammonia at ports and on ships are adequately trained. This includes emergency responders (both on and offshore).

Finally, public perception needs to be considered, since it will play a critical role in the development of an ammonia-fuelled economy. As an example, the Beirut explosion in 2020 is often raised in discussions of ammonia safety but the incident actually involved ammonium nitrate, not anhydrous ammonia: this creates confusion. Although ammonia’s history is

[17] https://www.atsdr.cdc.gov/toxprofiles/tp126-c1.pdf

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generally good in the refrigeration and agriculture sectors, its use as a fuel will bring other challenges. These need to be managed and technical solutions may need to be developed to mitigate risks.

Recent and Ongoing Safety-Related Research Activities

Various programs worldwide have been undertaken over the last few decades to explore the potential health and safety implications of using ammonia at a large scale. Most of these programs were aimed at improving our understanding of ammonia for transport and storage applications. They included the Desert Tortoise, FLADIS, INERIS and Jack Rabbit I experiments. A summary of these studies can be found in the review by Batt[18].

The Jack Rabbit III research program is currently ongoing and is focused on improving our understanding of anhydrous ammonia releases. Recent work has included an international dispersion model inter-comparison exercise, using data from the Desert Tortoise and FLADIS trials[19]. HSE have recently been undertaking some further modelling work to examine the impact of humidity on dispersion of ammonia[20]. The coordinators of the Jack Rabbit III program (the US Department of Homeland Security and US Department of Defense) have also funded research on dry deposition of ammonia at the University of Arkansas. Future large-scale ammonia tests in the USA are in the early planning stage, tentatively scheduled for 2026-2027. Further information about the Jack Rabbit research program can be found on the Utah Valley University website[21].

Air Products funded a series of tests at DNV Spadeadam in 2022 on pressure-liquefied and cryogenic (temperature-liquefied) releases, known as the Red Squirrel trials. The main objective of these experiments was to improve our understanding of source and dispersion characteristics. The tests involved both two-phase jet releases and liquid spills onto concrete and water. Further details can be found in the paper by Dharmavaram *et al.*[22]

Yara Clean Ammonia are also currently working with the French national laboratory INERIS, the maritime institute CEDRE, and other French organisations to undertake experiments involving large spills of cryogenic liquid ammonia onto the sea, to improve our understanding

[18] Batt (2021) "Review of dense-gas dispersion for industrial regulation and emergency preparedness and response", Atmospheric Dispersion Modelling Liaison Committee (ADMLC) Report ADMLC-R13, https://admlc.com/publications/

[19] Gant *et al*. (2022) "Summary of results from the Jack Rabbit III international model inter-comparison exercise on Desert Tortoise and FLADIS", 21st International Conference on Harmonisation within Atmospheric Dispersion Modelling for Regulatory Purposes, Aveiro, Portugal, 27-30 September 2022 https://gant.org.uk/research/H21-095_Gant_Chang_paper.pdf

[20] Tickle *et al*. (2023) "Effect of humidity on the dispersion behaviour of pressure-liquefied ammonia jet releases", 27th Annual George Mason University Conference on Atmospheric Transport and Dispersion Modeling, 20-22 June 2023, http://camp.cos.gmu.edu

[21] https://www.uvu.edu/es/jack-rabbit/

[22] Dharmavaram *et al*. (2023) "Red Squirrel Tests: Air Products' ammonia field experiments", Process Safety 2023; 42(3): 481-498. https://doi.org/10.1002/prs.12454

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of the characteristics of the airborne and waterborne hazards. The research program is called ARISE and the trials are currently planned for 2024-2025.

SINTEF has also recently been awarded funding from the Research Council of Norway for a project involving laboratory-scale releases of ammonia onto water, and model development. Other ammonia projects involving SINTEF include MartimeNH3[23] and the Ammonia Fuel Bunkering Network for the Marine Sector[24].

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[23] https://www.sintef.no/en/projects/2021/maritimenh3-enabling-implementation-of-ammonia-as-a-maritime-fuel/

[24] https://www.sintef.no/en/projects/2021/maritimenh3-enabling-implementation-of-ammonia-as-a-maritime-fuel/