



# Alternative fuels: a shift in the response paradigm?

Andrew Le Masurier

ITOPF

ITOPF, Dashwood House, 69 Old Broad Street, London, EC2M 1QS

## **ABSTRACT**

The decarbonisation of shipping has become an increasingly prominent topic, and this is due to growing regulatory pressure, a changing climate of public opinion and investors demanding a faster energy transition as well as the industry's increased focus on sustainability.

This paper focuses on biofuels, liquefied natural gas (LNG), methanol, ammonia and hydrogen, all substances with extremely variable fates and behaviours when spilled. Biofuels behave in a similar way to conventional hydrocarbons albeit with less acute toxicity and higher rates of biodegradation. LNG, ammonia, and hydrogen are stored at temperatures below their boiling points or at pressure as they are gaseous in ambient conditions. When spilled they rapidly boil, causing visible clouds that sink on the surface of the water before dissipating into the atmosphere. Methanol is a volatile liquid that is fully miscible with water and therefore is lost to the atmosphere from its vapours and to water through dissolution. The behavioural variability of these substances is coupled with severe health and safety risks from fire and explosion, toxicity, corrosivity, cryogenic damage and asphyxiation, which could cause serious injury or death to the ship crew, bunkering and port



operators as well as spill responders. For these reasons, preparedness is key to mitigate the safety risks of personnel and to promote effective spill emergency response. Scalable contingency plans are an effective tool to assess the risks of different spill scenarios and to undertake modelling and sensitivity mapping to ensure that if a spill were to occur, responders would be sufficiently prepared. Finally, the paper discusses a possible three-fold paradigm shift relating to strategy, timeframes and receptors. Current clean-up strategies and techniques are established for oil; however, these do not translate to most alternative fuels (except for biofuels), as their residence time is so short that monitoring may be the only technique possible. Timeframes for receiving pertinent information following an oil spill can be lengthy and fragmented, whereas with most alternative fuel spills, the substance's hazards (e.g. toxicity, flammability) will be driving the initial response, and therefore information transfer needs to be immediate so that first responders are able to safely undertake their operations. Finally, after protecting human health, the primary oil spill response objective is reducing pollution damage, however with alternative fuels, pollution is expected to be short-lived and localised, however the risks and associated costs of property damage from an explosion may be far greater.

## **INTRODUCTION**

With the eyes of the world focusing on reducing human reliance on fossil fuels, the shipping industry is undergoing the largest fuel revolution since the obsolescence of steam-powered vessels in the 1950s. The push for decarbonisation is not just driven by the IMO's 2023 Greenhouse Gas (GHG) Strategy following Marine Environment Protection Committee (MEPC) 80, which aims to reach net-zero emissions from international shipping close to



2050, but also by a changing climate of public opinion and investors and charterers demanding a faster energy transition.

This is reflected in the current state of the global fleet's orderbooks with 51.3% of ships on order due to run on alternative fuels in comparison to the 6.52% of the world fleet by gross tonnage currently running on these fuel type. The percentage breakdown shows that of these 51.3% of ships on order, 40.3% are scheduled to run on LNG with 8.01% running on methanol (DNV-GL, 2023a). 13 ammonia-fuelled vessels are also on the official orderbooks, with eight to be bulk carriers, three will be gas carriers and two will be tug vessels (DNV-GL, 2024). These statistics indicate that the fuel technology transition is firmly underway with LNG leading the way, which had been anticipated as it is seen as a viable 'transition fuel' that is commercially mature with an established global bunkering infrastructure in place. It also shows that there are currently multiple different options when selecting the most suitable fuel to pursue. It should be noted that those 48.7% ships on order for conventional fuels may still look to run on 'drop-in' biofuels or be retrofitted to run on alternative fuels in the future.

### **ALTERNATIVE FUEL SPILL BEHAVIOUR**

As the current forecasts indicate that the shipping industry will have a multi-fuel future, the spill and emergency response community will need to be prepared to react to a number of different fuel types. These fuels all have different physical and chemical characteristics, which dictate how they interact with human and environmental receptors and, consequently, how spills of these fuels should be managed.



## **Biofuels**

From the list of alternative fuels covered in this paper, it is clear that biofuels will behave most similarly to conventional oils. Therefore, the more established spill response techniques and equipment that have been so effective in responding to oil spills over the past 60 years will likely still play a critical role following an accidental release into the marine environment. Fatty acid methyl esters (FAME) (also known as biodiesel) and hydrotreated vegetable oil (HVO) (also known as renewable diesel) are considered to be the most prevalent biofuels on the market currently. Demand for biofuels is set to grow with some predictions forecasting increases in global production from 11 million tonnes of oil equivalent (Mtoe) per year currently, to between 500 and 1,300 Mtoe by 2050 as shipping, and other transport sectors, look to decarbonise without significant reconfiguration of engines and auxiliary infrastructure (DNV-GL, 2023b). Although FAME and HVO's characteristics depend on the feedstock used to produce them as well as the amount of blending taking place, their processing means that their physical properties are very similar to petroleum distillates. They are both less dense than water and are insoluble and therefore will float and form a slick on the surface of the water when spilled (Jezequel et al., 2019). Like most alternative fuels, limited studies have been undertaken to demonstrate the catastrophic release of biofuels in the marine environment. However, FAME studies have shown that once released the main process of loss to the environment is biodegradation with 94% of pure biodiesel volume undergoing biodegradation over a 28-day period (Jezequel et al., 2019). This is likely due to the fact that biodiesel is composed of a simple, straight-chain carbon chain with two oxygen atoms at one end in a mono-alkyl ester group



and is more readily metabolised by bacteria that normally break down fats and oils in the environment. In contrast, petroleum diesel lacks oxygen and represents a very complex mixture of hydrocarbons with multiple double bonds, and many other branched, cyclic and cross-linked chains, making them more difficult to biodegrade. Despite a lack of studies undertaken to date on a spill of HVO on water, it is considered likely, due to its chemical structure, that it will also display high rates of biodegradation.

Due to FAME and HVO's relative persistence in the marine environment in comparison to other alternative fuels, and the fact that spills of these types are generally understood and do not pose an immediate threat to nearby receptors, the current mechanisms in place for responding are likely to remain practical and effective. Consideration as to the efficiency of equipment, such as skimmers, may be required, in a similar way to what has been observed since the widespread introduction of low sulfur fuel oil (LSFO) and the difficulties that have arisen with high pour point LSFO. For example, a consideration for FAME, which can also have high pour points, is the possibility that it will solidify when spilled. ITOPF has provided technical advice for several incidents involving the spill of vegetable oils, a common feedstock for FAME and HVO, and their behaviour when spilled is considered to be similar to biofuels. ITOPF attended a case in China in 2017, whereby refined palm stearin was spilled, started to solidify and due to its low plasticity, did not aggregate and instead formed lumps (up to 60 cm diameter on the second day of release), which remained in a relatively concentrated area before gradually breaking into small pieces and forming a small slick under the influence of the dominant currents and winds. On the third day, these broke down further into pea-sized lumps over a large area (approximately 200 – 300 km<sup>2</sup>), which made



the palm stearin significantly more difficult to recover at sea. The main at-sea response technique was an established oil spill response method: manual collection using nets and scoops with the shoreline response primarily undertaken using standard beach cleaning hand tools (e.g., rakes and shovels).

### **Gaseous Fuels**

The disparate behaviour of 'gaseous fuels' (LNG, ammonia and hydrogen) in comparison to conventional hydrocarbons, and even biofuels, will result in a considerable shift in the techniques and timeframes associated with a typical spill response scenario.

LNG (which principally contains methane (>85%) but also contains ethane, propane and butane), ammonia and hydrogen have boiling points of -161 °C, -33 °C and -253 °C respectively. As a consequence, when bunkering and storing these fuels, they have to be held below these temperatures in order for them to remain liquid. As ammonia has a higher boiling point than the others, it can be either transported as a refrigerated liquid, a compressed liquid or as a semi-refrigerated, compressed liquid, whereas LNG and hydrogen have much lower boiling points and therefore are typically stored cryogenically. Hydrogen can also be stored as a compressed gas if subjected to very high pressure (250 – 700 bar). These storage requirements (except compressed hydrogen) reflect what would occur in the event of a spill of these substances with all substances transitioning from a liquid to a gas when exposed to ambient conditions, albeit at differing rates. Table 1 displays the specific gravities of these fuel types in both liquid and gaseous states.

**Table 1 – Specific gravities for the alternative gaseous fuels**

Properties	LNG	Ammonia	Hydrogen
Specific gravity (liquid) @ boiling point	0.45*	0.68	0.071
Specific gravity (vapour) @ boiling point	1.5*	>1.0**	1.338
Specific gravity (vapour) @ ambient temperature	0.55*	0.60	0.067

\*As LNG can contain different compositions of substances, these are average values

\*\* In presence of water vapour

Although, the specific gravities of these substances' vapours are less than air in ambient conditions, LNG, hydrogen and ammonia (in the presence of water vapour) are denser than air at the cryogenic temperatures near their boiling points and, if spilled above the waterline, will immediately descend upon release. The moisture in the air that is exposed to these fuels' low storage temperatures will immediately condense, forming a dense visible white cloud of water vapour mixed with the substance on top of the water surface. In the case of ammonia, this vapour cloud is toxic and is likely to persist longer than LNG and hydrogen. If released below the waterline, LNG, hydrogen and ammonia will float to the surface of the water body before rapidly boiling and volatilising into the atmosphere as their temperatures increase to ambient conditions. The rate and extent to which this volatilisation takes place depends on the properties of the substance. For instance, ammonia has a higher boiling point and specific gravity in comparison to LNG and hydrogen and is also soluble in water. Therefore, when spilled, it is expected to boil at a less rapid rate, whilst the ammonia that encounters water will dissolve to form caustic ammonium hydroxide (NH<sub>4</sub>OH).

This has been demonstrated in limited studies, whereby surface and underwater spills of ammonia were carried out in laboratory and large-scale open water experiments. The



results indicated that only 5% of the spilled volume resulted in ammonia vapours reaching the atmosphere when spilled underwater with 95% remaining in the water column as caustic  $\text{NH}_4\text{OH}$  (Raj et al., 1974). Whereas for large surface spills, the partition ratio between ammonia in the water and in the atmosphere was generally between 0.5 and 0.6 for an instantaneous release of ammonia above the waterline. During this study, the vapour cloud formed was also identified as being very buoyant and in low wind conditions, was reported to rapidly rise vertically whereas it travelled horizontally in higher wind conditions. As a result, the toxic hazard at ground level was a higher risk in high wind conditions, although these conditions will allow stronger mixing and dissipation of  $\text{NH}_4\text{OH}$  in the water column. In the event of LNG being spilled above and near to the waterline, it will descend initially and, depending on volume spilled, lead to a shallow cryogenic pool on the surface of the water, which spreads out while violently boiling due to heat transfer from the warmer water below. A cloud of condensed atmospheric water vapour and methane will also form, before the temperatures rise, methane density decreases, and it travels into the atmosphere. Hydrogen will behave similarly to the previously mentioned gaseous fuels, but to a much greater extent. The difference between hydrogen's temperature while stored and the ambient conditions is so large (approximately 260 °C) that the boiling and volatilising would be so rapid and vigorous that the liquid hydrogen would undergo an extremely rapid phase transition to a gas, therefore becoming less dense than air and dissipating into the atmosphere. However, the visible condensed water vapour cloud is likely to persist for a longer period of time in comparison to the hydrogen plume.





LNG and hydrogen are also insoluble in water, and therefore no volume of spilled product will remain in the water column and lead to a caustic plume that an ammonia release would cause. Some localised impacts observed may include freezing of the water surface if the sea state is calm due to the rapid reduction in water temperatures in the immediate vicinity of the release as the sea is exposed to cryogenic liquid. As the ice layer thickness increases, the heat transfer rate will decrease, thereby somewhat reducing the rate of evaporation, despite the rate still expected to be rapid. However, due to the likely turbulent interface created by the cryogenic liquid and the water, significant amounts of water being frozen is unlikely and will most probably be confined to the immediate vicinity of the incident location.

The fate and behaviour of a spill of LNG has been the subject of studies with a focus on identifying the dispersion characteristics of the vapour clouds produced. A study reviewed experimental work performed on large-scale spills of LNG undertaken by Esso, Shell, the National Maritime Institute and the Lawrence Livermore National Laboratory (Luketa-Hanlin, 2005). The results indicated that the low-lying visible vapour cloud spread roughly at the same rate as the wind speed before becoming buoyant and dispersing into the atmosphere. The vapour cloud was likely to persist in the order of tens of minutes, however this depended on multiple factors such as the puncture size, location of the breach, discharge rate and environmental conditions at the time of the spill.

The study undertaken by Esso in 1973 of a spill of between 0.73 and 10.2 m<sup>3</sup> of LNG in Matagorda Bay, Texas demonstrated that the density of the condensed water vapour cloud was affected by the atmospheric humidity, with increased humidity resulting in lower



density vapour-air mixtures. A range of cryogenic pool radii were observed between 7 m and 14 m with a maximum distance to the lower explosive limit (LEL) measured at 442 m for a spill size of 7.12 m<sup>3</sup> and a wind speed of 4.9 m/s. However, there were some spill scenarios whereby the vapour cloud exceeded the sensor field meaning the maximum LEL distance for that scenario was unable to be measured. The longest distance to the last visible fog from the spill location was 1,372 m for a spill volume of 8.37 m<sup>3</sup> at a wind speed of 4 m/s (May et al., 1973).

Similarly, Shell undertook an exercise in the same year from a 75,000 m<sup>3</sup> capacity vessel whereby LNG was jettisoned from hoses 18 m above the waterline, 70 miles west of St. Nazaire, France (Kneebone and Prew, 1974). An interesting result was that no cryogenic pools formed on the sea surface and only isolated patches of ice formed on the largest volume spill. This feature of the spill is likely to have been caused by the LNG undergoing evaporation before reaching the sea surface as it was released 18 m above the waterline. It was also shown that for the highest volume spilled (193 m<sup>3</sup>) in 3.9 m/s winds, the visible plume appeared to have a height of 10 – 12 m and a maximum continuous width of 550 m and length of 2,250 m. The main purpose of this study was to investigate the possibility of jettisoning fuel from a vessel, and it was proved that this could be done without the vapour cloud engulfing the ship and without causing cryogenic damage to the ship (Kneebone and Prew, 1974).

In contrast to the studies of LNG, studies of spill scenarios from hydrogen are significantly more limited, most likely due to; the immaturity of this fuel type in comparison to LNG, the higher safety risks associated with flammability and explosion and, the likely expense



associated with experimental studies. However, NASA undertook hydrogen vapour cloud dispersion experiments in 1983 in order to obtain basic information regarding the physical factors dictating the dispersion of flammable clouds formed as a result of spills of liquid hydrogen (Witcofski and Chirivella, 1983). The results demonstrated that rapid liquid hydrogen spills would not lead to a cryogenic pool due to the significant temperature difference of  $>250$  °C between liquid hydrogen and ambient conditions. The spill scenario, taking place on land, resulted in the presence of a ground-level flammable cloud travelling downwind for a short period of time before hydrogen vapours rapidly mixed with air, dispersing to non-flammable concentrations, warming and become positively buoyant (Witcofski and Chirivella, 1983). Vapour clouds in the study were recorded travelling between 50 m and 100 m downwind, before undergoing a 0.5 – 1.0 m/s cloud rise rate. It was noted, as was also observed in other studies of LNG spills, that continuous, low-volume releases of hydrogen resulted in prolonged, ground-level vapour cloud travel. This was due to the fact there was less turbulence between interfaces (vapour cloud and ground) and the long-term cooling of the ground reduced the heat transfer rate and therefore the evaporation rate slowed.

### **Methanol**

Methanol is a liquid at typical ambient temperatures as opposed to LNG, ammonia and hydrogen. As a result, it does not require storage and handling at refrigerated or cryogenic temperatures and when spilled, will remain in its liquid state. If released in an unconfined environment, no plume of dense, toxic or asphyxiating vapour clouds will result following a spill of this fuel type. If spilled in a confined space, toxic vapours can cause risk to human



life for those within that confined space. Methanol belongs to the chemical family of alcohols and due to their chemical composition of having a hydroxide group attached to their carbon atom, these substances have a high affinity for water molecules. For this reason, methanol is fully miscible in water, meaning that it has no limit to its solubility and can never meet a point of maximum saturation (Machiele, 1989). This characteristic strongly dictates its fate and behaviour when spilled into the marine environment.

Once spilled into the marine environment, methanol, due to its specific gravity of 0.792 at 20 °C, would float, rapidly spreading on the sea surface and undergoing dissolution into the water body while simultaneously being lost to the atmosphere via evaporation. Methanol concentrations will rapidly decrease in the water body due to the spreading of the plume via advection and diffusion as well as biodegradation caused by micro-organisms in the water (Katsumata and Kastenber, 1996). The rate at which methanol will dissipate will depend on the amount of mixing in the aquatic environment, influenced by tidal flows combined with wind-induced wave action (Malcolm Pirnie, Inc, 1999). Depending on many environmental factors, a methanol release in open water will disperse to non-toxic levels (<1%) at a much faster rate than petroleum hydrocarbons with some studies giving a methanol half-life between one and seven days (Howard et al., 1991).

### **HEALTH AND SAFETY IMPLICATIONS**

In comparison to conventional hydrocarbon fuels, the majority of alternative fuels pose hazards that can lead to direct impacts on health and safety, mainly through flammability, explosivity, toxicity, cryogenic damage, corrosivity and asphyxiation. These risks are summarized in Table 2 with a comparison to a conventional marine fuel, marine diesel oil

(MDO). The table's colour scheme indicates increasing severity with green indicating negligible risk, orange denoting moderate risks under certain conditions and red denoting severe risks.

**Table 2 – Summary of safety risks from alternative fuels**

Safety risk	MDO	Biofuels	LNG	Ammonia	Hydrogen	Methanol
Flammability/Explosivity	Yellow	Yellow	Red	Yellow	Red	Red
Toxicity	Green	Green	Green	Red	Green	Red
Cryogenic damage	Green	Green	Red	Yellow	Red	Green
Corrosivity	Green	Green	Green	Red	Green	Green
Asphyxiation	Green	Green	Red	Yellow	Red	Red

Biofuels (FAME and HVO) have a very similar risk profile to conventional oils and therefore, training on handling and managing accidental spills of these oils is required for seafarers, responders and bunkering operators can remain as it is currently. The need for non-standard personal protective equipment (PPE) for a ship's crew, bunkering operators or responders is not necessary for these fuel types due to the similar risk profiles.

However, for LNG, ammonia, hydrogen and methanol, the risk profiles are significantly different and the health and safety implications of a spill of these substances are critical to understand before responding to such incidents.

### **Flammability**

Inside fuel storage tanks, the percentage of fuel is almost pure and, as such, the conditions are not in its flammable range. However, following a leak/rupture, a vapour cloud will form and once it has mixed with air, when its concentration reaches between the lower flammability limit (LFL) and the upper flammability limit (UFL), the mixture can sustain a flame if ignited. Therefore, when these fuels are spilled, the flammability risk will depend on



the breadth of the flammability ranges. Hydrogen (4 – 75 (v/v) %), methanol (6 – 36.5 (v/v) %) and LNG (5 – 15 (v/v) %) are more flammable than conventional fuels such as MDO, which has a much smaller range of approximately 0.5 – 5.5 (v/v) %. In addition, methanol has a flash point of 12 °C, meaning that 12 °C is the lowest temperature at which vapours emanate from methanol in sufficient quantities to form an ignitable mixture. These properties present risks in the event of an accidental release, especially in confined spaces where the vapours are unable to dissipate. This could lead to a flammable vapour cloud that, when in contact with an ignition source such as a static charge or hot surface, could lead to a flash or pool fire, which could possibly propagate back to the leak source until all the fuel is consumed below the LFL or it is extinguished. As the burning speed of hydrogen is nearly an order of magnitude higher than that of LNG, hydrogen fires will burn more rapidly, which can result in a short-lived fire but also allow the flames to propagate back to the source, leading to a pool fire or an explosion.

If a spill were to occur in unconfined conditions, it is likely that only a small area near the spill source would reach concentrations within the flammable range due to atmospheric dissipation of vapours. Vapour clouds can burn in two principal modes as either a slow burn back, also termed a flash fire, or as a fireball, the rapid burning of fuel characterised by high upward acceleration. Fireballs occur when fuel is atomised sufficiently to provide a mixture with air that can be rapidly consumed. They are more likely with a large rapid release of hydrogen or LNG resulting from a high momentum impact source. Fireballs are short duration events, in the order of seconds, but are still lethal within close proximity. It should



be noted that hydrogen and methanol flames are near invisible in daylight, which can lead to possible risks to responders if it is not clear as to the location of the fire.

Although ammonia has a flammability range of 15.5 – 27 (v/v) %, it has a high ignition energy and therefore, without a catalyst or the presence of combustible material, it is difficult to ignite.

### **Explosivity**

Those fuels that pose a high flammability risk will as a consequence, pose a high explosivity risk. When exposed to ambient conditions, spilled LNG and hydrogen may result in a rapid phase transition (RPT), which is a flameless overpressure due to a very fast change of phase, in this instance from liquid to gas. The vapour cloud expands so quickly that a sonic boom and localised overpressure occurs. These have been reported in the past but are unpredictable and not particularly well understood at this time. In particular conditions, LNG, hydrogen, methanol and ammonia could potentially undergo a boiling liquid expanding vapour explosion (BLEVE), which is an explosion caused by the rupture of a tank containing a pressurized liquid that has reached a temperature above its boiling point. This would be the case if the temperature of the tank were to rise and gas release systems were to fail (Alcaro et al., 2021).

ITOPF has attended two incidents involving methanol tankers that exploded during loading / offloading and methanol's low flash point is an important factor as to why these events occurred. Both incidents led to a constructive total loss of the vessel as well as a tragic loss of life for operators.



### **Toxicity / Corrosivity**

Ammonia is a toxic and corrosive substance that is also hygroscopic, meaning it has a high affinity for water. When spilled, it will seek water from the nearest source, which can include the human body and will react to form a caustic, corrosive solution,  $\text{NH}_4\text{OH}$ , with a pH greater than 11. This places the eyes, lungs and skin at greatest risk due to their high moisture content. Caustic burns can also result from ammonia dissolving into body tissue. The National Institute for Occupational Safety and Health has established that ammonia concentrations greater than 500 ppm in the atmosphere are considered immediately dangerous to life with thresholds as low as 25 ppm being classified as limits of exposure for longer time periods (Kass et al., 2021). Fortunately, the odour threshold for ammonia is around 20 ppm, which allows early warning for personnel that a release has occurred (Raj et al., 1974).

Methanol is another alternative fuel option that has toxic properties, and the routes of acute exposure are via inhalation of vapours or dermal contact. In the event of mild exposure to methanol and its vapours, the symptoms are similar to ethanol intoxication, with headaches, dizziness, nausea and blurry vision being commonplace. If the exposure was significant, there may be a latent period for 10–48 hours, until more serious symptoms such as violent abdominal pain, temporary or permanent blindness, coma and possibly death due to respiratory failure occurs (Machiele, 1989). The latent period, whereby treatment should be administered, is due to methanol being metabolised into formaldehyde and formic acid, which are the main toxic agents responsible for the above effects. It should be noted that for toxic effects to take place via inhalation and dermal contact, prolonged





periods of high methanol concentrations, (approximately 3,000 ppm for 8 hours or 20,000 ppm for 1 hour), would be required (Machiele, 1989).

### **Asphyxiation**

Like with any gaseous or low flash point substance, in a confined environment, high concentrations of vapours can displace oxygen in the air, decreasing oxygen availability and therefore leading to asphyxiation to those present in these confined environments. Therefore, it is considered that the gaseous alternative fuels and methanol, due to its low flash point pose high risks of asphyxiation in confined spaces.

### **Cryogenic Damage**

Exposure to the cryogenic temperatures that LNG and hydrogen are stored at will result in the freezing of any tissue upon contact and can cause materials to become brittle and lose their strength and functionality. This could be an important factor in the event that a hull underwent embrittlement, leading to structural damage and possibly sinking. The temperature at which ammonia is stored in (-33 °C) also has the potential to cause skin damage but to a lesser extent than LNG and hydrogen.

### **PREPAREDNESS, CONTINGENCY PLANNING AND TRAINING**

After assessing the hazards posed by these alternative fuels, it is evident that a response to an incident involving these substances will most likely not solely be undertaken by governmental agencies. Instead, the incident management team would need the assistance of technical experts, private organisations and the wider response industry. Therefore, preparedness and efficient communication between these parties will be essential in



promoting an effective response, with a particular emphasis on health and safety aspects such as monitoring, PPE and decontamination.

If carried as bulk cargo, these fuels would be categorised as contributing cargo under the 2010 HNS (Hazardous and Noxious Substances) Convention (when in force), however, this convention does not take into account HNS used as bunkers. Despite this legislative difference in terminology, these substances are HNS and current regulations and guidance in place will greatly assist those responding to an incident. For instance, the 2000 OPRC-HNS Protocol highlights the need for preparedness through contingency planning, prompting states to develop bottom-up, scalable spill response plans so that each emergency plan is compatible with one another from a single facility to an international response. To assist with the objectives of the OPRC-HNS Protocol and following requests by multiple UN Regional Activity Centres (REMPEC, Bonn Agreement and HELCOM), the Marine HNS Response Manual was developed by Cedre, ISPRA and ITOPF and can play a vital role in assisting contingency planners, government agencies, port operators and the emergency response industry to prepare for spills involving alternative fuels.

In order to develop an effective contingency plan, it should be based upon a robust risk assessment that is created with the cooperation of multiple relevant stakeholders. In the case of an alternative fuel spill response plan, this risk assessment should consider the most probable spill scenarios, coupled with the possible consequences of such an event, with a primary focus on the risks to human health. For instance, if the Port of Singapore became a regional hub for ammonia bunkering, a risk assessment based on an ammonia bunkering incident would be one of the most likely spill scenarios. Therefore, within the



contingency plan there could be a requirement for regular ammonia spill training workshops with all port operators; a requirement for suitable, chemically compatible PPE and HAZMAT equipment to be readily accessible; modelling showing the predicted direction and distance of any vapour or  $\text{NH}_4\text{OH}$  plume in the water; a requirement for UAVs/ROVs attached with ammonia detectors / pH sensors to be readily available to monitor any vapour or  $\text{NH}_4\text{OH}$  plumes; and; mapping of any sensitive environmental and economic receptors that may be impacted.

This example is for a single port, however, for regional and national plans, models can be used to analyse the number of alternative-fuelled vessels entering their jurisdiction. This information can feed into a risk assessment to identify any significant substances that have not been covered or included within the contingency plan.

As this paper has discussed, the varying ways alternative fuels behave and the potential catastrophic impacts that could occur if not managed correctly shows that regular training for all involved in the response is vital in order to reduce the risks posed by these fuels. In order to work together as a coherent unit, all responders need to understand the contingency plan in place and the roles and responsibilities of themselves and others in implementing the plan effectively. Clear communication channels during these training workshops and exercises facilitates information exchange in the future and allows relationships to be built prior to a spill occurring.

### **PARADIGM SHIFT OF STRATEGIES AND TIMEFRAMES**

The spill response industry works within the paradigm that the substance that is spilled is possible to clean-up. This model has been the case since the industry's inception, as it has



been set up with oil in mind, following significant spills from the 1960s onwards. It is only relatively recently that more focus has been placed on HNS response, although still minor in comparison to oil spill response. However, with shipping's decarbonisation journey approaching and these volatile alternative fuels being introduced to the global fleet, the response paradigm that has been constant, may be starting to shift.

Although oil will still be traded and shipped globally in the long-term, the possible reduction in the volume of oil shipped and the introduction of new fuels may see declining numbers of oil spills and increasing numbers of alternative fuel spills. As a result of this, the timeframe of a protracted oil spill clean-up lasting months to years over large areas may be replaced with spills lasting minute to hours over a confined area. Another shift will be the minimum level of information required at the beginning of an incident in order to ensure the safety of responders and nearby populations.

In the initial emergency phases of conventional oil spill response, timeframes are constricted and despite knowing limited details of the incident, in most cases assumptions can be made safely. For example, it can be assumed that in most cases the oil will be less dense than water and will therefore float on the surface where it will spread and travel under the influence of metocean conditions. A trajectory model can be generated in minutes, which can be used to formulate a general idea of the direction of the slick and whether it is heading for the shoreline or offshore. When notified in the emergency stages of an incident, it is rare to be able to obtain all the information that is requested in order to provide bespoke, accurate technical advice. A good example of this is the fact that it is often a matter of days before the oil specification is provided and accurate fate modelling is able to take place.



However, due to the nature of oil spill response it is more of a frustration than a barrier to initiating a response as the experience gained over 55 years of responding to oil spills means that from a photograph of the oil's appearance, visual assessments can be made as to how the oil will behave at-sea and when it impacts the shoreline. In addition, during mobilisation of resources to a casualty releasing oil, the aim is to attend to the incident location and deploy resources as quickly as possible in order to minimise any further uncontrolled loss of oil. This is a possibility due to the relatively low hazards to human health posed by oil releases.

However as has been discussed, for alternative fuels, their potentially flammable, explosive or toxic nature requires a minimum level of information amongst responders in order to safely attend the casualty. This is especially relevant for 'first responders', namely salvors and firefighters, who are often immediately mobilised to assist the crew and to reduce any damage to the vessel. Crucial information would be the type and quantity of bunker fuel on-board, the weather and sea conditions (primarily wind speed and direction) and signs of bunker spillage (e.g., visible vapour cloud, plume, indicative odour, etc.). Other pertinent information that would likely be requested by a technical expert are as follows:

- Date and time of incident (specifying local time or GMT/UTC)
- Position (e.g., latitude / longitude or distance from nearest port / landmark)
- Cause of incident (e.g., collision, grounding, explosion, fire, etc.) and nature of damage
- Description and quantity of cargo on-board (e.g., dangerous goods, reactive substances)



- Estimated volume of quantity spilled or likelihood of spillage
- Location of breaches to bunker tanks (above or below waterline (estimated distances))
- Capacity and if possible current level of any bunker tanks impacted
- Estimate of the size of any breaches to bunker tanks
- Type of resources that may be at risk (e.g., fisheries or residential areas)
- Distribution of cargo and bunkers and location relative to damage.

Accurate, rapid information acquisition would, in the first instance, allow safety zones to be demarcated so that no vessels are downwind of a possible flammable, explosive or toxic plume, could inform authorities on possible evacuation of population centres and would also inform responders as to what appropriate PPE / respiratory protective equipment (RPE) should be worn. Innovative technology that is being used more during incidents are UAVs that can investigate the casualty closely with real-time footage being relayed to responders from a safe distance. Additionally, if fitted with sensors, they could also confirm the presence or absence of any atmospheric plumes. These devices can act as the ‘canary in the coal mine’ to ensure that it is safe to travel closer to the casualty.

Gathering the key information detailed above during an emergency is likely to be difficult but is a vital step in identifying risks and assisting with their mitigation. For this reason, facility, regional and national spill exercises should focus on the availability and transmission of information, rather than the typical deployment of all response resources. Following the gathering of this data, it is also crucial to disseminate this information among relevant stakeholders. A possible solution would be to have a central online dashboard whereby



information can be shared in real-time as, with many spill response cases, it is likely that different parties (e.g., salvors, national agencies, shipowners, charterers and technical experts) have access to different pieces of information that would fit together and allow for rapid robust risk assessments.

There is also a possibility that a shift might occur relating to moving from mitigating environmental damage to mitigating risks to property damage. This is due to the fact that pollution risks related to alternative fuels are likely to be more localised and short-lived, whereas the risk of property damage and possibly personal injury and economic loss risks from an explosion are significant. For instance, methanol is short-lived in the marine environment and is expected to only cause localised pollution impacts, whereas a methanol explosion leading to the destruction of a large area of a port and the costs associated with that would push the priority to economic rather than environmental sensitivities.

## **CONCLUSION**

This paper has demonstrated the variability of these alternative fuels, not only in comparison to conventional fuel oils but also to each other. The relative similarity of biofuels (FAME and HVO) with conventional hydrocarbons indicates that many of the same response strategies and techniques will still be suitable. In contrast, the lack of response strategies available for spills of LNG, ammonia, hydrogen and methanol indicates a shift in the response paradigm where monitoring and evaluation is likely to be the only technique possible. The human health risks to seafarers, port operators as well as nearby populations and responders are significant and for this reason, preparedness in the form of robust contingency plans, regular exercises and specialist training is key to mitigate against these



risks as much as possible. The shift to hazard-driven decision-making following reports of a spill means that rapid information transmission and dissemination to all relevant stakeholders is key, unlike the current delays in acquiring oil spill information until days after the incident. Due to the non-persistence of many of these alternative fuels, the focus may shift from reducing pollution damage, which is likely to be relatively short-term and localised, to reducing property damage impacts, which may prove to be significantly more costly.

Although, alternative-fuelled vessels are likely to make up only a small portion of the global fleet over the next few years, it is essential that the spill response community invests in research, shares experiences from previous incidents and promotes communication with parties, such as ship designers and builders, class societies and alternative fuel manufacturers as there are still significant research and knowledge gaps for the industry to address, so that it is advancing alongside these fuel technologies and not playing catch-up.



## REFERENCES

Alcaro, L., Brandt, J., Giraud, W., Mannozi, M., Nicolas-Kopec, A. 2021. MARINE HNS RESPONSE MANUAL Multi-regional Bonn Agreement, HELCOM, REMPEC. Project WestMOPoCo, Bonn Agreement, London, UK, 2021: 321.

DNV-GL. 2024. Alternative Fuel Insights Platform. DNV-GL. Høvik, Norway <https://afi.dnv.com/> (last accessed: 26.02.24).

DNV-GL. 2023a. Energy Transition Outlook 2023: Maritime Forecast to 2050, DNV-GL. Høvik, Norway. <https://www.dnv.com/energy-transition-outlook/download> (last accessed: 01.03.24).

DNV-GL. 2023b. White Paper: Biofuels in Shipping, DNV-GL. Høvik, Norway. <https://www.dnv.com/maritime/publications/biofuels-in-shipping-white-paper-download> (last accessed: 24.02.24).

Jezequel, R., Duboscq, K., Valladeaud, F., LeFloch, S. 2019. Fate, Behaviour, and Impact Assessment of Biodiesels in Case of an Accidental Spill. In: Proceedings of the 42<sup>nd</sup> AMOP Technical Seminar, Environment and Climate Change Canada. Ottawa, Canada, 42: 919-939.

Howard, P.H., Boethling, R.S., Jarvis, W.F., Meylan, W.M., Michalenko, E.M. 1991. Handbook of Environmental Degradation Rates, Lewis Publishers Inc. Michigan, USA.

Kass, M. D., C.S. Sluder, B. Kaul. 2021. Spill behaviour, detection, and mitigation for emerging nontraditional marine fuels. Oak Ridge National Laboratory. Report no. ORNL/SPR-2021/1837. US Department of Energy, Washington D.C., USA.



Katsumata, P.T., Kastenber, W.E. 1996. Fate and Transport of Methanol Fuel from Spills and Leaks. In: Hazardous Waste and Hazardous Materials 13 (4), 485–498.

Kneebone, A and L.R. Prew, Shipboard jettison test of LNG onto the sea. In: Proceedings of the 4th International Conference on LNG, Algiers, Algeria. 1974: 1–25.

Luketa-Hanlin A. 2006. A review of large-scale LNG spills: experiments and modelling. J Hazard Mater. 2006 May 20; 132(2-3): 119-40.

Machiele, P.A. 1989. A Perspective on the Flammability, Toxicity, and Environmental Safety Distinctions Between Methanol and Conventional Fuels. US Environmental Protection Agency, Washington D.C., USA.

Malcolm Pirnie, Inc. 1999. Evaluation of the Fate and Transport of Methanol in the Environment. Report: 3522-002. California, USA.

May, W.G, McQueen, W., Whipp, R.H. 1973. Spills of LNG on water, American Gas Association, Operation Section Proceedings, Paper 73-D-9.

Raj, P.K., Hagopian, J., Kalelkar, A.S. 1974. Prediction of Hazards of Spills of Anhydrous Ammonia on Water. Report No. CG-D-74-74, US Coast Guard, Washington D.C., USA.

Witcofski, R.D., Chirivella, J.E. 1984. Uses of the mechanisms governing the dispersion of flammable clouds formed by liquid hydrogen spills. International Journal of Hydrogen Energy 9 (5), 423–435