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Spill Behavior, Detection, and Mitigation for Emerging Nontraditional Marine Fuels

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Buildings and Transportation Science Division

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ABBREVIATIONS

DME	dimethyl ether
HFO	heavy fuel oil
IR	infrared
LNG	liquified natural gas
MDO	marine diesel oil
SAR	synthetic aperture radar
SVO	straight vegetable oil
UAV	unmanned aerial vehicle
UV	ultraviolet
VLSFO	very low sulfur fuel oil

FORWARD

In this report, we describe the predicted impact of large spills or releases of alternative marine fuels. The fuels covered in this report are those that have been identified as potential future fuels for the marine shipping sector by industry experts and government agencies overseeing the development of renewable and low-carbon fuels. Several of these fuels are already in use, such as liquified natural gas, renewable diesel, ethanol, methanol, and biodiesel. Other fuels are hydrogen, dimethyl ether, ammonia, and bio-intermediates, such as catalytic fast pyrolysis bio-oils and hydrothermal liquefaction bio-crudes. The property databases of these fuels are extensive enough to form predictive assessments. Other potential marine fuels, such as lignin ethanol, have not been extensively evaluated and are therefore not included is this study. For each fuel chemistry, we have surmised the spill profiles and environmental impacts based on existing studies and relevant properties. The technologies used to detect spills (especially those for crude oil detection) are also reviewed for their applicability with alternative fuels, and in some instances, recommendations to improve these technologies for use with a particular fuel chemistry are put forward. Finally, current containment and remediation technologies are reviewed and assessed for their efficacy at handling these alternative fuels.

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EXECUTIVE SUMMARY

BACKGROUND

The use of nontraditional fuels in the marine sector is expected to increase significantly in the next 30 years. This development is being driven by the International Maritime Organization goal of reducing greenhouse gas emissions from marine shipping by 40% in 2040 and 50% in 2050 (compared with 2008 levels). Near-term carbon dioxide reduction targets are being met through more efficient ship designs and operations, but the 2040 and 2050 targets will most likely require the use of a low-carbon or renewable fuel. Fuels being actively evaluated and considered include liquified natural gas, biofuels (such as bio-alcohols, biodiesel, renewable diesel, and pyrolysis oils), and zero-carbon fuels (such as hydrogen and ammonia). The potential impacts and hazards of many of these fuels in the event of a spill (or release) are not known and need to be assessed before any alternative fuel chemistry can become established. Petroleum spills are often associated with ruptures of large crude oil tankers or offshore well releases that make global headlines; however, spills of fuels used to power the engines are more commonplace. While the spilled volume is lower than that associated with a crude oil spill, it can still be quite significant considering that the fuel tanks may hold up to 3,500 m^3 (more than 900,000 gal) of heavy fuel oil (HFO; usually composed of residual oil blended with lighter components to be near 380 mm^2/s at 50°C). Similar to crude oil, HFO is highly stable and detrimental to the environment. HFO is usually denser and is less flammable than crude oil, which can make containment and cleanup (via in situ burning) more difficult.

Accidental releases occur during refueling, collisions, or sinking. Most spills that occur during refueling are relatively small. However, releases caused by collisions and sinking also occur and in these cases, the released volume can be as high as the fuel tank capacity. More than two dozen large vessels are lost at sea every year. The hazards associated with large spills of HFO are fairly well understood since HFO has been used as a marine fuel for more than 70 years. Experience and knowledge gained from the large releases of crude oil have also contributed to an understanding of the environmental impacts and detection of HFO at sea. However, the spill behavior (including the physical state), hazards and reactivity of many nontraditional fuels are drastically different from HFO or distillate marine oils. In many cases, even small releases (e.g., hydrogen, ammonia, alcohols) can be serious safety concerns. Additionally, the technologies and methods currently used to detect releases of crude oil or HFO are not likely to be suitable for many alternative fuels. Before a nontraditional fuel can be widely used to power marine vessels, its spill behavior needs to be assessed. Additionally, the ability of established detection, containment, and cleanup technologies for large spills needs to be evaluated for each fuel type under consideration. The purpose of this report is to provide a comprehensive summary document on what can be expected from a large release (spill) of nontraditional marine shipping fuels.

SPILL BEHAVIOR OF NONTRADITIONAL MARINE FUELS

When HFO is spilled from a ship at sea, it will form a dense, highly viscous slick that will expand outward from the release point. The spread rate will be relatively slow because of the high viscosity of the HFO, and the slick will be characteristically thick. If its density is less than the surrounding seawater, it will float; otherwise, it will be suspended in the water column. The inherently high viscosity and stability of HFO will likely prevent the formation of an emulsion with the surrounding water, but globules may form as a result of wave action. Over time, the HFO will slowly oxidize, which will increase its density, thereby causing the spill to eventually sink in the water column. The depth will depend on the density or degree of oxidation. In contrast, a distillate or marine gas oil spill has a much lower viscosity and density than HFO. It will rapidly spread on the sea surface and have a low film thickness, which become thinner the further the spill spreads. In this section, non-traditional fuels and their properties will be discussed relative to HFO.

Renewable Diesel, Biodiesel, and Vegetable Oil

The only alternative fuel options that will approximate the behavior of the HFO or distillates are those that are liquid under ambient conditions. Renewable diesel, also known as "hydrotreated vegetable oil," is similar to petroleum distillates such as marine gas oil and its spill profile will behave similarly. It is considered nontoxic and will biodegrade at a faster rate than marine distillate fuels. Biodiesel will also have a similar spill profile under ambient conditions where the outside temperature is above 10°C. It is also relatively nontoxic and will biodegrade quickly when released into the environment. If released into a cold environment where the outside temperature is near 0°C, biodiesel will gel, which will subsequently increase the thickness of the slick. The spill profile, toxicity, and degradation rate of vegetable oil is expected to be analogous to biodiesel. It is less processed than biodiesel and is therefore more susceptible to gelling and solidification when released into a cold environment.

Bio-Intermediates (Bio-Oils and Bio-Crudes)

The spill profile of bio-intermediates will depend heavily on whether they are in the raw condition or have undergone additional processing to remove water and oxygenates. In the raw forms, they are usually heavier than water and can be expected to sink in the water column when released. A fraction of the bio-oil is soluble and will rapidly dissolve into water. The insoluble component has high viscosity and will remain as a thick slick below the water surface that may eventually separate into globules. Wave action may also emulsify the bio-oil, and it will take on the appearance and consistency of peanut butter. Over time, the slick or globules will slowly polymerize, which will further increase the density such that the slick may coat the shoreline and sea floor. Any sea life coming into contact with a bio-oil will become coated with it. Bio-oils are toxic to aquatic life and will not degrade as quickly as biodiesel or renewable diesel. It has the potential have long-term effects on marine life. The properties of hydrothermal liquefaction oils, also known as "bio-crudes," are less well known, but their spill behavior is expected to behave similar to bio-oils. In general, bio-crudes tend to be more viscous than bio-oils, so a thicker slick can be expected.

Alcohols

Ethanol and methanol have high partition coefficients and will dissolve rapidly into the surrounding seawater when spilled. They will also rapidly dissipate into the atmosphere if released on deck; however, immediately after spilling, the surrounding air will be displaced and suffocation is possible, especially if the spill is confined in a small area. The risk of fire is also high because these fuels are highly volatile and flammable. Both methanol and ethanol are toxic, and marine life in close proximity to the release point is vulnerable. Fortunately, neither ethanol nor methanol will bioaccumulate in the ecological food chain. Because of the high rate of dissipation, they will not remain in high concentrations for long and will likely be dissipated before clean-up activities can begin.

Dimethyl Ether

When used as a transportation fuel, dimethyl ether is stored as a liquid (under moderate pressure). When released suddenly, a visible vapor cloud of condensed water vapor may form at the release point. It will form a dense gas on the water surface, where it will spread and dissipate rapidly. Dimethyl ether will behave similarly to the alcohols, except that it is insoluble with water and will not disperse in the water column. Because dimethyl ether is denser than air, suffocation is a risk for marine life at the water surface near the release point. It is highly flammable and therefore, fire is a high risk.

Liquified Natural Gas and Hydrogen

The spill behaviors of liquified natural gas and liquified hydrogen over water have been the subject of numerous studies. Natural gas and hydrogen are stored under cryogenic conditions to improve their energy density and reduce the storage volume. These gases are lighter than air under ambient conditions, but they are heavier at the very cold temperatures near their boiling points. Therefore, they will sink immediately upon release and will form a white vapor cloud at the water surface. Neither of these fuels are highly soluble with water and they will remain on or above the surface until they mix with the surrounding air, heat up, and dissipate upward. The dissipation process is rapid, and the visible vapor cloud will disappear within 30 min for large discontinuous spills. One consequence of this rapid dissipation is that released gas cloud does not spread beyond 100 m on the water surface from the release point. Their spill profile is wind-dependent. Under very low wind speeds, the vapor clouds will not extend beyond 30 m on the water surface from the release point. More moderate to high wind speeds will push and expand the vapor cloud footprint on the water surface. As a result, fire and suffocation risks are much higher under windy conditions. Because hydrogen is lighter than natural gas, it will not spread as far as a liquified natural gas release. However, hydrogen is much more flammable than natural gas and the released heat energy is higher. Suffocation is a risk for aquatic and human life in the cloud zone.

An added potential risk associated with the sudden release of LNG or liquified hydrogen over seawater is that a rapid phase transition will occur when these liquids contact water. The rapid and violent boiling of these fuels may cause a cold explosion due to the rapid volume expansion as the liquid fuel transitions to the gas phase. As a result, the immediate vicinity of where the liquid fuel contacts the seawater may be subjected to a damaging shock wave.

Ammonia

Similar to dimethyl ether, ammonia is stored as a liquid under pressure. When released suddenly, a white vapor cloud containing condensed water vapor will form near the release point. Ammonia is lighter than air and will eventually dissipate into the atmosphere, but if it contacts the water, it will react to form highly soluble ammonium hydroxide. Both ammonia and ammonium hydroxide are highly toxic. The water surface where this reaction takes place will become heated as this reaction proceeds. The newly formed ammonium hydroxide is lighter than water and a layer will form on the water surface near the release point. At further distances, it will dissipate in the water column because of diffusion. Ammonia is not flammable. The main safety concerns will be associated with its toxicity and suffocation.

DETECTION AND MITIGATION

Established detection and mitigation methods will have limited use for many nontraditional marine fuels. Radar-based detection is the most common means of remotely identifying a spill of crude oil or HFO. This method detects surface wave attenuation caused by a floating viscous slick. The only alternative fuels that have similar properties are bio-intermediates. However, because these fuels are usually denser than water, they will not likely float. They may, however, still attenuate waves if they do not sink far below the water surface. Visual observations can be made of opaque surface slicks formed by fuel in water emulsions or if the alternative fuel forms a sheen. Cryogenic (and compressed) fuels can be identified by their vapor clouds at the release point, but the impacted area will not be large and these vapor clouds will not last long. Current infrared (IR) imaging techniques are turned to specifically image crude oil and HFO spills. This approach may be successful at detection of biofuels and cryogenic fuels. For cryogenic fuels, IR imaging will need to have high resolution to detect the cold regions on the ship and in the water near the release point. IR imaging of slick forming nontraditional fuels may be possible but requires further studying to determine if a detectable IR signature exists.

Current detection methods based on laser-induced fluorescence will not work for the alternative fuels listed in this study. Because these fuels do not contain aromatics, they will not be excited by the currently used laser signatures. The laser frequency may potentially be adjusted to excite a molecular structure inherent in a given alternative fuel, but further investigations are needed to assess the efficacy of this approach.

Chemical analysis of the water and air offer a potentially viable means of detection. The detection of fuel compounds becomes difficult the further the detector or sample is from the release point because of dilution. The technologies used to identify individual compounds are expensive and require contact with the air or water sample. Therefore, this type of detection is more likely applicable to port regions.

CONTAINMENT AND REMOVAL

With the exceptions of renewable diesel, biodiesel, and bio-intermediates, the dissipation of a sudden release of a gaseous fuel or alcohol will happen too rapidly for a containment and removal strategy to be employed. The slick-forming fuels can be contained with traditional booms, but bio-intermediates may not be close enough to the water surface for a boom to effective. In situ burning is not likely to be effective since the slick-forming fuels do not have flammable components. However, in situ burning could possibly be useful if a flammable fuel is added to the slick. Fortunately, many of these slick-forming fuels are not highly toxic and are readily degraded by bio-organisms. Bio-intermediates can be especially challenging because they will likely be suspended in the water column and are not expected to degrade rapidly.

SUMMARY STATEMENT

During a large, sudden release at sea, few of the nontraditional marine fuels examined in this study are expected to behave in the same manner of crude or residual fuel oils. Fortunately, fuels capable of forming surface slicks have low toxicity and are readily decomposed. Alcohol spills and releases of gaseous fuels (whether compressed or cryogenically stored as liquids) will create hazards (fire/explosive risks, toxicity, suffocation) during and immediately following a release. These fuels will dissipate quickly. Ammonia is highly toxic and is expected to be detriment to aquatic life near the spill zone. Bio-intermediates are likely to sink below the water surface, where their toxicity and slow rate of decay will be problematic to aquatic life.

The spill detection and remediation methods used to monitor and remove spills of crude oil will not work as effectively for alternative fuels. Gaseous and alcohol fuels will rapidly dissipate before any cleanup technologies can be employed. Biodiesel and vegetable oils will be visible for a short time after being spilled, but they will readily be dispersed in the water column, where they cannot be ignited nor captured effectively by boom-type methods. Bio-oils and bio-crudes will also not be easily detected and their heavier density relative to water means that traditional detection and remediation technologies (developed for surface slicks) will not be effective.

1. INTRODUCTION

1.1 PURPOSE

The chief purpose this document is to provide an assessment of the impacts of a sudden large release (or spill) of an alternative fuel at sea or in port from a marine vessel. Alternative fuels are being explored as substitutes for heavy fuel oil (HFO; usually composed of residual oil blended with lighter components to be near 380 mm^2/s at 50°C) to minimize environmental impacts associated with the combustion of heavy petroleum, namely greenhouse gas, oxides of nitrogen (NO_X), and particulate matter emissions. They include low-flashpoint fuels such as hydrogen, liquified natural gas (LNG), dimethyl ether (DME), methanol, ethanol, bio-intermediates, biodiesel, renewable diesel, and ammonia. The chemistries and physical properties vary widely depending on the fuel type and in many cases are drastically different from HFO, which is the primarily fuel used to power large merchant vessels. Spills of HFO, which is typically used to power large marine ships, are of high concern since they are highly stable and often cause long-lasting environmental damage comparable to spills of raw crude oil. The impacts and risks of spills of alternative fuels to the environment, along with their detection and cleanup, are not well understood. The information and recommendations contained within this report are expected to help the community better understand the risks associated with alternative fuel use on marine vessels. This report seeks to document and assess the spill characteristics, hazards, and efficacy of existing detection and remediation methods that have been developed for releases of crude oil and HFO. Many of the approaches currently used to detect, contain, and clean up large releases of HFO and crude oil are not expected to be applicable. Alternative approaches and recommendations are put forth to help address these issues.

1.2 BACKGROUND

Since the 1950s, HFO has been the predominant fuel used to power large marine vessels of all types, including cargo vessels, cruise ships, and some merchant and fishing vessels (Wankhede 2020). The driving factors for expanded HFO use have been low cost and relatively lax emission regulations. HFO is derived primarily from the crude oil residual fraction and therefore contains high levels of sulfur, ash, and water. Marine vessels consume more than 300 million metric tons of HFO and distillate fuel per year, resulting in significant generation of greenhouse gases and particulate emissions (Kass et al. 2018). The fuel tanks of cargo vessels can hold up to 2.5 to 3.5 million gallons in capacity and, therefore, the potential for serious environmental damage is high when the bunker tanks are breached. Additionally, HFO is also transported as cargo in even larger quantities. A review of recorded spill incidents of heavy marine fuels shows that these incidents are relatively common. As reported by Ansell et al. (2001), approximately 40% of all oil spill incidents in the 25 years preceding 2001 were HFO spills. Several of these incidents caused serious harm to the environment and therefore, ships powered using HFO are currently banned from the Antarctic and restrictions are being considered for Arctic transport.

In 2005, the International Maritime Organization, along with government and state agencies, initiated regulations designed to reduce sulfur emissions from HFO-fueled vessels operating in coastal regions known as emission control areas (Kass et al. 2018). For deep sea cargo vessels, these new requirements were met by switching from HFO to distillate fuel when entering emission control areas. These regulations do not preclude ships from switching back to HFO when operating outside of emission control areas, and therefore have little effect on total global shipborne emissions. The International Maritime Organization acted in 2020 to limit sulfur emissions at sea through reducing the sulfur content in HFO from a nominal level of 2.5% to 0.5%. The new 0.5% sulfur fuel is often referred to as very low sulfur fuel oil (VLSFO); it and marine diesel oil (MDO), a blend of HFO and distillate diesel fuel, will not be considered separately from traditional high-sulfur HFO for the purpose of this report, as the spill properties are similar. For simplicity, all of these fuels will be referred to as HFO throughout this report regardless of sulfur content. Similarly, marine gasoil, a distillate diesel fuel, is not substantially differentiated from on-highway diesel fuels from a spill impact/response perspective: all references to diesel fuel should be read as applying to petroleum-based distillate diesel fuels in general.

As part of its future strategy, the International Maritime Organization has put together a framework with the stated goal of a 50% reduction in greenhouse gas emissions (compared with 2008 levels). The organization is also pursuing efforts to eliminate greenhouse gas emissions entirely. The marine shipping community is aggressively evaluating alternative (low-carbon) fuels to meet these targets (Thepsithar 2020, DNV-GL Maritime 2018). These targets are also being pursued by the marine shipping community primarily through the use of low- and net-zero carbon fuels.

One pathway that is gaining attention is the use of biofuels as a means of reducing carbon intensity (Kass et al. 2018, Kesieme et al. 2019, Abbasov 2018). Biofuels are considered a significant step toward carbon neutrality since the plant feedstock uses atmospheric carbon dioxide to promote cellular growth. They are also inherently low in sulfur (in most cases) and, in the case of oxygenated biofuels, can significantly lower particulate emissions. Traditional biofuels include biodiesel and ethanol. These fuels are established as engine fuels (usually as blends) to power on-highway vehicles. Less traditional biofuels include pyrolysis-derived bio-oils, hydrothermal liquefaction bio-crudes, DME, bio-derived natural gas, methanol, and renewable diesel. Methanol is also of high interest because it is currently produced at a large scale and has good combustion properties. Pathways to net-zero carbon emissions have predominantly centered on ammonia and hydrogen, which can be synthesized without using biomass as a feedstock.

Some alternative fuels are used in the marine sector today. The most common are LNG and methanol, which are used to fuel the ship engines of tankers used to transport these chemicals. LNG is also being considered as a fuel for dry cargo vessels since it is low in sulfur and has significantly lower particulate emissions than HFO or distillate.

Before a new fuel is approved for broad commercial use, its environmental impacts need to be evaluated. One of the most serious concerns is the sudden release from a vessel. The primary focus of spill studies has been on crude oil releases from offshore rigs and the large tanker vessels that transport crude petroleum from the production sites to the refineries. For the large ship-based spills, the cargo hull (containing crude oil) is usually breached rather than the actual ship fuel tank (containing HFO). Spill volume and release rate influence the initial spill characteristics (Shaw's Environmental and Infrastructure Group 2011). Spills from oil tankers can be massive. For example, the *Exxon Valdez* released 10 million gallons to the environment, making it the largest tanker spill in the United States.

The chemical and physical properties of many alternative fuels differ substantially from crude oil and HFO. As a result, the spill characteristics (e.g., appearance, slick thickness, spread rate, volatility, toxicity) will be dramatically different, especially with respect to crude oil and HFO. Spills of non-petroleum products have also been recognized by the US Environmental Protection Agency (EPA 1999), which recognizes the potential threat from large releases of biofuels and vegetable oils.

1.3 DIFFERENCES AMONG CRUDE OIL, HFO, AND ALTERNATIVE FUELS

Historically, spills of crude oil have been the primary concern for detection and mitigation efforts because the potential volume of released crude oil is much higher than for releases of engine fuels. For instance, the largest oil tankers can contain up to up to 150 million gallons of crude oil, while releases from off-shore rigs can be massive as evidenced from the approximately 210 million gallons of crude oil released from the Deepwater Horizon rig in 2010 (Pallardy 2011). However, spills of HFO are not negligible as was seen in the *Prestige* oil spill, which released 17.8 million gallons of HFO off the coast of Spain and Portugal (Camphuysen et al. 2002), causing serious environmental and economic damage. To put this spill into context, it was larger than the volume of crude oil released during the *Exxon Valdez* incident.

At first glance, HFO, which is primarily composed of the heavier molecular weight fraction of crude oil, appears to be quite similar to crude oil. However, key differences exist. Crude oil typically contains a large fraction of hydrocarbons, including volatiles, which do not exist in HFO. HFO is also denser and more viscous than most crude oils, making it less prone to emulsifying with the surrounding water. These features also cause HFO to persist longer in the marine environment and travel further. The thickness of HFO slicks range from 0.5 to 1.0 cm, in contrast to crude oil, which can vary from 1 to 5 mm (Fritt-Rasmussen et al. 2018). (The lighter-weight and more volatile components of crude oil have slick thicknesses of <1 mm). The higher viscosity of HFO means that its slicks will be thicker and spread less than those of crude oil. Mechanical booms, which have rails extending beneath the water surface, are the most effective means of mitigating HFO spills.

Current spill detection and mitigation methodologies and technologies were developed to address spills of crude oil. The properties of crude oil are highly variable depending on the source, but the vast majority of crude oils have densities equivalent to or less than that of water. Therefore, crude oil spills will typically float on the sea surface, which allows for detection using several technologies. Because of its higher density, HFO is neutrally buoyant near the surface or in the water column. This inability to float much above the surface makes it difficult to visually see and contain with some skimmers that are specifically designed for lighter crude oil (Ansell et al. 2001). Because crude oil and HFO are highly stable, their degradation rates are low; thus, they can remain in the environment for long periods, especially in colder climates. HFO will eventually break down into smaller tar-like masses that polymerize over time. Emulsification can occur slowly under high mechanical agitation of the surrounding water. The level of agitation required to emulsify HFO is higher than other marine fuels because of its high viscosity.

Studies examining the effectiveness of spill recovery technologies and methods have shown that mechanical recovery mechanisms (booms) are the most effective means of containment (Fritt-Rasmussen et al. 2018). In situ burning is not effective because of the lack of light (volatile and flammable) hydrocarbon compounds and the suspension of much of the HFO mass in the water column. These two factors also preclude the use of existing chemical dispersants.

The technologies and methods established for spill detection, containment, and mitigation have been developed predominantly for releases of crude oil and are unlikely to be effective for many of the alternative fuels being considered. Of the alternative fuels being considered, only LNG and ammonia have been extensively studied for their spill behavior and impact associated with sudden large release at sea. (However, it is important to note that alcohol spills have been evaluated for terrestrial and inland water scenarios.) The high volatility and partition coefficients of these fuel types preclude any of the containment and cleanup technologies established for crude oil. These approaches are likely also unsuitable for many of the other alternative fuels. The purpose of this report is to elucidate the expected spill behaviors of these alternative fuels and their impacts to the environment and human health. This report seeks to provide a ready source of information to gain insight into what happens when a major release of an alternative fuel occurs at sea.

Hydrocarbon fuels, especially alcohols, oils, and distillates, will degrade naturally, both by oxidation reactions and by microbial degradation, which is usually the more predominant mechanism. Natural chemical degradation is widely studied by environmental scientists. The rate of degradation of a substance is referred to in terms of half-life (the time it takes for half of a substance to become decomposed). Temperature is an important factor because microbes are less effective in colder climates than in warm ones. Releases in the polar regions are particularly problematic and long-lasting. Natural decay may take decades to occur for large spills of crude oil; however, the natural remediation of alternatives fuels is not as well understood. Another factor heavily influencing the degradation rate is the surface area of the slick. High surface areas usually accompany low-viscosity, low-density slicks. The high surface area relative to volume accelerates the processes associated with degradation (photooxidation, evaporation, microbial degradation) of the spill.

This study assesses the impacts of alternative fuel spills by examining their properties (physical and chemical) in relation to the expected spill or plume characteristics. Key characteristics include spill (or plume) profile, physical state, and the stability of the released fuel. Dissolution, evaporation, and degradation kinetics are discussed alongside the potential resulting hazards, which include fire risk, suffocation (by air displacement), contamination, and toxicity. While toxicity of the fuel will not influence the spill profile, it can have a detrimental impact on human health and the environment (in terms of dead and dying marine life). Marine life can also be harmed if oxygen is removed from the surrounding water during decomposition.

2. CHEMICAL AND PHYSICAL PROPERTIES AND THEIR IMPACTS ON CHARACTERIZING FUEL SPILLS

The chemical and physical properties of a fuel, as well as the storage conditions, govern the spill behavior and profile of the released gas or slick (EPA 1999). Gaseous fuels such as natural gas, DME, hydrogen and ammonia, are pressurized to maintain a liquid state and reduce storage volume. In the case of hydrogen and natural gas, the stored liquid is also kept at ultralow (cryogenic) temperatures. When a container of pressurized fluid is breached or vented, the release rate will be extremely rapid with the liquid phase immediately boiling to become vapor. In this scenario, a complete loss of fuel is expected. Fuels that are liquid under ambient conditions (e.g., alcohols, biodiesel), will remain the liquid state when released, though some (such as alcohols) will volatilize over time.

Physical properties, such as viscosity and density, are well-established factors shaping the thickness and spread rate of a slick. Most fuels have densities lighter than water and are therefore visible on the surface of the water. For oceanic spills, the spread rate is proportional to the oil-water density difference and reduced viscosity (also known as "Fay spreading") (Fay 1971). Fay spreading was derived for oil-type fuels that do not readily dissolve or volatize. Therefore, the relationships will generally hold for fuels such as biodiesel, vegetable oils, and renewable diesel. For fuels that readily dissolve in seawater and are volatile, the forces governing solubility and evaporation will govern the spill profile and behavior.

Solubility is intrinsically a chemical property that relates to the weak bonding forces that govern dissolution. For fuel spills, solubility with seawater is a critical parameter and is denoted by the partition coefficient or ratio, which is a means of assessing how readily a fuel will dissolve (or partition) into the water. Substances that can readily dissolve into water will disperse at a high rate, whereas those that are insoluble will remain intact and separate from the surrounding water. Stronger chemical reactions such as oxidation and polymerization also play a role by increasing the density of heavier fuels, which can cause them to drop in the water column, making detection and cleanup difficult. When heavy fuels age and sink, they may accumulate on the bottom of shallow regions, such as shorelines. Highly volatile fuels such as alcohols, natural gas, and hydrogen are extremely flammable and easily ignite. Highly flammable fuels necessitate differentiating safety precautions than diesel-type fuels.

2.1 ENVIRONMENTAL FACTORS

The environment plays a key role in determining the characteristics of a spill (Fritt-Rasmussen 2018, Fay 1971, Fingas and Brown 2014, 2017). These factors include wind, wave action, temperature, geography, and cloud cover. Wind greatly affects the spill direction and slick shape. It has been shown to be the key factor influencing the profile of released gaseous fuels. Wave action is necessary for mixing and subsequently emulsifying the spill. Emulsification of the spill complicates containment and cleanup since the spilt fuel is now dispersed in the water column. These dispersions allow the oil to become more readily available and therefore hazardous to marine life and the ecosystem. However, emulsions have been shown to be less prone to adhering to solid objects, such as shorelines (Fritt-Rasmussen 2018). The rate of dispersion is directly proportional to wave action. This action will also increase mixing and subsequently dissolution of nonaqueous surface liquids. Wave action also affects visual observation; however, some detection methods rely on wave effects for detection. Ambient temperature is another key controlling feature as mentioned earlier. Spill degradation rates are often accelerated by photooxidation, which is derived from sunlight. As a result, nightfall and cloud cover can extend spill life. The other important degradation mechanism is via microbes, which feed off the fuel. Microbial action is highly temperature-dependent and can be expected to be highest in warm tropical regions and weakest in the cold polar regions.

2.2 ALTERNATIVE FUELS CONSIDERED, FUEL PROPERTIES, TOXICITY, AND COMPARISON TO CONVENTIONAL MARINE FUELS

The alternative fuels examined in this study can be classified into two broad categories based on their volatility. Highly volatile fuels, such as alcohols, natural gas, DME, and ammonia, will quickly evaporate and undergo rapid dissemination in the environment. Less volatile fuels, such as renewable diesel, biodiesel, and vegetable oils, will remain in liquid form under ambient conditions and can be expected to remain in the environment for extended periods. Water solubility is also an extremely important factor contributing to dissipation and environmental concerns. The key physical properties are summarized in Table 1 for the nontraditional fuels examined in this study. As can be seen from the table, only the alcohols and ammonia are highly soluble in water. The overall solubility level of the bio-intermediate fuels is not known with any precision, but an appreciable amount of their constituents will go into solution. Another general observation is that, except for the bio-intermediates, the fuel densities are lower than the surrounding sea water. For the gaseous fuels listed in the table, natural gas, hydrogen, and ammonia are lighter than air and will be expected to rise. The only gaseous fuel evaluated in this study which is heavier than air is DME.

Table 1. Properties affecting spill profile for selected nontraditional marine fuels.

Fuel type	Density (g/ml)	Boiling point (°C)	Flashpoint (°C)	Water solubility	Kinematic viscosity at 40°C (mm^2/s)
Renewable Diesel	0.77 - 0.8	280 - 330	52	Negligible	2.0 - 4.0
Ethanol	0.789*	78.2	14	High	0.011
Methanol	0.792*	64.7	10 - 11	High	0.006
Biodiesel	0.82 - 0.88*	315 - 350	100 - 170	Negligible	3.5 - 5.0
Vegetable oil	0.91 - 0.95*	~300	250 - 340	Negligible	25 - 50
Bio-oil	1.1 - 1.3*	>300	Decomposes	Moderate	40 - 80
Bio-crude	0.97 - 1.04*	>300	Decomposes	Moderate	~70
DME	$2.1 \cdot 10^{-6}$**	−24	-41	Negligible	N/A
LNG	$0.717 \cdot 10^{-6}$**	−161	-188	Negligible	N/A
Ammonia	$0.8 \cdot 10^{-6}$**	−33.3	132	High	N/A
Hydrogen	$0.093 \cdot 10^{-6}$**	−252.9	N/A (highly flammable)	Negligible	N/A
* at 25°C					
** at 0°C					

In most cases, the spill profiles and risks were obtained from literature sources based on controlled observations and modeling results. For fuel chemistries not previously studied as releases, the spill characteristics were obtained based on the properties listed in Table 1. These characteristics are discussed in detail in this section and are summarized in Table 2 at the end of this section.

2.2.1 Renewable Diesel

Renewable diesel is also widely known as “hydrotreated vegetable oil” (Engman et al. 2016, REG 2019). The feedstock is highly variable and the hydrotreating process produces a paraffinic fuel that has physical properties very similar to petroleum distillates. A key noteworthy difference is that renewable diesel does not contain any of the aromatic structures present in petroleum. Because it does not contain aromatics, it is considered to be less toxic than distillates. The spill profile is expected to be similar to diesel since it has similar viscosity. Also, because it is colorless, renewable diesel will form a clear oily slick on the water surface. Limited studies have shown that renewable diesel has low toxicity to key marine organisms, though additional studies are recommended to confirm responses on a wider range of marine and shore life (McKone et al. 2011). The degradation rate of renewable diesel in the environment has not been studied in detail. Based on its composition (and the lack of aromatic compounds), it will be more susceptible to biodegradation than petroleum-derived distillates. Its predicted degradation rate is somewhere between that of biodiesel (which is composed of fatty acid methyl esters) and petroleum diesel.

2.2.2 Ethanol

Ethanol is an established transportation fuel for on-highway vehicles. Since its introduction in the 1970s, ethanol has almost always been blended with gasoline at levels ranging from 10% to 85%. Because of its history of extended use, a large body of research is associated with ethanol fuel properties, including those associated with safety and compatibility (Howard 1991, Renewable Fuels Association 2016, GSI Chemical Database 2020a). As shown in Table 1, ethanol boils at 78°C, but its relatively high volatility means that it will eventually evaporate over time if left in the open. Ethanol is also completely soluble with water, and when dissolved in water, it becomes much less volatile. According to one study, when released into surface water areas, a portion of ethanol will initially float as a light nonaqueous liquid film (Shaw’s Environmental and Infrastructure Group 2011). Given ethanol’s high solubility with water, this surface film will rapidly disappear because of evaporation to the atmosphere and dissolution into water (Shaw’s Environmental and Infrastructure Group 2011). Notably, dissolution is the more dominant process, and the majority of the ethanol spill will end up dissolving into the surrounding water. Once in the water phase, ethanol will rapidly disperse and subsequently be destroyed via microbial action. Ethanol is known to be toxic to aquatic organisms, but because of rapid dispersion, only those organisms located close to the source of the release point will be impacted. It also has a low bio-concentration factor, meaning that it will not bioaccumulate in the ecological food chain.

When a large volume of ethanol is released suddenly, it will immediately collect on the water surface because it is less dense than water and is heavier than air. It also has a low viscosity and will spread rapidly. Immediately upon release, there will also be a vapor phase immediately above the nonaqueous liquid surface phase. These phases are shown graphically in Figure 1. These phases will be short-lived, but while present, air will be displaced at the surface region. Given the high dissolution rate, surface-based suffocation due to air displacement is unlikely to occur much beyond the release point. Ethanol is also toxic at high concentrations, but because of rapid spreading and water diffusion, areas not in the immediate vicinity of the spill will likely be unaffected. A more serious concern is the risk of fire. Ethanol is highly flammable, and liquid or vapors collected on the ship's deck or near the release point can readily ignite. Any resulting fire will be hazardous to the ecosystem in the vicinity of the fire, not to mention the ship's crew or nearby personnel. At sea, the fire can potentially burn the ship, while a spill in a port location will also be a fire hazard for the port infrastructure and population.

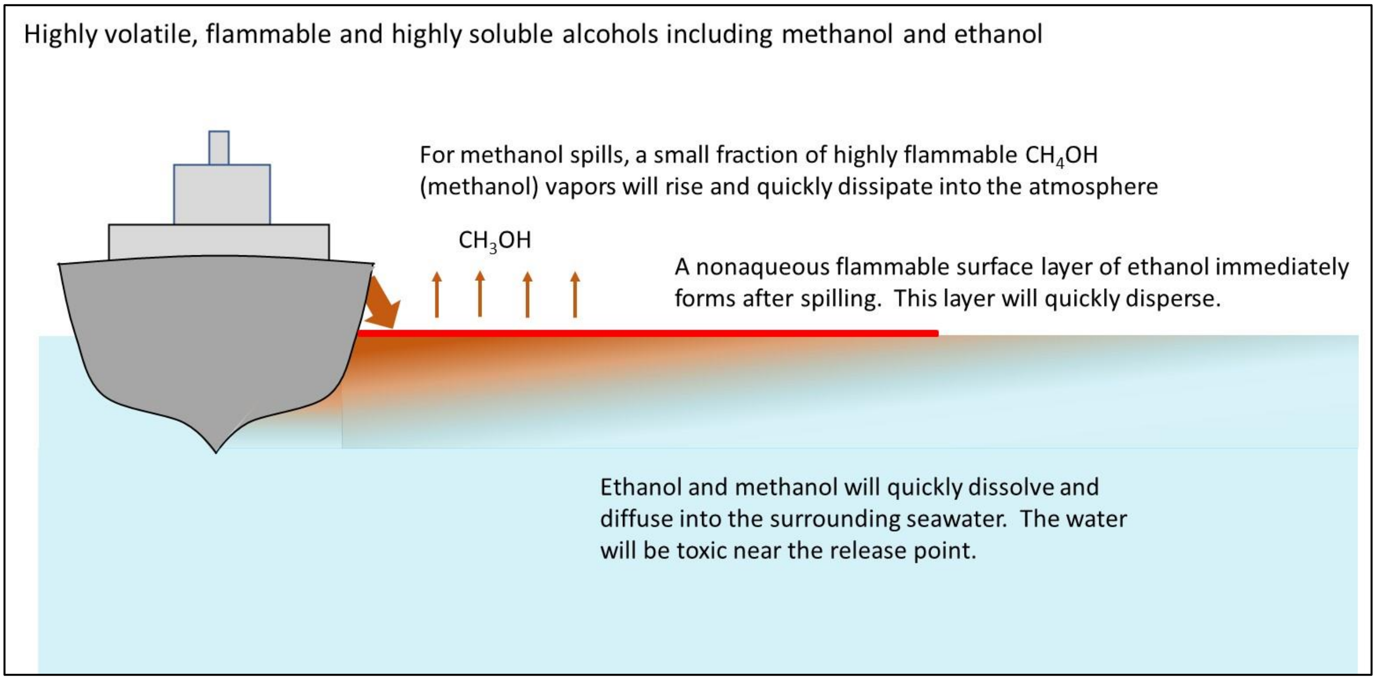

Figure 1. Ethanol and methanol are water soluble and will dissolve into seawater and form a cloud of flammable gases above the surface.

The half-life of ethanol spilled onto surface water based on photooxidation ranges from 6.5 to 26 h. Incidentally, the biodegradation half-life of ethanol dissolved in water is also 6.5 to 26 h (Howard 1991). The exact rate will depend greatly on the environmental conditions, such as wind and temperature.

2.2.3 Methanol

Similar to ethanol, methanol has been used as an automotive fuel blend with gasoline for spark-ignited engines. As such, a lot of knowledge is associated with methanol regarding material compatibility, fuel system needs, and combustion properties (GSI Chemical Database 2020b, Machiele 1989, Malcolm Pirnie 1999, Brynolf et al. 2014, Katsumata and Kastenberg 1996, Andersson 2019). Methanol is seeing increased use and production, and with increased use, the potential for accidental releases to the environment also increases. The possibility of a large release of methanol at sea is tangible, and methanol tankers capable of holding 30 million gallons have been commissioned for methanol transport (Malcom Pirnie 1999).

Methanol spill behavior will be similar to that of ethanol since the properties are similar. However, it is more volatile and will therefore evaporate more quickly than ethanol. As seen in Figure 1, methanol vapors will quickly rise and disperse. However, the immediate region of the spill will be highly flammable while the spill is ongoing. The majority of the spilled methanol will quickly dissolve into the surrounding water. It is completely miscible with water and will rapidly spread from the release point and quickly partition into water. In surface water, the methanol half-life ranges from 1 to 7 days based on aqueous aerobic biodegradation. Many microorganisms can process methanol into formic acid. Rapid degradation in the environment is expected, and a large spill would only have impacts near the release point (Andersson and Marquez Salazar 2015). Methanol is toxic and a high concentration of methanol (e.g., at the release point) may inhibit microbe activity in this locality. However, the concentration will dilute quickly over time (Katsumata and Kastenberg 1996).

Methanol has high diffusivity in air and therefore will disperse rapidly, more so than ethanol. When airborne, methanol will photooxidize with a half-life rate ranging from 3 to 30 days. Given both the high diffusivity and high level of water partitioning, methanol is unlikely to accumulate on the water surface. Computer simulations have shown that a 10,000 ton release of methanol at sea would reach a concentration of 0.36% within 1 h of the spill (Machiele 1989). In other words, a large methanol spill will degrade faster than it could be cleaned up.

As with ethanol, the key risk will be that of a fire or explosion during the release event or immediately thereafter.

2.2.4 Biodiesel and Vegetable Oils

Biodiesel has been evaluated as an alternative fuel in several marine vessel field trials (Biomass Magazine 2020, Maersk 2020). In these trials, biodiesel was evaluated either as a blend with diesel or with HFO. Biodiesel is manufactured by the transesterification of vegetable oils and animal tallow into fatty acid methyl esters. Biodiesel is inherently more stable and less viscous than vegetable or animal oils and is therefore more widely used. However, unprocessed vegetable oils also known as “straight vegetable oil” (SVO) have shown potential as engine fuels (Griipma 2018). Notably, in a 1997 ruling under the Clean Water Act, vegetable oils are considered oils, such as petroleum (Clean Water Act section 311(a)(1)). However, this view is not universal (for instance, France classifies biodiesel as a food). Biodiesel and SVO are similar in that they are both lighter than water, are insoluble, are biodegradable, and have low toxicities (ITRC 2011). When released, they will float on the surface as a slick as shown in Figure 2 (ITRC 2011). Because SVO has a much higher viscosity than biodiesel, it will form a much thicker slick and will not spread as rapidly and as far as biodiesel.

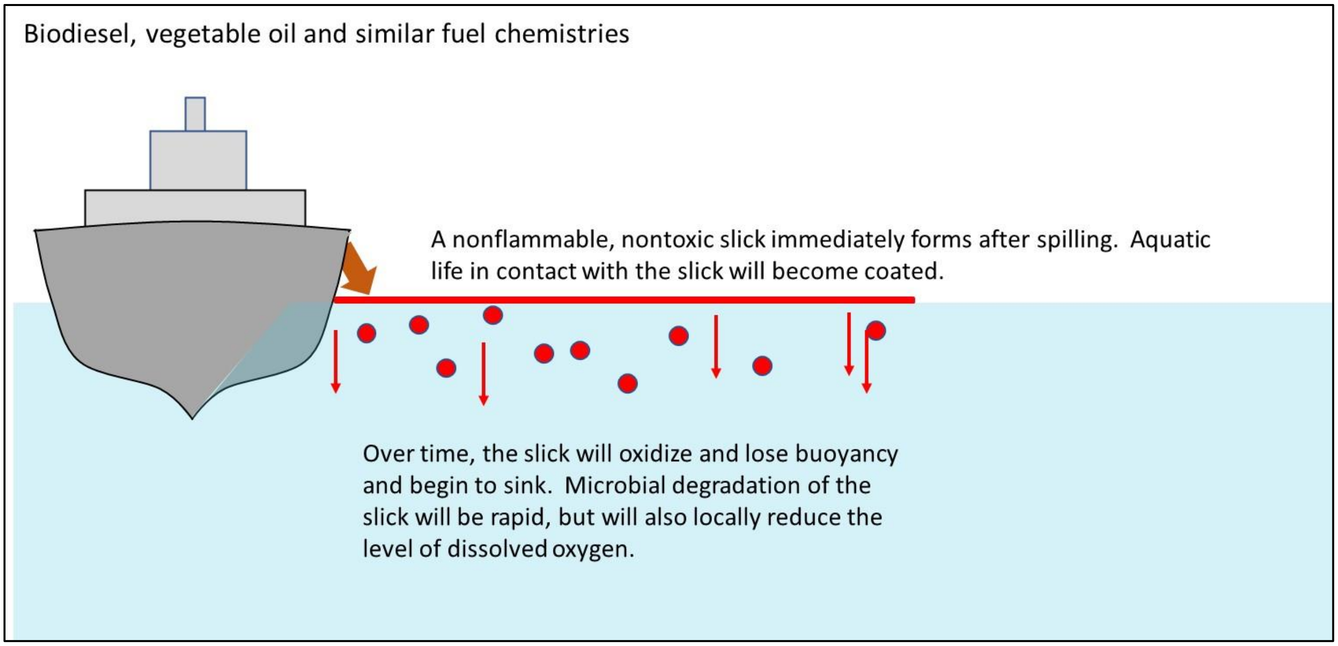

Figure 2. Biodiesel and vegetable oils are likely to initially float on the surface of the sea but will sink as they are oxidized.

Temperature significantly affects the viscosity of biodiesel and SVO, and therefore, the slick characteristics will vary considerably with temperature. The pour point (also known as the "gel point") is the temperature at which biodiesel gels; it can range from −10°C to 10°C (Kimble 2016). These temperatures are common in cold environments and the implication here is that a large release of biodiesel in a cold environment will result in a highly viscous slick and therefore have high film thickness (Kimble 2016). The viscosity of SVO increases almost exponentially with decreasing temperature and can solidify when the temperature drops below 15°C (Blin et al. 2013). When used as a fuel, SVO is typically heated above 40°C to achieve proper flow. A release into the sea will likely result in a solid floating mass when the SVO contacts the water. Biodiesel spills are prone to emulsification with moderate wave action.

Biodiesel and SVO will degrade rapidly in aquatic environments (Demirbas 2008, Zhang et al. 1998). Biodiesel is estimated to degrade approximately 4 times faster than diesel fuels (Kimble 2016). Biodiesel degradation will proceed primarily along two lines: the fatty acid methyl esters making up the biodiesel will degrade into peroxides and short chain acids due to oxidation. Temperature greatly accelerates this oxidation and it will proceed relatively rapidly under most ambient conditions. Biodegradation via microorganisms is the other predominant mechanism. Studies have shown that various fatty acid methyl esters were degraded in an aquatic environment between 85.54% and 88.49% in 28 days (Demirbas 2008). For comparison, diesel was degraded around 26.24% under similar conditions over 28 days (Zhang et al. 1998). In another study, the half-life was determined to be less than 4 days (at 17°C), which is twice as fast as diesel (von Wedel 1999). Since SVO is not processed, it will degrade even faster than biodiesel in the environment by both oxidation and microbial action.

Because of its inherent polarity and high solubility with other oils, biodiesel is sometimes described as a solvent. Its soluble nature means that any aquatic birdlife in direct contact with freshly spilled biodiesel may lose its water repellency because of the loss of its protective oil coating on its feathers. Any marine organism that comes into contact with a biodiesel slick may also become coated. This coating (while less toxic than diesel or oil) will negatively impact the insulating properties of fur or feathers and therefore, the animals will be at a heightened risk of exposure. Foraging behavior will be also be impacted. The treatment of coated wildlife is expected to be similar to that of oil spill treatment (Kimble 2016). In 1994 through 1996, a series of tests were conducted to examine the toxicity of biodiesel released into surface water (of a pond). The concentration required to kill 50% of the fish population was 578 ppm versus 27 ppm for diesel fuel. For larval invertebrates (shrimp), the concentration required was 122 ppm for biodiesel versus 2.9 ppm for diesel. Other studies have confirmed the lower toxicity of biodiesel (von Wedel 1999). SVO is considered to be relatively nontoxic.

2.2.5 Pyrolysis Oils and Hydrothermal Liquefaction Oils

Pyrolysis oils (also known as “bio-oils”) are derived from the fast heating of biomass (often woody feedstocks) to high temperatures in the absence of oxygen. Bio-oils are complex mixtures and contain hundreds of compounds with a large range of molecular weights (Paasikallio 2016). Raw bio-oils contain high levels of water (around 25%) and exist as a dispersion (emulsion) of insoluble components suspended in the continuous aqueous phase. If left to settle in a tank, bio-oils will stratify, such that the water concentration decreases from the top to the bottom. The heavier oily bottom phase will contain more of the water-insoluble components, of which approximately 22 wt % of the bottom fraction are dominated by high-density lignin (oligomer) macromolecules (Basu 2018, Lindfors et al. 2014, Duan et al. 2017). Because of its inherently high-water content, the aqueous phase has low value as a fuel because of its low energy density. The higher energy-rich insoluble fraction is of interest even though it also contains significant water levels. Raw bio-oils refer to this insoluble fraction. The main components of bio-oils are carboxylic acids and sugars and small levels of aldehydes, ketones, furans, phenols, ethers, and alcohols (Ren 2014). In the raw state, bio-oils are being evaluated as a renewable option for residual oils, such as HFO. However, to be considered for distillate use, they must be heavily upgraded (hydrotreated), which is expensive. The upgrading process reduces the density of the starting bio-oil, such that it may be less dense than water for highly upgraded bio-oils.

As shown in Table 1, bio-oils have a slightly higher density than water (though the actual value depends heavily on the processing conditions). As a result, bio-oils will not float on the surface, but rather will be suspended in the water column either as slick or dispersion. Any wave action will produce a dispersion or globules of dense matter. Over time, bio-oils will polymerize and increase in density, causing the slick globules or dispersion to sink. Slicks of bio-oils are shown graphically in Figure 3. The impact of large releases of bio-oils on water has not been evaluated, but some behaviors can be determined based on composition. The sugar, alcohol, and lignin components can be expected to be undergo biodegradation. For the sugar and alcohol components, degradation will be rapid. For the more predominant lignin fraction, decomposition will take longer. Because lignin is more stable than biodiesel, it is expected to remain in the environment for a longer time period.

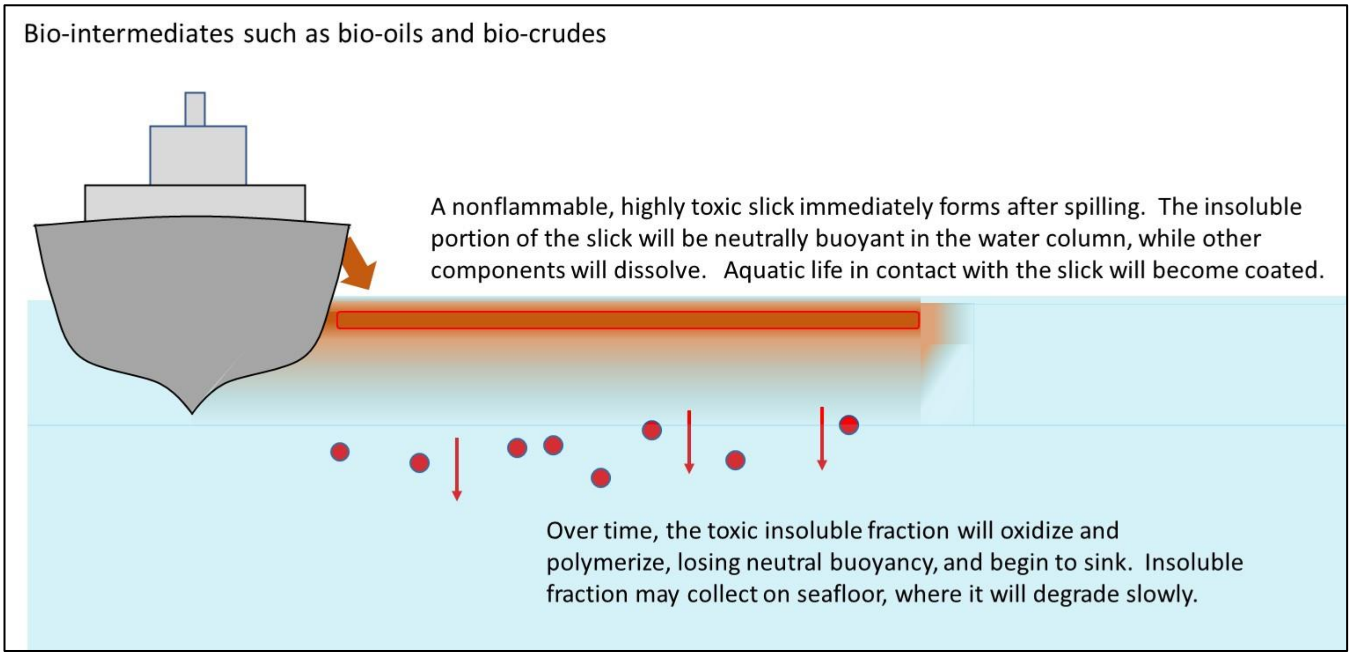

Figure 3. Bio-oils will form a nonflammable but highly toxic slick upon spilling. There are likely to be components of the spill that will dissolve into seawater, while others will float in the water column with neutral buoyancy.

The toxicity of bio-oils is primarily attributed to naphthalene, phenanthrene, and anthracene components. Many of these highly toxic substances exist in levels that cause harm to aquatic life. An ecotoxicology assessment reported by Chevron Phillips lists pyrolysis oils as being very toxic to aquatic life with long-lasting effects (Chevron Phillips Chemical Company 2020). Pyrolysis oils readily adhere to surfaces they contact and can therefore be expected to coat any marine organisms that come in direct contact.

Hydrothermal liquefaction oils (also known as “bio-crudes”) are similar in appearance to bio-oils (Ramirez et al. 2015, Yang et al. 2019, Golakotaa et al. 2018). However, they are less dense (as shown in Table 1) and will float on the water surface. They typically have high viscosities and can be expected to form a floating slick that is relatively thick. Chemically, bio-crudes does not contain high levels of water, but similar to bio-oils, they are partially water-soluble. The toxicity of bio-crudes is not well known, but because they contain aromatics similar to bio-oils, they likely have a similar toxicity to bio-oils.

2.2.6 Lignin Ethanol Oil

Lignin ethanol oil is being evaluated as a potential marine fuel. The production process involves blending lignin with ethanol. Properties on these fuels have not been readily available. Our understanding is that ethanol is used to liquify lignin into an oil having good combustion properties. Without further information on the chemistry and properties, it is difficult to assess precise spill characteristics and environmental impact. Without additional property information forthcoming, our best guess is that lignin ethanol oil will behave in a manner similar to biodiesel in both spill profile and environmental impact.

2.2.7 Pressurized Gaseous Fuels

A key characteristic of pressurized fuels (whether kept at cryogenic conditions or not) is a sharp drop in temperature when released suddenly in the atmosphere due to volumetric expansion. This sudden drop in temperature will cause water vapor in the surrounding air to condense and form a visible white cloud. An example is shown in Figure 4 for LNG spillage during refueling of a vessel. The higher density of the condensed water vapor relative to the surrounding air means that this cloud stays on the surface and does not rise. Because the driving forces for the cloud formation are the chilled fuel vapors, the cloud will disappear once the fuel vapors heat up and dissipate. This cloud is readily visible during daylight.

Figure 4. White cloud formed during the release of LNG.

LNG and liquid hydrogen are unique in that they are stored under cryogenic conditions to maintain as liquids and, as vapors, they have densities lighter than air under ambient conditions. However, the densities of these gases increase with a decreasing temperature, and at the exceptionally low temperatures accompanying the release of the liquid phase, they will be denser in the gaseous phase than the surrounding air. As such, when released, the gas vapors will immediately sink to the ocean surface (Witcofski and Chirivella 1984). Because of their low solubility in water, they will spread rapidly on the water surface. The rate of spreading depends on the size and nature of the release, boiling point, and the degree of sub-cooling (Thyer 2003). However, the wind conditions will greatly affect the vapor cloud profile, which has implications for safety and environmental impact. Vapor cloud profiles for released LNG and liquid hydrogen have been determined from several studies (Ivings et al. 2016). The influence of wind speed is shown in Figure 5 for low wind speeds (<5 mph), and Figure 6 for higher wind velocities (>5 mph) (Lin et al. 2019, Sklavounos and Rigas 2005, Thyer 2003, Witcofski and Chirivella 1984). When the wind speed is low, the vapor cloud length advancing on the sea surface is restricted since more of the vapor movement will be vertical as the gas mixes with the surrounding air to become warmer and less dense. Higher wind speeds will push the vapor cloud along the water surface as shown in Figure 6. As can be seen, a consequence of higher wind speeds is an expansion of the cloud footprint on the water surface resulting in an expanded hazardous region.

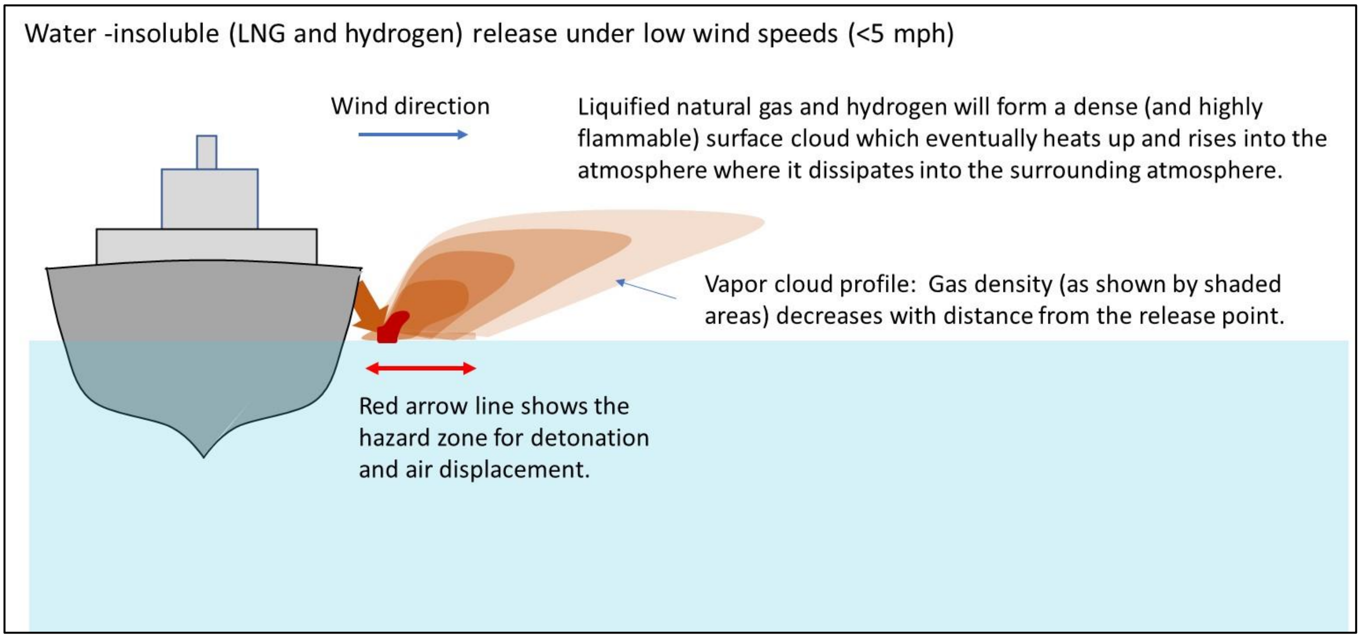

Figure 5. General vapor cloud profile of a sudden release of LNG or liquid hydrogen under low wind speed (<5 mph).

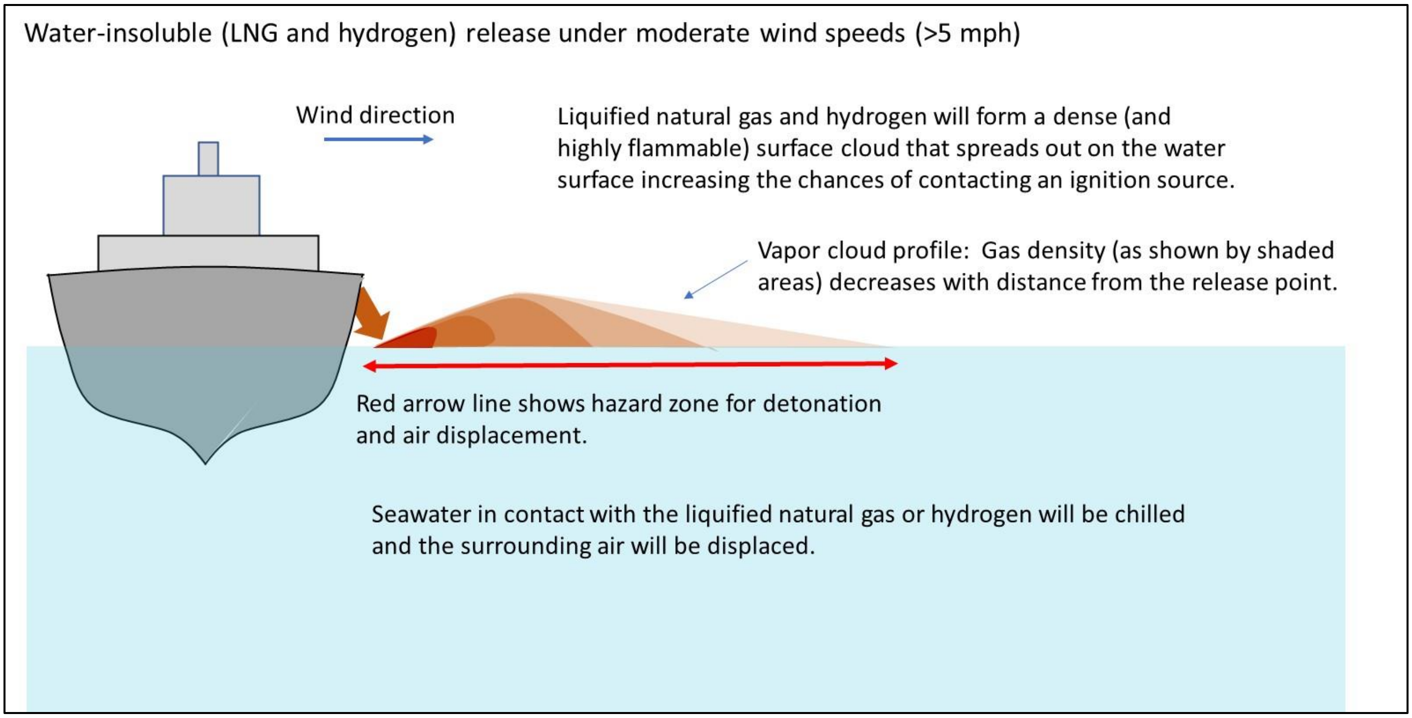

Figure 6. General vapor cloud profile of a sudden release of LNG or liquid hydrogen under moderate wind speed (>5 mph).

2.2.7.1 LNG

The impact of large releases of LNG at sea and on land has been a topic of interest for more than 30 years (Luketa et al. 2008). The primary driver for this research is the flammable and potentially explosive nature of leaking natural gas (Luketa et al. 2008). LNG tanker ships routinely cross the oceans; these ships use the LNG cargo to fuel the engines. Natural gas is predominantly composed of methane, which is lighter than air. Natural gas is liquified extremely low temperatures and is maintained as LNG at −162°C during storage and transport.

As stated previously, a white cloud of condensed water vapor resulting from the much colder methane will form immediately and will be readily visible as a flat white cloud. Since methane is not highly soluble with water, little dissolution will occur into the sea. The natural gas molecules rapidly warm up from contact with the much warmer air, causing the natural gas to rise and diffuse quickly in the atmosphere. The methane cloud in its cold state is the most dangerous since it will ignite when it comes into contact with an ignition source. The maximum height of this cloud has been determined to be around 12 m (Sklavounos and Rigas 2005). However, the length and resulting profile highly depends on the wind conditions. Wind will reduce the cloud height and will spread the cloud to further lengths. As a result, the flammable zone becomes increased and therefore, the ignition risks increase, as well.

It has been surmised that the released natural gas will not form a liquid pool on the water surface, but this has not been conclusively determined. Models developed at Sandia National Laboratories show that large spill volumes (41,000 m^3) will disperse between 10 and 25 min depending on the spill rate (Luketa 2008). For natural gas releases, the main concerns are with fire and detonation. Here, the risks are categorized according to three zones as follows:

Zone 1: This zone is labeled as high risk and is associated with narrow harbors, channels, or ports where the release point if within 250 m of people or infrastructure.

Zone 2: This zone is associated with broader channels and larger harbors. These sites are graded as less severe risk environments having a distance of 500 to 1,600 m to populated sites.

Zone 3: This zone is associated with bays or open water where the distances to populated localities greater than 1,600 m.

2.2.7.2 Liquid Hydrogen

The released behavior of liquid hydrogen has been shown to be similar to LNG, but because it is lighter and more volatile, it will rise faster (College of the Desert 2001). Therefore, the resulting vapor cloud will have a much smaller sea surface footprint and will have a smaller overall flammability zone than LNG. The dissipation rate is also higher. However, because molecular hydrogen is highly reactive, it will more readily ignite than natural gas. While hydrogen is nontoxic, it can displace the surrounding air and cause suffocation. The biggest concerns with released hydrogen are its explosiveness and flammability. Exposure to air will allow it to be readily ignited by any hot surface or spark (including static electricity). A large release of hydrogen from a vessel is highly likely to be ignited by a hot surface. If the escaping hydrogen is ignited, no cold cloud of condensed water vapor will form. When ignited, more heat will be released per mass and volume than LNG; as a result, the distances identified for Zones 2 and 3 identified for LNG are not likely to be appropriate for liquid hydrogen.

2.2.7.3 DME

DME is a second-generation biofuel. It can be made from biomass as well as shale and natural gas. It has a better energy density than other alternative fuels and has been shown to blend well with diesel and reduce the formation of particulate matter when combusted. Because DME is gaseous at temperatures above −24°C, it will not remain as a liquid in the event of a spill. When released, the temperature of the escaping gas will drop and the possibility of a white vapor cloud is likely. Gaseous DME has roughly twice the density of air and is also insoluble. Therefore, it will form a vapor phase on the water surface that will effectively displace the surrounding air as seen in Figure 7. This gaseous plume will spread rapidly on the water surface provided it is not contained in some manner. Unlike natural gas and hydrogen, DME will not rise into the atmosphere, but rather will remain on the water surface, even if the white vapor cloud is not present. This factor increases the potential for contacting an ignition source. Suffocation of marine life is possible at the surface near the point of release. Fire and explosions are another key risk. DME is extremely flammable with an autoignition temperature of 350°C. The risk to fire and explosion is expected immediately after the release occurs because the DME vapors will quickly spread over the water surface, where they will rapidly dissipate. This dissipation will occur quickly and is accelerated with wind and wave action. Therefore, a DME spill will be diffused before any cleanup could arrive.

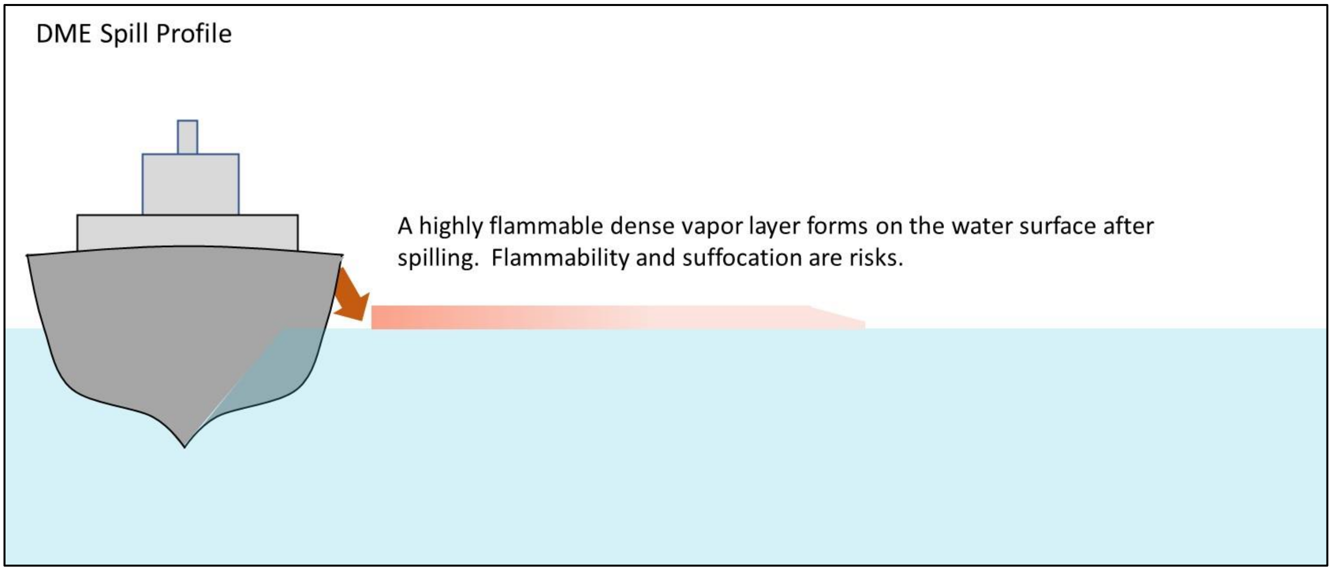

Figure 7. Surface vapor profile associated with a large sudden release of DME.

2.2.7.4 Ammonia

Ammonia is of interest in marine shipping as a net-zero carbon emitter (Karikoglou 2019, de Vries 2019a, 2019b) and has been evaluated periodically as a fuel for internal combustion engines. As shown in Table 1, ammonia boils at −33.3°C, but it does not require cryogenic storage (Dincer and Bicer 2018). However, it will rapidly cool when released, and a portion of the gas may revert back to the liquid phase. Ammonia gas is highly toxic to humans and marine life, and a shipborne release may have dire consequences for the ship crew and any nearby population. A report detailing the impact of large ammonia spills over bodies of water was published by Arthur D. Little for the US Coast Guard in 1974 (Raj et al. 1974). This report was the result of a series experimental studies looking at the dissolution kinetics and chemistry of controlled releases of ammonia. Ammonia is highly soluble with water, and around 70% of a surface spill volume will quickly go into solution with water as shown in Figure 8. Upon contact with the water, ammonia (NH_3) will immediately react with it to form highly toxic ammonium hydroxide (NH_4OH). Any liquid ammonia that does not contact water will quickly volatize. Since ammonia gas is lighter than air, it will quickly dissipate in the atmosphere and eventually react with water vapor to form ammonium hydroxide. Ammonium hydroxide is lighter than water and will spread on the water surface. The heat released during the reaction will cause the newly formed ammonium hydroxide to be hot. This heated and toxic surface region will threaten marine life in the spill zone (EPA 2013). The dissipation rate of ammonium hydroxide on the water surface will depend on the spill site. At sea, dissipation will be rapid, but a more contained locality may allow for the toxic ammonium hydroxide surface layer to exist for a longer period. The exact rates of dissipation are unknown at this time. Both ammonia and ammonium hydroxide are difficult to ignite and burn, so the risk of a fire hazard is low with an ammonia spill.

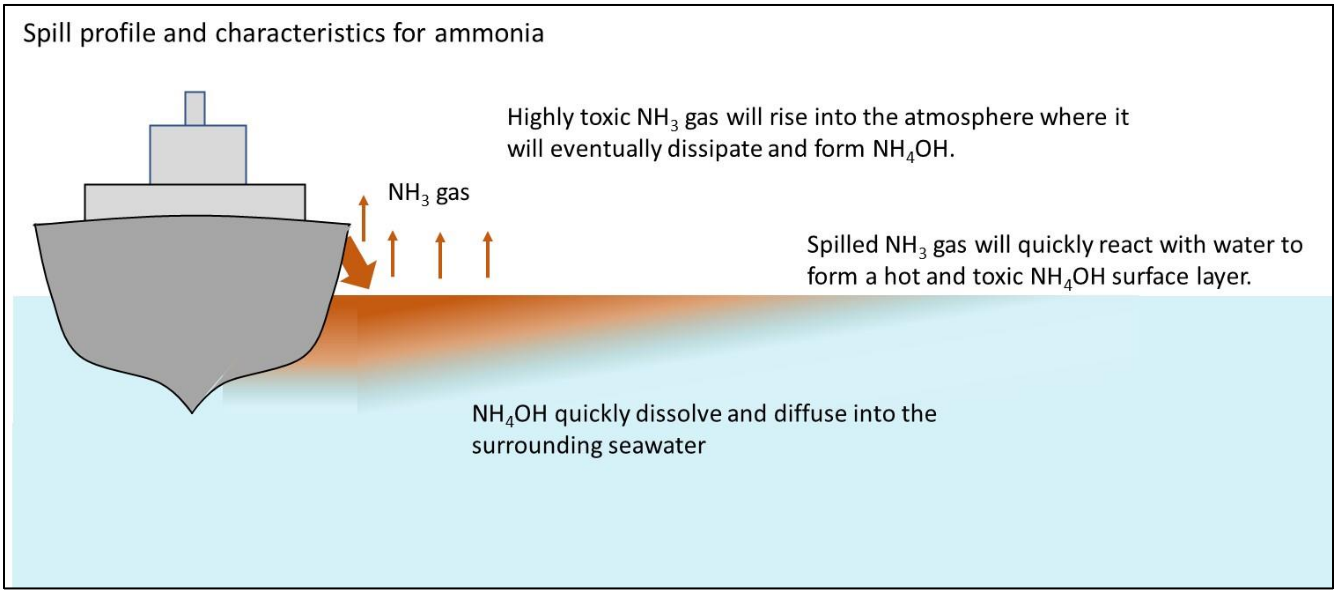

Figure 8. Ammonia reacts chemically with water, producing ammonium hydroxide. The resulting ammonium hydroxide is toxic but will rapidly diffuse into the surrounding seawater.

2.2.8 Blends with HFO

Of the alternative fuels being considered, only a few may be considered as blends with HFO. These include biodiesel, bio-intermediates, and possibly DME. The performance of these fuels will depend heavily on blend level and whether the added fuel exists as a soluble component or as an emulsion. For the purposes of this study, we only considered blend levels containing up to 30% of the alternative fuel. Upon release, the spill profile will take on that of HFO, which is a heavy slick. The density of HFO is variable and may be heavier than water, resulting in HFO sinking into the water column. Because DME, biodiesel and vegetable oils are less dense than HFO, the probability of these blends (with HFO) floating on the surface increases, especially if the blended constituent is greater than 20% of the total blend volume. In contrast, the more-dense bio-intermediates will have less impact on the overall density of a blend with HFO.

The added fuel will not significantly impact the degradation rate or toxicity of HFO. If the blended component exists in a separate phase as an emulsion, its degradation rate will be relative unaffected by the HFO. However, if the added alternative fuel is incorporated as a soluble component, its degradation will be slowed by the attractive forces with HFO.

Table 2. Summary of spill characteristics of large, sudden releases of each alternative fuel.

Fuel type	Behavior when spilled	Dissipation or degradation Rate	Ecological impacts	Flammable/ explosion risk	Toxicity	Air displacement and suffocation risk to crew	Spill cleanup	Detection probability with current practice
Renewable diesel or HVO	Will behave as a diesel spill and rapidly spread out as a clear oily film	Moderate: Expected to take up to a week or more	No long term impacts are expected. Aquatic life may become coated	Low	Low	None	Boom containment is most optimal	Moderate
Ethanol	Will rapidly spead out and dissolve into water	Fast	No long term impacts, but aquatic life in contact with spill may be poisoned	High	Yes, but limited to spill zone	Possible	Will dissipate before cleanup can begin	Low
Methanol	Will rapidly spead out and dissolve into water	Fast	No long term impacts, but aquatic life in contact with spill may be poisoned	High	Yes, but limited to spill zone	Low	Will dissipate before cleanup can begin	Low
Biodiesel	Will form a slick on the water surface	Moderate: Can take up to a week or more	Aquatic life may become coated	Low	Low	None	Boom containment is most optimal	High
Vegetable oil	Will form a slick on the water surface	Moderate: Can take up to a week or more	Aquatic life may become coated	Low	Low	None	Boom containment is most optimal	High
Bio-oil and bio-crude	Will be suspended in water column and will eventually sink.	Slow	Aquatic life may beome coated and poisoned	Low	High	None	TBD	Moderate
DME	Will form a vapor cloud on the water surface	Fast, unless contained	No long term impacts, but marine life at the water surface in the spill zone may suffocate	High	Low	Possible	Will dissipate before cleanup can begin	Low
LNG	Will form a cold cloud on the water surface	Fast	Marine life at the water surface in the spill zone may suffocate or become chilled	High	Low	Possible	Will dissipate before cleanup can begin	Low
Ammonia	Will partition into water forming a heated surface layer of ammonium hydroxide	Fast	No long term impacts, but marine life near the spill zone may be burned and poisoned	Low	High	High	Will dissipate before cleanup can begin	Low
Hydrogen	Will form a cold cloud on the water surface	Fast	No long term impacts, but marine life at the water surface in the spill zone may suffocate or become chilled	High	Low	Possible	Will dissipate before cleanup can begin	Low

3. SPILL DETECTION AND MONITORING TECHNOLOGIES AND THEIR APPLICABILITY TO ALTERNATIVE MARINE FUELS

Remote spill detection has been a critical component for locating large releases of crude oil or heavy residual fuel oils. The accuracy and ability of these methods highly depend on geography and weather conditions. Remote sensing is now routinely employed to map spills and their growth and movement, detect illegal releases, and gather information pertaining to a release (Fingas 2018, Robbe and Hengstermann 2006). The methods and technologies are primarily based on interactions of the spill with the water surface or detection of optical property differences. Detection technologies are categorized as passive if they are based on ambient observations or sensors only. Examples include visual observations and infrared (IR) cameras. Active technologies are those that actively send out an energy beam (e.g., laser or microwave radiation) that interacts with the environment to generate a signal that can be used to differentiate the slick from the background.

For these technologies to be effective in detecting alternative fuels, they must be able to survey potentially smaller areas than crude oil spills for two reasons. First, the volume of stored crude oil is massive compared with the volume of the fuel storage container. This means that less fuel will correspondingly be released during the event of a spill. Second, many of the alternative fuels, especially the alcohols and gases, will dissipate quickly once released into the environment and therefore, the area will be smaller relative to a large stable oil spill. Therefore, instead of resolutions in the tens of meters, the pixel resolution will likely need to be around 1 m. This is especially true for satellite-based detection, where the resolution may not be fine enough to detect small releases. In the context of remote oil spill detection, satellites are useful for obtaining images (visual or IR), but their use in actively sensing spill is limited to radar-based methods. In particular, the images generated from synthetic aperture radar (SAR) satellites have been shown to be successful at oil slick detection. Both passive and active sensing technologies are used in aircraft surveys.

Instrument technologies for detecting and monitoring hydrocarbon spills at sea are presently in use. Each technology has limitations; no single technology delivers information on all of the important attributes of an oil spill with certainty (ITOPF 2014, Pilzis and Vaisis 2016, Fingas 2018). Since contact with seawater that may contain oil can degrade or foul sensors, spill detection and monitoring is typically accomplished by non-contact optical sensors. In most cases, deployment of these sensors is accomplished with the use of manned aircraft, unmanned aerial vehicles (UAVs, or drones) or by satellites. These deployments are used to determine and monitor the extent of an oil slick on the water. A key challenge with satellite imagery is that it takes a long time to deliver images because of the high levels of data processing. Another issue is overpass time; newer imagery systems can pass over areas every several hours, but this frequency is still too low to capture releases of fuels that dissipate quickly. Systems mounted on aircraft and ships are much more responsive and available; however, they are unlikely to capture releases at sea and are currently only useful in port locations or onboard the ships themselves.

In this section, current detection technologies are discussed in the context of detecting the spills of alternative marine fuels. A summary of spill detection methods and their applicability with the alternative fuels considered in this study is shown in **Error! Reference source not found.**.

Table 3. Summary of detection methodologies with fuel type.

Fuel type	Visible	Radar	Infrared	Fluorescence	Chemical analysis
Renewable diesel	Possible if sheen is formed	No	Potentially yet	Unknown	Yes, but limited to spill zone
Ethanol	No	No	No	No	Yes, but limited to spill zone
Methanol	No	No	No	No	Yes, but limited to spill zone
Biodiesel	Potentially yes	Yes	Potentially yes	Unknown	Yes
Vegetable oil	Potentially yes	Yes	Potentially yes	Unknown	Yes
Bio-oil	Yes	Potentially yes	Potentially yes	Potentially yes	Yes
Bio-crude	Yes	Potentially yes	Potentially yes	Potentially yes	Yes
DME	Yes. Will form a cold cloud on the water surface that will quickly dissipate	No	Potentially yes. Depends on the temperature reduction of ship and water surface	Unknown	Yes, but only by sampling surface airspace
LNG	Yes. Will form a cold cloud on the water surface that will quickly dissipate	No	Potentially yes. Depends on the temperature reduction of ship and water surface	No	Yes, but only by sampling surface airspace
Ammonia	Yes. Will form a cold cloud on the water surface that will quickly dissipate	No	Potentially yes. Depends on the temperature reduction of ship and water surface	Unknown	Yes
Hydrogen	Yes. Will form a cold cloud on the water surface that will quickly dissipate	No	Potentially yes. Depends on the temperature reduction of ship and water surface	No	Yes, but only by sampling surface airspace

3.1 PASSIVE DETECTION METHODS

Passive optical sensing technologies are analogous to photography. In photography, objects partially reflect visible light emitted from the sun. This reflected light is captured in a photograph, providing a visible-light image of the object. Similar images can be produced using ultraviolet (UV) light, IR light, or microwaves. These forms of electromagnetic radiation are also reflected or emitted from objects including the sea surface, biofilms, and slicks. UV imaging is prone to error caused by sun glints, wind slicks, and the presence of biogenic material, and so is not used as often as IR imaging, which is less susceptible to these issues and can additionally provide qualitative information about the thickness of the slick. Thin slicks appear lighter than the surrounding seawater, whereas thicker slicks appear darker. One weakness of IR imaging techniques is that if the image includes areas of shoreline or waters that are covered in substantial amounts of seaweed, differentiating these areas from areas that contain spills may be more difficult. This condition is a good example of why multiple techniques for petroleum detection are often employed. Oil slicks emit greater amounts of microwaves than seawater, allowing a microwave image to detect slicks, and can provide information about their thickness. Microwave detection of slicks is degraded if the oil has emulsified.

Passive observation is based on spectral reflectance and is usually conducted using cameras capable of imaging visible and UV spectra. Collecting images from multiple spectral bands, which can be analyzed to improve accuracy, is common. The spectral signature of a spill depends greatly on lighting (sun angle), sea conditions (wave action), spill geometry (thickness) and the optical properties of both the spill and the surrounding water (Kolokoussis and Karanthanassi 2018). Another key factor is the angle of the detector (Carnesecchi et al. 2008). Oil has only a moderately larger reflectance than water but can be remotely imaged under favorable conditions. Carnesecchi et al. (2008) showed that thin films (sheens) are more easily detected at viewing angles near the sunglint zone (i.e., where sunlight reflects off the surface of the ocean at the same angle that the detector or camera is viewing the surface). Near the sunglint angles, smooth ocean water reflects as a silvery mirror, whereas rougher surface waters appear dark. In contrast, very thick films are more readily detected at viewing angles away from the sun. These details are important for alternative fuels that form surface slicks. To improve detection, hyperspectral imaging may be employed. Here, the spectrometer collects multiple images at different wavelength regions (spectral bands). Information from each bandwidth is then processed to improve detectability. The large data sets and computational needs of hyperspectral imaging can require significant amounts of processing time, which may preclude its use.

Oil films have a polarizing feature that can be exploited to improve contrast. This method has not been examined for alternative marine fuels, and studies are needed to confirm that slick-forming fuels have a unique polarization feature. This approach has been used by both satellites and aircraft. One of the challenges of satellite imagery is that images are limited to the position of the satellite, whereas aircraft can be flexible in regard to gaining quicker access. The ground resolution of several imaging satellites available for the public is less than 0.5 m, which is suitable for the detection of small spills. However, the large sets of data that must be processed and analyzed requires enormous time and resources. The utility of satellite imagery is thus relegated more toward identifying illegal discharges. The length of time required to process the data precludes the use of satellites to assist in quick cleanup operations. Aerial photography is likely to be more effective since the sensing technologies in many cases may be more advanced, and the resolution and clarity are better.

3.1.1 Visual Observations

Visual detection, either by the eye or camera, is the most straightforward means of detecting releases. Crude oil spills are identified as a dark floating mass that contrasts to the lighter coloration of the ocean. Wave action (or interference) will make observation more difficult. In many cases, the oil slick will have a sheen that contrasts with the surrounding water. These differences can be readily seen directly by the human eye or by images transmitted from cameras and satellites. They can appear as a sheen, a metallic reflection, or as darker region on the surface. Visual observations are limited to spills that remain on the water surface. Spills that sink below the surface are not readily detectable above or at the surface. Since several nontraditional marine fuels form surface slicks that are not darker than the surrounding water, other visual cues will likely be limited to sheen-based images (or perhaps a metallic reflection). Compressed gaseous fuels (such as LNG, liquified hydrogen, ammonia, and DME) are not visually detectable, but they will readily create a cold vapor cloud composed of water droplets above the water surface when they are released suddenly (Figure 4). Once the fuel vapor temperature rises and the cloud disappears, the gases will not be visible.

Other fuels that quickly dissolve into water, such as ethanol and methanol, are not expected be distinguishable by remote imagery. Eye detection is not likely either. The camera (or observer) will need to witness the spill event up close for it to be recognized. Once the fuel is released into the surrounding sea, visual detection is not likely. Fuels that will form slicks, such as is the case for many biofuels (e.g., vegetable oils, biodiesel, renewable diesel, bio-oils, and bio-crudes), can be observed to varying degrees. A series of potential alterative liquid fuels is shown in Figure 9. As can be seen in the photograph, alcohols such as ethanol and methanol are clear and cannot be visually distinguished on the water surface prior to dissolution into the adjoining seawater. Renewable diesel and biodiesel appear similar to diesel, except with lighter coloration. Unfortunately, the inherent visual transparency of these fuels will make distinguishing on the water surface challenging based on visual coloration alone. If they form an oily sheen, the sheen could possibly be distinguished depending on the viewing angle and the sun location. The ability of these fuels to form a visible sheen is not established and therefore, studies are recommended. Bio-oils and bio-crudes are opaque and dark, and visually appear similar to HFO. The dark color and opaqueness contrast highly with the surrounding seawater and therefore, bio-oils and bio-crudes have good potential to be visually detected under ideal daylight conditions. Because of the agitation normally present on the ocean surface, emulsions of these fuels will likely form. Photographs showing several fuel emulsions with water are shown in Figure 10. A key feature of emulsions is their opaque appearance. The appearance of the resulting emulsions varies from milk white (for biodiesel) to peanut butter for bio-oils. (Interestingly, the HFO did not appreciably change color as a result of the mechanical action and it is highly unlikely that an emulsion was formed.) Because they are opaque, and in many instances highly reflective, they will readily contrast with the surrounding water. Because emulsions contain seawater, they will be heavier than the pure fuel. Therefore, they will not float as high on the water surface. More likely, they will be neutrally buoyant at the water surface.

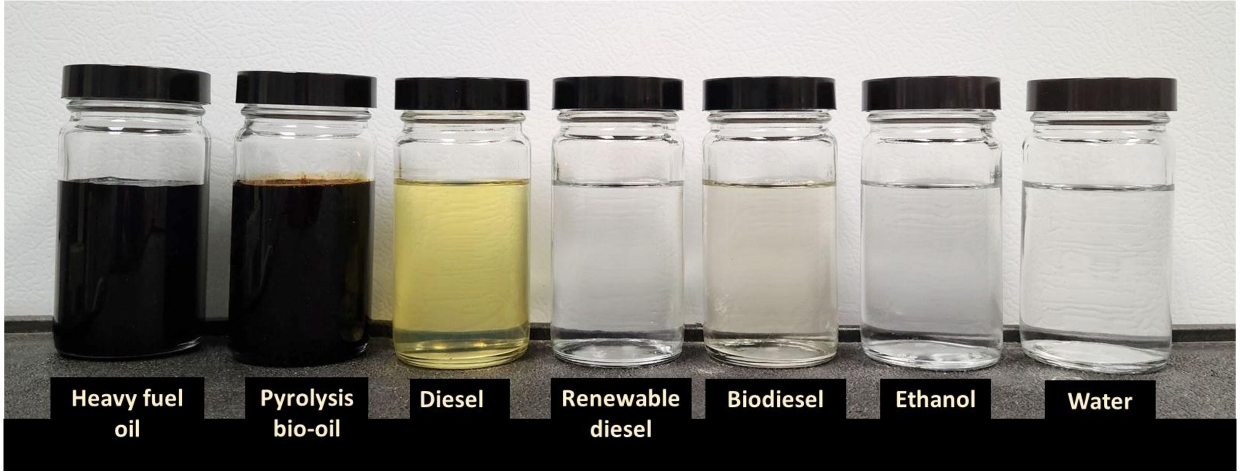

Figure 9. Photograph of selected alternative liquid marine fuels compared to water.

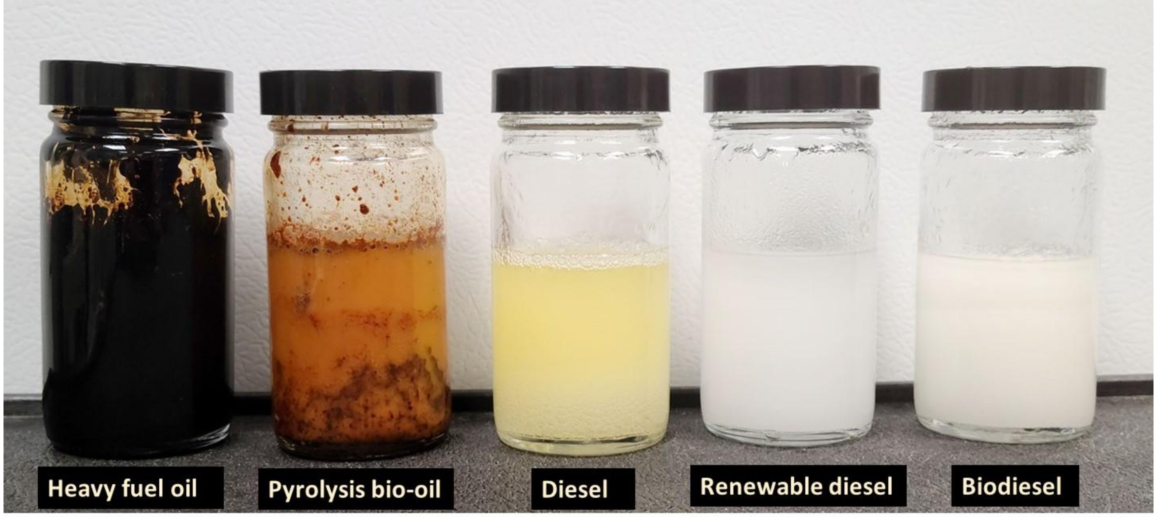

Figure 10. Photograph of selected alternative liquid marine fuels emulsified with water. The fuel to water ratio for each emulsion was approximately 2:1. The emulsions in the photo were prepared by mechanical action.

A key aspect to visible detection is the thickness of the film or slick. Research is needed to determine the detectability of these fuel types via spectral imaging. The ability to discern based on the environmental conditions will need further study. None of these methods will work under cloudy or dark conditions.

3.1.2 IR Detection

IR imaging works on the same principal as visible daylight cameras, except that thermal imaging makes pictures of IR radiation due to heat or thermal energy instead of visible light (Daniels and Hover 1994). IR sensors capture light in the IR spectrum, which is emitted due to thermal energy, and convert it into a visible image. IR imaging resolution is typically lower than an equivalently sized visible light imager because of the larger IR wavelengths, which necessitate larger sensing elements. During the daytime, the slick absorbs light, which is subsequently emitted as IR radiation. For crude oil, light in the visible spectra is absorbed and then partially re-radiated in the IR band. Oil (when heated by the sun) will emit IR radiation more than the surrounding water because of the higher IR emissivity of oil. The use of IR highly depends on slick or film thickness, and thick oil films will appear hotter than the surrounding water. Interestingly, some intermediate thickness layers of oil (between 50 and 150 µm) can appear to be cooler because of the destructive wave interference with the seawater. Films that are thinner than the intermediate thicknesses are not distinguishable from the surrounding seawater.

During the nighttime, the slick will not receive any light energy and IR detection will not work unless the slick is thick enough to be able to retain the heat for an extended period. For slick-forming fuels, such as biodiesel, vegetable oils, and bio-crudes, this approach may work depending on the emissivity of the biofuel and the film thickness. A key requirement for this method is that the slick forms on the surface of the water. Biofuels that are suspended in the water column, as would be the case with bio-oils and fuel emulsions, will not be detectable via IR because of the quenching effect of the water. Readily dissolved fuels such as alcohols and ammonia will also not be detected by IR imaging.

IR detection of cryogenic fuels has excellent potential since these fuels will be at a much lower temperature than their surroundings immediately after a release. The cold vapor cloud should be readily detectable by IR methods. Also, the surrounding seawater in the immediate vicinity will also be a lower temperature. Any ship surface in contact with the fuel will also register as cooler than the surroundings and will subsequently be detectable. Because of the temperature differential between these fuels and the surroundings expected to be high, detection would be readily achieved without the need for sunlight to provide heating. As previously stated, these fuels, when released, will quickly warm up (due to interaction with their surroundings) and therefore, the affected area will not be as large as with a surface slick. This means that the resolution of the detectors will need to actually register and spatially resolve the chilled vapor cloud and surrounding areas. In general, the resolution of satellite imagery ranges are as follows:

- High to very high resolution is between 30 cm and 5 m/pixel;
- Medium resolution is between 10 meters/pixel and 30 meters/pixel; and
- Low resolution is typically more than 60 m/pixel.

Low resolution may not be suitable for detection of most releases of cryogenic fuels. The detector should be capable of high to very high resolution to effectively capture the event. Aerial photography is likely to be more effective since the sensing technologies in many cases may be more advanced, and the resolution and clarity is better. Other compressed gaseous fuels such as ammonia and DME are also likely to form vapor clouds. However, because they are not as chilled, their vapor clouds will be dramatically smaller than those associated with released LNG or liquified hydrogen, and they will dissipate faster in the environment.

3.1.3 Passive Microwave Use to Assess Slick Thickness

Passive microwave use applies the principal that microwave emissions from oil slicks have a higher intensity than the surrounding seawater. Because this technology is limited to slick-forming fuels, the only alternative fuels that will be relevant are renewable diesel, biodiesel, vegetable oils, and low-density bio-crudes. The microwave band emissivities of these fuels will need to be determined to assess the efficacy of passive microwave film thickness detection for these alternative fuel chemistries.

3.2 ACTIVE SENSOR DETECTION

As stated previously, active sensors actively send out a signal to elicit a response from a target, and the signal is reflected back to the sensor to provide information. Examples include laser fluorosensors and radar. With the exception of radar, these sensing technologies are limited to aircraft-based observations.

3.2.1 Laser Fluorosensors

Fluorometry uses a laser or xenon lamp to produce a beam of UV light that is directed toward the water surface. If aromatic hydrocarbons (benzene, toluene, and other ring-structed hydrocarbons) are present, they partially absorb the UV light. Absorbing the UV light causes these molecules to enter an energetically excited state, and they give up this excess energy by emitting visible light, typically in the blue/violet color range. This phenomenon is called “fluorescence.” The UV light and visible light given off by the hydrocarbons penetrate through seawater, so this technique can detect aromatic hydrocarbons on top of and below the water surface (Chase and Roberts 2008). The color of the light released by the hydrocarbons is specific to certain molecular structures. Thus, fluorometry can be used to gain information about the makeup of the hydrocarbon compounds in the slick. If the slick composition is known, this information can also provide information about the thickness of the slick (Pilzis and Vaisis 2016). Some naturally occurring compounds in seawater fluoresce when exposed to UV light, so some sensors incorporate the ability to discriminate between these natural sources and compounds that are typically present in petroleum spills (Fingas and Brown 2017). Fluorometry has been successfully used as a continuous monitoring technique to rapidly detect localized spills from near-shore operations, such as refueling (Chase and Roberts 2008).

Laser fluorosensors are based on laser-induced fluorescence, whereby a laser light is shone on a substance, causing the atom or molecule to be excited to a higher energy state. When the molecule de-excites, it will emit light (fluoresces) at a wavelength that is longer than the excitation wavelength of the laser. The fluorescent light is then detected by a sensor consisting of either a photomultiplier tube or photodiodes. This method is currently limited to aircraft or shipborne surveillance, where it is used to detect oil seepages or spills. Because it does not depend on daylight, it can be used in darkness. For oil detection, the excitation laser wavelength is selected to excite the aromatic compounds of oil. Bio-oils and bio-crudes contain appreciable levels of aromatics and may be detectable with current systems. However, the other alternative fuels (renewable diesel, biodiesel, SVO, and alcohols) do not have aromatic structures and therefore, existing fluorosensing systems will not work for these fuel chemistries. This approach may still have utility with these fuels pending tuning of the excitation laser wavelength to a molecular structure present in the alternative fuel (Ying et al. 2007, Fan et al. 2015). One wavelength will not be applicable to all fuel chemistries. Also, the molecular structure selected for excitation must not be common in the surrounding environment. This technology has much potential, but research and development will be needed to adapt it to alternative fuel chemistries.

3.2.2 Radar

Radar, especially SAR, is one of the most prominent means of oil slick detection (Li et al. 2018, Akkartal and Sunar 2008, Alpers et al. 2017). This is an active sensing technique whereby an energy source emits microwave radiation via an antenna. The microwave radiation interacts with the targeted area, which then reflects part of the radiation signal back toward a sensor. By measuring the level of microwave energy received and recording the time between signal generation and reception, a two-dimensional image can be constructed. Large water body (ocean or sea) capillary waves reflect microwave (radar) signals, which produces an illuminated image. Floating objects on the surface, including oil slicks, attenuates the capillary waves, which subsequently reduces the reflected signal and reduces illumination in the image. This principle is shown in Figure 11. For an unencumbered sea surface, a detectable and measurable level of microwave energy is reflected back to the satellite sensor. The amount of the reflected energy depends on wave characteristics, specifically the height (trough) and length of the surface waves. A dense slick effectively dampens (or attenuates) the wave height, causing more of the incoming microwaves to scatter in directions away from the satellite detector. As a result of the reduction in the returning microwave energy to the detector, the image appears darker than the surround sea area. To detect a spill, two conditions must be met. First, a slick has to form and cover an area within the resolution of the detectors, and second, the slick must be large and viscous enough to alter the wave character. Fuels that are unable to impact wave motion (such as gaseous fuels), or those that readily dissolve, or sink will not be detectable. This limits the usefulness of radar detection to fuel spills of biodiesel, vegetable oils, and bio-intermediates such as bio-oils and bio-crudes.

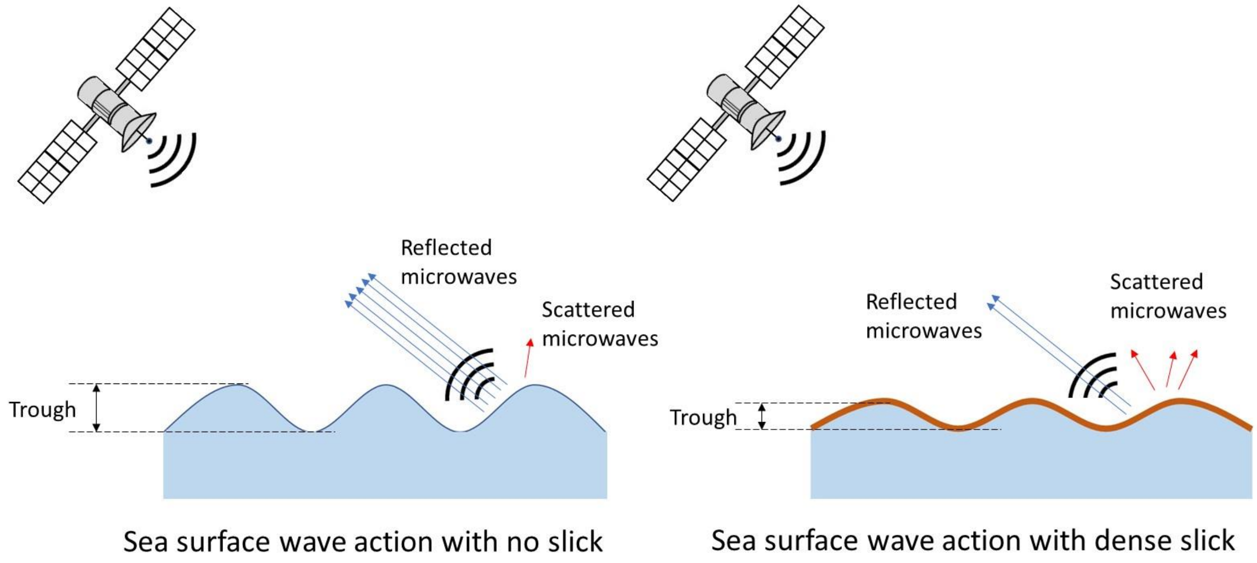

Figure 11. Schematic showing the impact of a slick on wave attenuation and subsequent reduction of reflected microwave energy. The wave height (or trough) is reduced when the surface is covered in a dense slick. As a result, more microwave radiation is scattered away from the spacecraft by the wave geometry, thereby reducing the strength of the returned signal.

For satellites, the resolution of the detector will dictate whether a spill can be detectable. As of 2005, the satellites having the highest SAR resolution were capable of detecting objects down to

30 m (Brekke and Solberg 2005), which was not likely to be sufficiently high enough to detect small spills. Newer satellites with SAR capability, such as the TerrSAR-X, have resolutions exceeding 0.5 m, which is within the range needed for small spill detection (Earth Observing System. 2019). Radar detection is the standard, most widely used means of detection of oil spills. It works well in daylight or darkness and is transparent to cloud cover. In addition to satellite-based surveillance, airborne and shipborne mounted systems are widely used.

3.2.3 Chemical Analysis

Careful analysis of water and air chemistry is a potentially valuable means of spill detection. It has the advantage of enabling detection when other detection methods, such as those based on optics, microwaves, or fluorescence, are not suitable due to environmental conditions, such as high wind speeds, large biofilms, poor sun angle, and unfavorable pass-over times. Chemical analysis can also be effective at detection of submerged fuels which cannot be seen by airborne methods. A number of analytical chemical techniques and methods are available for chemical detection; they all require direct contact with or collection of air or water samples. Common analytical methods include the use of mass spectrometry, gas chromatography mass spectrometry, fluorometry, IR spectroscopy or other methods to identify compound signatures. For a port location, sampling can be achieved on the shore or in port. Ship-mounted sensors or automatous surface, or underwater, samplers can provide continuous measurement. Many of these methods can detect substances in the parts-per-million range, but further dilutions are not likely to be detectable. Currently, chemical analysis is not commonly used for the detection of oil or fuel spills because of the relatively high capitals and operational costs, but this is likely to change in the future.

3.2.4 Fuel Taggant

One means of facilitating detection is to add a readily detectable taggant to the fuel. Examples include substances, such as highly visible colorants, or those that readily fluoresce, such as aromatic hydrocarbons or quantum dots. A fuel taggant can improve detection, but to be universally effective, fuel suppliers must be required to “tag” their fuels and not provide untagged fuels. The incorporation of a taggant into a liquid fuel is straightforward (as long as it can be readily dispersed in the liquid fuel). The applicability of a visible taggant for cryogenic fuels is less understood; however, an odorant (such as mercaptan in natural gas lines) is a viable alternative. A low-cost taggant would need to be developed and legislation would be necessary to ensure effectiveness.

3.2.5 Summary and Recommendations

A summary of detection methodologies and their potential to detect a particular alternative fuel chemistry is shown in Table 3. As summarized in the table, visible imagery, which is effective at spotting HFO or crude oil under certain conditions, will not be as effective for alternative fuels. With the exception of bio-oil and bio-crude, which have a high visible contract with the surrounding water, the remaining slick forming fuels will be more challenging to see visibly since they are transparent and do not provide much contrast with the background. Their contrast improves if emulsified, but this may not always occur. Compressed gaseous fuels, especially LNG and liquid hydrogen, will form a highly visible white cloud when released. However, the size of the cloud will be smaller than a slick of the same volume and in most cases, the cloud will disappear within 30 min after being released. Radar-based methodologies that are well established for oil slick detection are only viable for dense, slick-forming fuels. Therefore, they will be limited to biodiesel, SVO, and bio-intermediates, such as bio-oils and bio-crudes. IR detection has the highest potential of the detection methods surveyed for detectability of a wider range of alternative fuels, but several caveats exist. Detection will need to be recalibrated to identify cold spots associated with the release of cryogenic or highly compressed fuels. Since the cold footprint may not extend beyond the vessel structure, the detectable area will be smaller than for a crude oil spill. As a result, the resolution may need to be higher than current IR systems. Current IR detection methods are tuned to detect the emitted IR wavelengths from crude oil spills, but their utility at detecting slicks of alternative fuel chemistries is not known and warrants further study.

Laser fluorescence is a developing method that currently detects the aromatic structures present in crude oil or HFO. Because bio-oils and bio-crudes contain aromatic compounds, they may be detectable with existing systems, but fuels not containing aromatics will not be detectable. Studies will need to be conducted to ascertain whether other molecular structures are susceptible to fluorescence to determine the overall efficacy of this method. Chemical analysis methods offer the best approach for the detection of the widest range of fuel chemistries, but this approach is the least remote of the detection capabilities and requires that the sensor or sampling device be in relatively close proximity with the spill.

Because of the unique chemistries, spill profiles, and safety aspects of many alternative marine fuels, we recommend the following:

- Refueling of compressed fuels only under low–wind speed conditions
- The ability of slick-forming alternative fuels to form detectable sheens should be determined
- Investigation of slick-forming fuels for their emissivity profiles and ability to fluoresce
- IR detectors should be developed with increased resolution
- Expanded research and development of chemical analyses methods should be undertaken. This needs to include air and water sampling approaches
- Potential fuel taggants should be evaluated

4. SPILL CONTAINMENT

Because oil and petroleum slicks tend to float near the water surface, existing spill containment technologies are designed to be effective for addressing buoyant pollutants. Floating barriers, called “booms,” are the most widely used means for containing a spill (EPA 1999). Booms are deployed to surround an oil slick, preventing it from spreading. Figure 12 shows a deployed boom separating an oil slick from uncontaminated water.

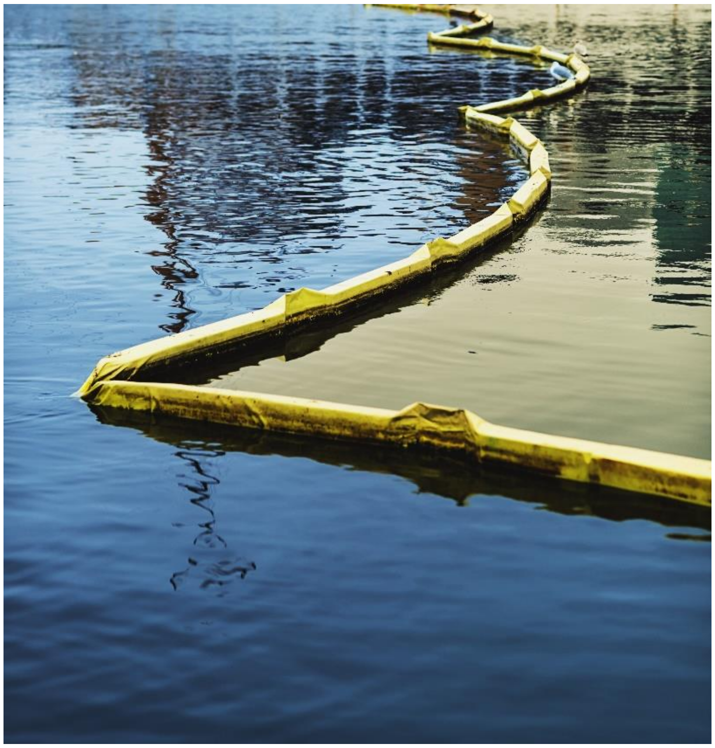

Figure 12. Floating booms contain an oil slick, preventing it from spreading into uncontaminated water. (Photograph from iStock/Getty Images Plus.)

Various boom designs have advantages and disadvantages; these can include ease of deployment, appropriateness to differing weather conditions, and effectiveness at containing slicks, for example. The most appropriate boom design depends on the specific conditions of a given spill. All booms share four basic characteristics:

- A freeboard floats on top of the water surface, which reduces the amount of oil that can escape over the top of the boom due to wave action, and which can provide a means of separating oil from the surface of the water.
- A flotation device keeps the freeboard on top of the water.
- A skirt extends below the water to contain the oil and reduce the amount of oil that can escape under the boom.
- A longitudinal support strengthens the boom against wind and wave action. This support is frequently a chain or cable that runs along the bottom of the skirt, additionally providing ballast to keep the skirt fully extended below the surface.

Improvised booms are sometimes used until better equipment can be deployed to a spill site. These booms use materials that are available at the spill site to rapidly contain oil or to exclude it from sensitive areas.

4.1 OIL SPILL CLEANUP

There are two means of mitigating an oil spill. The first is through separation of oil from water and subsequent disposal of the oil. This method makes use of the fact that oil and water tend not to mix well, forming layers that can be separated mechanically, or through separation of the oil by an absorbent. The second approach is to mitigate the oil spill in place using chemical or biological agents or in situ burning.

4.1.1 Separation Technologies

Mechanical separation of oil from water makes use of the buoyant nature of an oil slick. Some booms are designed to allow wave action to carry the top layer of the slick into a trough on top of the boom for subsequent disposal while preventing this oil from escaping completely over the top of the boom. Mechanical skimmers are powered devices that operate in a similar fashion by removing the top layer of the slick for disposal, but they do not rely simply on wave action.

Some boom and skimmer designs incorporate an absorbent material to trap and remove oil from water. Absorbent materials used for this purpose are most effective if they selectively trap oil and not water, meaning that they are oleophilic and hydrophobic. These types of absorbents are usually polymers. Some improvised absorbents use organic materials such as hay bales to trap oil, but these types of materials are also likely to absorb water. Booms incorporate absorbent materials onto the floating portion of the boom. Absorbing the oil rather than relying entirely on mechanical separation results in the oil being trapped in a solid material rather than as a slurry or liquid phase. This difference can make handling and disposal of the trapped oil more convenient.

4.1.2 In Situ Treatment

Treating the oil spill in place without separating the oil from the water is the second approach to spill mitigation. This approach is often used in areas where weather or sea state make mechanical containment and separation difficult or inefficient. Chemical or biological treatment agents are frequently applied in this scenario to speed up natural processes that decompose the oil. Ships or aircraft may be used to spread the agents over the oil slick (Figure 13).

Figure 13. Ships or aircraft may be used to spray chemical or biological agents onto the oil slick to speed up natural process that decompose the oil. (Photograph from iStock/Getty Images Plus.)

Chemical agents, often called "dispersants," break up the oil slick into smaller droplets that disperse through the water column. The smaller droplets are more susceptible to natural degradation processes and are less likely to reach a shoreline. Chemical agents are most effective in warm waters and when they are applied soon after a spill has occurred before the light hydrocarbons have evaporated (EPA 1999).

Biological agents are also used to enhance natural degradation of oil. Biological agents may include enzymes, nutrients, or organisms, such as bacteria. Bacteria and enzymes break down the oil, removing it from the environment. Nutrients are used to increase the population of bacteria and other organisms that are already present in the area of the slick to accelerate hydrocarbon breakdown (EPA 1999).

In situ burning involves the controlled ignition and burning of the oil slick on the water surface. This approach is most effective when the oil contains a substantial amount of light hydrocarbons. Heavier oils may require the addition of an accelerant (such as gasoline) to be used. All burning involves the use of a high-temperature ignition source and therefore poses an elevated risk for the personnel involved in the spill response. Furthermore, burning introduces a large amount of particulate matter and polycyclic aromatic hydrocarbon pollution into the air. For this reason, this approach is usually restricted to oil slicks that are at least several miles from human population. Sea conditions, weather, and the nature of the oil spill influence a decision to use in situ burning in lieu of or in addition to other mitigation approaches (EPA 1999).

4.2 SPILL RESPONSE FOR NONTRADITIONAL FUELS

4.2.1 Ammonia Spills

Ammonia is a gas at atmospheric conditions. It is usually stored as a pressurized liquid (similar to storage of propane) to increase the amount of ammonia that can be stored in a given space. If released above the waterline, ammonia will produce a dense toxic cloud. Ammonia released below the waterline (or ammonia that drops into the water before evaporating) reacts with water to form ammonium hydroxide.

In the event of a release of ammonia that forms a gas cloud, little can be done to mitigate the release. The resulting cloud will dissipate through diffusion into the atmosphere, with the rate of dissipation dependent upon prevailing environmental conditions. In this case, the most important spill response is to evacuate personnel from the affected area and areas downwind that are likely to experience toxic levels of ammonia in the atmosphere. 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 or health; thresholds as low as 25 ppm have been established as limits of exposure of longer time periods (Centers for Disease Control and Prevention web site). Ammonia is flammable but difficult to ignite at low pressures and concentrations. This fact causes the toxic characteristic of ammonia as a gas to be more important in terms of spill response than the hazard posed by fire or explosion.

In the event of a spill into the sea, opportunities to mitigate the spill are also limited. Ammonia that contacts the sea will react to form a solution of NH_4OH. Ammonium hydroxide is soluble in water, and the plume of NH_4OH will also dissipate through diffusion into the sea. As with dispersion of an NH_3 cloud, the dispersion rate of the NH_4OH plume depends on prevailing conditions, such as current, wave action, and temperature. Importantly, NH_4OH is chemically basic, which causes it to be corrosive. Hazards associated with corrosivity, such as the potential for chemical burns and impacts to aquatic life, are likely near the source of the release and become less likely at increasing distances from the source.

Ammonia is used extensively in commerce and as a result, commercial sensors for NH_3 detection are readily available. These sensors tend to use an IR absorption or electrochemical measurement technique. These techniques are not appropriate for use as a standoff monitoring method for airborne ammonia plumes but could readily be adapted for use on UAVs to monitor the extent of the local hazardous area surrounding an ammonia release. Similarly, deployment of commercial pH meters on UAVs or on watercraft may be useful for determining the extent of a hazardous area of the sea due to NH_4OH formation.

In the open ocean, it is unlikely that large-scale spill response will be effective in the event of ammonia spills because of the tendency for the ammonia to dissipate into the environment. In bodies of water such as ports, inlets, and bays, dissipation may not occur as rapidly as desired. The addition of weak acids, such as dilute acetic acid (vinegar), can neutralize NH_4OH. This approach may be useful to prevent encroachment of an NH_4OH plume into a sensitive area, for example, or to accelerate dissipation in a port. Using a weak acid, such as dilute acetic acid, is important because adding stronger acids to water or an NH_4OH solution may cause a vigorous chemical reaction and/or may be more hazardous or environmentally destructive than the original spill.

4.2.2 Methanol and Ethanol Spills

Methanol and ethanol belong to the chemical family of alcohols. Alcohols are molecules that have a hydrocarbon structure that includes an oxygen-hydrogen group attached to the carbon backbone of the molecule (Figure 14). The oxygen-hydrogen group is chemically attracted to water molecules, so most alcohols will dissolve at least partially into water. Both methanol and ethanol are miscible in water, meaning that they can exist in solution with water at any concentration. When spilled, these compounds will diffuse into water at a rate that depends on their temperatures. Warmer water will promote faster diffusion.

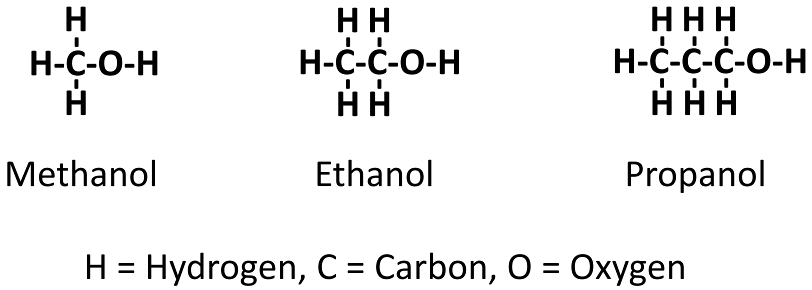
$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}O{-}H}$ $\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}O{-}H}$ $\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}O{-}H}$

Figure 14. Methanol, ethanol, and propanol are examples of alcohol molecules. All alcohols have an oxygen-hydrogen group attached to the carbon backbone of the molecular structure.

Because of their ability to dissolve into water, methanol and ethanol will not form a buoyant slick on top of the water. This key difference makes detection of a spill more difficult when using established detection technologies. Radar techniques are not likely to be useful in detecting methanol and ethanol spills since they would not have the same effect on surface wave height as oil spills. Similarly, the IR emission characteristics of methanol and ethanol differ from those of oil spills. UV detection may remain useful but likely requires adaptation for use with ethanol and methanol.

Perhaps the greatest issue in detecting and monitoring spills of ethanol and methanol is that these chemicals diffuse into water, unlike most of the petroleum-based chemicals in an oil slick. This difference means that the concentration of ethanol and methanol decreases as the distance from the source of the spill increases. Thus, optical instruments may be able to detect these pollutants near the source but are likely to be less able to monitor the extent of the spill as it moves away from the source because of decreased concentration and greater optical similarity to water than is the case for oil.

Techniques that may be useful in the detection of ethanol and methanol spills in channels, inlets, and ports include optical measurements of thermal diffusivity and measurement of fluorescence. The fluorescence technique is similar to techniques for detection of oil spills. The wavelength of fluorescence for ethanol/water solutions is approximately 425 nm, which is within the wavelength range used for some oil slick detectors. Suitable sensors may be able to detect both alcohol- and oil-based fluorescence, but the ability to differentiate one from the other will likely require additional engineering development. Another technique that may be useful for monitoring spills in ports and inlets is detection of differences in thermal diffusivity using a thermal wave resonator cavity (Matvienko and Mandelis 2005). This approach uses the differences in thermal properties to provide a measurement of ethanol or methanol concentration in water. However, it relies on a flow-through sample chamber that may be subject to fouling by biofilms or other contaminants in a port environment.

The characteristics of methanol and ethanol that reduce the effectiveness of spill detection technologies also render current separation technologies much less effective. The cleanup technologies discussed previously rely on differences in chemical and physical properties to enable separation of oil from water. Methanol and ethanol (and to some degree, other alcohols) are much more chemically similar to water than to oil. Separation based on buoyancy difference will not be effective for alcohols. Developing absorbent materials capable of separating alcohols from water may be possible, but they are likely to be different from those used for oils and may not be able to achieve similarly high separation efficiencies.

Separation technologies for alcohols are likely to be more effective when deployed near the source of the spill, where the concentration of the pollutant is high, and much less effective further from the source of the spill. Since diffusion of methanol and ethanol into water occurs relatively rapidly, deployment of a separation technology must also occur rapidly if substantial recovery of the spilled material is to be accomplished.

In situ burning, although possible in some cases, is likely to be more hazardous than when it is used with oil slicks. The flashpoint of alcohol and water mixtures depends on the concentration of the alcohol in the sea. Since both ethanol and methanol diffuse readily into water, the flashpoint for a given spill will be highest at the source of the leak and will decrease with distance from the source. Pure ethanol and methanol have flashpoints of 12.5°C and 9.5°C, respectively. Thus, these compounds can produce flammable conditions sufficiently near the source of the leak even when ambient temperatures are relatively low. As concentrations of these alcohols drop to about 50%, the flashpoint for both compounds increases to approximately 20°C. The flashpoints for these compounds rise above 50°C for concentrations of about 3% for methanol and 7% for ethanol (Ha 2015). Moreover, the concentration of these compounds decreases much faster with distance in the air than in the water. Hence, the zone where a flammable mixture of these compounds with air exists is likely to be close to the water surface and very near the point of release. Since mixing of ethanol and methanol with water and air is also influenced by local conditions, including wind, currents, and other factors, it may be very difficult to reliably determine the area that may be encompassed in flame if an ignition source was introduced. Similar to its use in oil slicks, in situ burning of alcohol spills would need to be initiated quickly after the spill occurs. In the case of alcohols, however, the window of opportunity to use this approach might close before the vessel experiencing the leak could maneuver clear of the affected area. Finally, initiating the burn could result in an explosion rather than a controlled flame, posing a great risk to the vessels involved.

Both ethanol and methanol experience natural degradation processes. Microorganisms (such as acetobacter) that degrade both methanol and ethanol are widespread in the environment. Enhancement of these natural decomposition mechanisms can be encouraged through the use of nutrient additions, such as those used in remediation of oil slicks. Microbial decomposition of methanol and ethanol consumes oxygen dissolved in the water. In the open seas, sufficient movement of water and oxygen may occur rapidly enough to prevent depletion of the dissolved oxygen. Barges equipped with oxygenation devices may be useful to prevent depletion of dissolved oxygen in inland waterways, bays, inlets, channels, and ports.

4.2.3 Natural Gas, Hydrogen, and DME Spills

Natural gas, hydrogen, and DME are discussed as a group because of the similarities in spill response that they require. Spills of these fuels will result in an airborne cloud of gas that is highly flammable. Although none of these gases are toxic, they can result in oxygen displacement that additionally creates a suffocation hazard. The cloud is likely to persist near the water surface and spread horizontally more than vertically until the gas reaches ambient temperature. This cloud will quickly diffuse into the atmosphere, with little if any absorption into the water column. Similar to ammonia that escapes into the atmosphere, little can be done to mitigate a natural gas, hydrogen, or DME spill except to monitor its extent and direction of motion (wind direction) so that personnel can be evacuated from the affected area.

Methane is the predominant gas species that makes up natural gas. Methane is a strong absorber of IR light; this characteristic is what makes methane a potent GHG. Methane leak detection based on IR light absorption is a mature technology. Numerous instrument designs exist for detection of methane leaks into the atmosphere at standoff distances from meters to kilometers. These instruments are in wide use for monitoring natural gas pipelines, for example (Cosofret et al. 2004). UAVs equipped with a methane detection capability is also a mature technology; commercial implementations are in use for field monitoring in the oil and gas industry. These solutions could be readily deployed for monitoring of methane releases at sea or in port. Satellite monitoring of the Earth’s surface is also a demonstrated capability for detecting methane plumes.

DME also absorbs IR light, making this a potentially useful means of atmospheric detection. Commercial use of DME is not as prolific as that of methane, and thus few if any commercial gas detectors that are specific to DME exist. Nevertheless, it is likely that instruments similar to those used for methane detection could be developed without undue difficulty.

Unlike methane and DME, hydrogen is not readily detectable using IR absorption. Hydrogen leak detection monitors are available commercially, but none are applicable to stand-off measurements such as those that would be needed to effectively monitor a large hazard zone around a spill at sea. Commercial detectors could conceivably be deployed on UAVs or watercraft to accomplish point measurements of hydrogen concentration, but many measurements would be needed at a range of locations and altitudes to adequately map the boundary of a hazard area.

4.2.4 Vegetable Oil and Biodiesel Spills

Vegetable oil and biodiesel spills are likely to require spill response measures similar to one another. As previously discussed, these fuels will form a slick on the sea surface upon release, with wave action causing emulsification with sea water over time. Traditional spill response and cleanup processes discussed previously for petroleum spills are likely to be very effective in mitigating spills of vegetable oils and biodiesel. Because they float on or near the sea surface, spills can be contained with booms to prevent their spread. Since both vegetable oils and biodiesel have lower environmental toxicity than petroleum oils, in situ clean up methods may be the preferred approach since these methods do not generate material that must be treated as hazardous waste. In situ burning is not likely to be successful because of the relatively low volatility of vegetable oils and biodiesel.

4.2.5 Spills of Bio-Oils and Bio-Crudes

Bio-oils and bio-crudes can contain a mixture of components, only some of which are soluble in seawater. Similar to ethanol and methanol spills, there is likely not a means of recovering the soluble components of bio-oils and bio-crudes once they have dissolved in seawater. Some of the components of these fuels may remain buoyant enough for spill mitigation efforts used for petroleum spills to be at least partially effective. Booms may be effective for containing the buoyant portion of the spill near the sea surface, at least until emulsification with sea water and other mechanisms of agglomeration begin to cause portions of the spill to sink. Similarly, in situ methods for mitigating the spill may be at least partially effective but are not likely to completely remove the spilled material from the environment.

5. CONCLUSIONS

Spill response in ports and at sea is an important safeguard for people and the environment in the event of an unintended release of hazardous materials. Spill response tools and techniques have long been in use to mitigate the impact of petroleum spills, but the potential deployment of new fuels to lessen the environmental impact of shipping likely require the development or adaptation of tools and techniques to adequately respond to spills of these new fuels. Although many of these chemicals may be new to the shipping industry as fuel for marine vessels, they are not unfamiliar as cargo. Hence, in many cases, there is extensive experience with safety protocols and response scenarios for port operations.

- **Ammonia:** Existing tools and procedures for petroleum spills are not likely to be effective because ammonia spills form a toxic cloud in the atmosphere and/or chemically react to form NH_4OH in the water. Ammonia spills will rapidly dissipate into the environment but create significant hazards, particularly near the point of release. Existing sensor designs for point-monitoring of ammonia may be adaptable to provide localized monitoring of the hazard area to facilitate evacuations. In sensitive areas, the use of mild acids, such as vinegar, may be a useful tool for accelerating degradation of ammonium hydroxide that has spilled into waterways.

- **Methanol and ethanol:** Existing tools and procedures for petroleum spills are also not likely to be effective in combating spills of alcohols such as methanol and ethanol. These alcohols dissolve very quickly into water, making subsequent separation very difficult. Additionally, methanol and ethanol can create a hazard area where airborne concentrations are high enough to create an explosive hazard under some conditions. Similar to ammonia, these alcohols will readily dissipate into the environment and degrade through natural processes. In sensitive areas, it may be possible to enhance environmental degradation through the addition of nutrients that accelerate the growth of microbes that degrade these alcohols.

- **Natural gas, hydrogen, and DME:** These fuels create a gaseous cloud that dissipates rapidly into the atmosphere when released. As a result, there is little chance of effective spill response beyond evacuation of personnel from the hazard area. Hydrogen and natural gas are in wide commercial use, which has spurred the development of a range of detection devices that may be adaptable to monitor the hazard area near a spill. Similar devices could conceivably be developed for DME detection. The principal hazard with these fuels is their potential to create an explosive cloud, although localized oxygen displacement can also create the potential for suffocation near the point of release.

- **Vegetable oils and biodiesel:** The spill response measures currently used for petroleum spills are likely to be effective for spills of biodiesel and vegetable oils. These fuels are expected to have a lower environmental impact than petroleum fuels because they are readily degraded by environmental mechanisms.

- **Bio-oils and bio-crudes:** These fuels are made up of a mixture of components, some of which are similar to petroleum and some of which are not. Because of this dichotomy, existing spill response measures used for petroleum releases are expected to be partially but not fully effective at containing and mitigating spills of bio-oils and bio-crudes.

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