

Comparative threat from LNG and fuel oil maritime accidents

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ABSTRACT

The U.S. Energy Information Administration estimates a 3-4% increase in U.S. production levels of natural gas in 2017 from 2016 production rates, themselves increased from 2015. While much of this increase will be used domestically or sent by pipeline to Mexico, some will need to be shipped as a cryogenic liquid to distant ports on specially designed ships. Spill responders are familiar with the hazards faced from unplanned fuel oil releases but have less experience with the threat of a large maritime liquefied natural gas (LNG) accident. Fortunately, considerable new research has been done assessing such threats.

Based upon such research, it is now possible to compare expected hazards from fuel oil and LNG tanker accidents. The paper compares behavior of both fluids in no-fire and fire-involved scenarios. LNG shows significantly different behavior than traditional oil products in either situation. In the no-fire case, LNG presents less of a direct environmental chemical hazard than fuel oil since methane, its main hydrocarbon constituent, is relatively benign compared to many of the hydrocarbons in typical fuel oils. However, it offers new safety threats to crew and vessel due to (1) its cryogenic behavior and (2) over-pressure caused by rapid phase transition of liquid to gas.

The fire/explosion hazards between the two fluids are also quite different. While

fuel oil fires have larger footprints and can generate a large airborne particulate hazard, LNG burns relatively cleanly with little soot. However, heat radiation from LNG is much larger, increasing the risk of secondary fires and increased damage to the vessel itself. Moreover, confined natural gas or LNG undergoing rapid phase transition can lead to an internal detonation overpressure in the vessel, also expanding the damage. Experts are divided on a boiling liquid expanding vapor explosion (BLEVE) risk from LNG maritime operations.

THE UNIQUE NATURE OF LNG

The U.S. Energy Information Administration estimates a 3-4% increase in 2017 U.S. production levels of natural gas in 2017 from 2016 production rates, themselves increased from 2015. While much of this increase will be used domestically or sent by pipeline to Mexico, some will need to be shipped as a cryogenic liquid to distant ports on specially designed ships.

To understand both the increased demand and method of transport, it is necessary to understand the basic properties of the hydrocarbons that constitute natural gas. Methane, the simplest hydrocarbon molecule with four hydrogen atoms surrounding a single carbon atom, makes up more than 90% of most natural gas mixtures, with the remaining 10% consisting of heavier hydrocarbons such as ethane, propane, and butane. Its density at room temperature is lighter than air although cold gas from vaporizing liquid is negatively buoyant so it is possible to have colder gas pockets collect near the ground. Since it is used as a fuel, natural gas is of course highly flammable with a flash point of 20° F and a flammability range of 5-14%.

Like all fuel gases, unless transported by pipeline, it must be concentrated to be economically feasible to ship (Lehr, 2007). Unlike larger hydrocarbons such as propane and acetylene, methane, with a critical point of -115°F and 45 atmospheres, cannot be compressed at room temperature to form a liquid. In order to compress methane to form a supercritical fluid with a density similar to liquid methane would require impractical pressure levels of over 1000 atmospheres. Instead, LNG is formed by cooling the gas to below its boiling point of -258°F .

The resulting liquid is buoyant, having a specific gravity of less than half that of seawater. In fact, if LNG is carefully spilled onto calm water, it will form a thin vapor layer between the two liquids, rapidly spreading due to Fay gravity-inertial forces (Fay, 2007). An interesting phenomena happens in such releases when the methane preferentially boils off from the LNG, leaving heavier components such as ethane that come in direct contact with water, causing an energetic phase transition from a liquid to a gas. The end result is a series of 'geysers' from the surface slick.

A more typical, and more dangerous, situation is when there is turbulent interaction between the LNG and receiving water of sufficient volume. Liquid water is well above the superheat temperature of liquid methane so that when liquid methane comes into contact with liquid water it undergoes a vapor explosion called a rapid phase transition (RPT). While not combustion related, it can produce significant overpressures. A 1980 field trial by Lawrence Livermore National Laboratory at the Naval Weapons Center at China Lake, California resulted in a rapid phase transition that caused a 27 kg metal plate to be thrown 50 meters from the LNG release point and 227 kg concrete slab to be moved backward over half a meter.

Methane is the least threatening of fossil fuels from the perspective of increased greenhouse gas from combustion. Oxidizing (burning) methane produces two water molecules for every carbon dioxide molecule generated. This contrasts with coal where burning produces large proportions of carbon dioxide as a waste product. Methane gas is relatively non-toxic to humans with its non-fire hazard being displacement of oxygen that may result in a suffocation risk to responders. In its liquid form, methane presents a skin contact hazard due to its cryogenic nature. Cryogenic liquids can produce effects on the skin similar to a thermal burn.

Unconfined methane vapor clouds generated from LNG evaporation can ignite if in contact with a heat source, producing a deflagration, an expanding sub-sonic flame front traveling at more than 1 m/sec with overpressures slightly less than an atmosphere. The resulting fireball could be a serious heat radiation hazard, but not a detonation threat, where the explosive overpressure front travels at supersonic speeds. One of the authors participated in a series of experiments using plastic explosive as an ignition source in an unsuccessful attempt to get detonation of unconfined methane. However, confined methane vapor clouds or vapor clouds formed with excessive amounts of non-methane hydrocarbon gases may not have this limitation. Ignition in such cases can lead to detonations where the overpressure front travels at supersonic speeds.

VESSEL SPILL RISKS

While ultra large crude carriers can transport as much as 2 million bbl, the more typical medium-size oil tankers of the Aframax class can carry less than half that amount at maximum capacity. Similarly the largest LNG carriers, the Q-max class, have a maximum capacity of 266, 000 cubic meters, the equivalent volume of 1.7 million bbl,

while the new Panamax class vessels designed for the expanded Panama canal transit are limited to approximately the equivalent of a million bbl. For both traditional oil shipment and LNG transport, safety has been an important factor in new ship design. A common LNG carrier may have 4 to 6 inside containment tanks, either of the moss spherical design or the membrane prismatic design, surrounded in whole or part by an outer hull, similar to the double hull concept for oil tankers. A common tank size used for past hazard calculations has been 12, 500 cubic meters but the new larger vessels have tank sizes of over 50, 000 cubic meters, indicating the potential of larger spills.

Unfortunately, enough oil tanker accidents have happened in the past that a typical spill scenario can be hypothesized. This is not the case for LNG vessels where there is a lack of major spill incidents. Sandia (Hightower et al., 2004) estimated that a collision of a large ship, travelling at 12 knots, with an LNG carrier would be expected to produce an effective hole area of one square meter. Perhaps because of the increased terrorist threat, much of the interest in LNG spills has centered on possible intentional, rather than accidental, releases. The same Sandia report calculated that an intentional breach might produce a hole size of between 5 to 7 square meters. A recent DOE report to Congress (2012) increased the maximum initial breach size to 15 square meters. Depending upon the breach location, LNG spillage would be accompanied by water ingestion. As discussed above, this could lead to localized RPT's, possibly further compromising the already damaged vessel. McRae (1984) estimated that a large methane RPT will produce a detonation shock wave with an overpressure of more than 30 atmospheres. Hightower et al (2004) considered that cascading damage events could cause the rupture of up to three tanks in a typical LNG vessel.

This conclusion illustrates the fact that external factors not present in a standard oil tanker accident may increase potential LNG release volume during an accident. Another factor that may increase the vessel damage and LNG release rate is if fire is involved. For example, a second vessel impacting the LNG carrier may itself contain a flammable cargo. Havens and Venart (2008) determined that commonly used polystyrene insulation material could completely liquefy in as few as 10 minutes exposure to fire, causing LNG boil-off that would exceed pressure relief valve capability by an order of magnitude. Fire response teams familiar with oil tanker fires might not recognize this new and significant threat to their safety. Fortunately, a series of experiments done by Sandia National Laboratories (Morrow, 2012) showed that exposure up to 40 minutes of intense heat radiation, 270 kW/m², to two common LNG cargo systems did not cause sufficient damage to the insulation that would result in dangerous levels of overpressure in the tanks. However, should the insulation be displaced during the breach incident, the expected heat radiation level could easily exceed the critical radiation intensity limit for structural steel.

One of the authors served on an expert panel assembled by the U. S. Government Accountability Office (GAO, 2007) to consider, among other questions, whether a fire-caused overpressure event such as discussed above could lead to a boiling liquid expanding vapor explosion (BLEVE), or, in layman terms, a rapidly expanding fireball. While the opinions of the experts at the time were not unanimous and the topic is still open to some disagreement, the majority was supportive of the study by Pitblado (2006) that the structural design of marine vessels would prevent a BLEVE from happening in

LNG marine transport. If a BLEVE were to occur however, the structural integrity of the vessel could be jeopardized and lead to a larger release.

A related threat would be an interior combustive detonation between the outer hull and the inner tank. Water ingested from the outside could heat leaking LNG, causing, besides the RPT discussed earlier, a stoichiometric methane vapor concentration (~10%) in a confined space. The potential for ignition sources would be high. The overpressure from any subsequent combustive explosion increases rapidly with containment space to obstacle volume ratio (almost to the cubic power according to Eggen,1995) while flame speed of the burning mixture then increases with overpressure. Once sonic speed limits are reached, a detonation occurs. The resulting shock wave can cause significant damage to the vessel.

Cryogenic structural damage caused by liquid LNG in direct contact with metal is probably less of a problem. Based on some limited DOE (2012) analysis, ice formation should insulate the outer hull in a major incident such that structural damage caused by rapid cooling should not be a major threat.

LNG POOL FIRES

For both LNG and fuel oil, spilled product that is not consumed by onboard fire or explosion will form a pool on the water surface. Leak rate will depend on the nature, size, and location of the breach. Assuming a 5 square meter breach from a 12,500 cubic meter tank at the 13 m above the water line, ABS Consulting (2004) estimated that drainage would be mostly finished in slightly over a minute. This would hold for either LNG or fuel oil.

This should be considered a maximum release rate scenario as some of the LNG or fuel oil would be restricted inside the vessel structure, and the breach would be irregular in shape, causing a smaller discharge coefficient (Lehr, 2007) than the ideal unit value used in the ABS calculation.

Spilling LNG would likely pool outside the vessel. Using the above scenario, a non-burning pool might, depending on conditions, form a slick of between 150 to 300 m. in diameter (ABS Consulting, 2004; Quest Consultants, 2003). The research by Fay (2007) indicates that the LNG will spread faster than fuel oil because of the vapor cushion between it and the water. Fay noted that LNG spreading would more closely resemble a liquid spreading on a smooth hard surface than a non-cryogenic, buoyant liquid spreading on water. However, an early study by Opschoor (1980) concluded that the LNG would also stop spreading sooner than spilled fuel oil with a final average thickness that is an order of magnitude greater than oil, producing a smaller slick footprint.

However, for large burning pool fires, the controlling factor in pool size is probably not gravitational force on the spreading liquid (Fay spreading) but rather the loss of product due to combustion. As the gravitational head inside the breached tank decreases, so does the fuel spill rate. However, as the area of the pool gets larger, more oil or LNG is burned, causing Fay spreading to slow down. At some point, burn loss equals or exceeds spill rate and the spreading slows and finally stops. The pool area reduces (Lehr and Simecek-Beatty, 2004) to a pool size such that leak rate matches burn mass loss rate. The circumstance when this occurs is different for fuel oil and LNG. LNG has burn regression rate of between 0.3-0.35 mm/sec (DOE, 2012). A typical fuel oil #2

might have a burn rate of .03 mm/sec, an order of magnitude smaller. Hence, all else being equal, the fuel oil pool will grow larger and burn longer. Luketa (2011) concluded a burning and spreading pool of LNG on calm water generated from a 5 square m. breach in one tank would result in 300 m diameter pool if unrestricted. The fuel oil pool area would be expected to might be several times this size. Of course, actual pool size would depend upon specific conditions such a sea state and surface obstructions.

THERMAL RADIATION HAZARD

A bigger pool footprint for the fuel oil fire does not necessarily translate into a greater heat radiation hazard. An LNG pool fire has a much larger emissive power, 200-300 kW/m², than the average fuel oil fire, at 140 kW/m² or less, and also produces much less obscuring smoke, meaning that the peak radiant heat danger from an LNG fire is significantly higher (Lehr and Simecek-Beatty, 2004). However, since it burns faster, any subsequent fire will be extinguished more rapidly.

Flame height from pool fires is often estimated by using some form of the Thomas equation (Thomas, 1963). The equation assumes that the flame height increases as the burn regression rate raised to the six tenths power, but only to the four tenths power for increasing pool diameter. Hence, the flame height increases more quickly due to the increased LNG burn regression rate than does the height increase due to the increased fuel oil surface spread. More importantly, the flame surface radiation emissive power per unit area is much larger for LNG than for burning fuel oils. LNG emissive power increases slightly with the size of the fired, minus a slight decrease due soot formation. Luketa (2011) recommends 286 kW/m² as a nominal value for LNG emissive power. Emissive power of burning fuel oil is significantly less, plus the burning oil will

produce considerably more obscuring smoke than would burning natural gas. Past experiments for large JP-4 fires (Lees, 2001) indicate that smoke blockage accompanying such fires will reduce the fraction of radiated heat by 90% or more. An unwanted side effect of this larger soot production is increased particulate inhalation risk to nearby personnel.

Based upon the above observations and recognizing that individual circumstances will vary, the authors recommend a rule-of-thumb for LNG pool fires. Such fires will produce a cleaner but much shorter burn with an order of magnitude more radiation heat flux compared to the heat radiation of an equivalent fuel oil fire, increasing the risk of secondary fires but reducing the risk from particulate inhalation. Fire suppression and mitigation procedures need to take this into consideration.

CONCLUSIONS

While LNG vessels have an excellent safety record, it is prudent to prepare for possible spill incidents of this product. LNG's unusual properties bring increased damage risk to the vessel if a breach were to occur, including rapid phase and/or combustive detonation, potentially increasing the size of the release. Accidents involving external fires might cause tank failure and possible BLEVE if the insulation is compromised. While methane, the main component of LNG, presents little toxicological concern, the increased intense heat radiation from an LNG pool fire presents a hazard larger, but of a shorter duration, than typical fuel oil fires.

DISCLAIMER

The contents of this paper reflect the personal views of the authors as spill experts and may not reflect the opinions and conclusions of NOAA or the U.S. government.

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