Argent Marine

LNG Bunkering Issues

An Overview of LNG Properties and their Safety Implications

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Introduction and Executive Summary

This paper gives a comprehensive overview of the hazards associated with LNG. The hazards differ from those arising from handling conventional marine liquid fuels; indeed, some hazards are unique to liquefied gases and have no comparison with those from conventional fuels. It is vital if the LNG small-scale industry is to develop that these hazards are fully recognised. This is important for establishing the regulatory framework and for setting training standards both for operating staff and for emergency responders. At the end of this paper a rational process for determining safety distances and exclusion zones is explained and some comments on training requirements are included.

LNG Properties

The physical properties of LNG are markedly different from those of conventional marine liquid fuels (distillate and residual) and full cognizance of these differences must be taken when proposing projects to facilitate the development of the LNG bunker industry. Some of the hazards (including the most consequential) are specific to liquefied and/or cryogenic gases and comparable hazards do not exist with conventional liquid fuels. For this reason, it would be imprudent to assume that mariners who are highly trained and familiar with conventional marine fuels are also aware of some or all of these hazards. Hence a comprehensive review of hazards associated with the handling of LNG is given.

The large-scale bulk LNG business has a remarkable safety record which has been achieved in large part by operators being fully aware of these properties and the attendant challenges. The LNG marine transportation industry can rightfully claim, since its inception some 50 years ago, that there have been no fatalities due to spillage or loss of containment of LNG. Studies to assess the cumulative volume of accidental release, whilst imprecise, yield figures totalling no more than 40 m3 over the course of 50 years. Similar studies on the conventional marine fuels tell a different story.

A USCG report titled "Evaluation of Accidental Oil Spills from Bunker Tanks" (US Coastguard Ships Structure Committee—2003) records that, over a 15 year period, there were 472 spills of marine fuel greater than 40 m3 internationally. Within the US over the same period for all reported spills, including those involving a few litres, there were over 10 000 incidents of spillage. 7% of these were assessed as 'structural', i.e. collisions or groundings, 93% were operational, i.e. overfilling tanks and careless draining before disconnection.

The key point to understand from this is that engagement of the existing major players in the LNG industry is predicated upon levels of operational safety being equivalent to those of the existing large-scale industry. The reputational risk to these players should an accident result in injury to members of the general public is unacceptable. Whilst the industry could theoretically develop with small-scale producers of LNG, the fact that the 'major players' were not participating would present serious regulatory challenges to the promoters.

For 'equivalent levels of safety', there should be a recognition that all technical measures for safety in the large-scale industry may not transfer directly to the small-scale, but the societal risk from small-scale activities must be no worse on a probabilistic basis than from the large-scale industry.

The conclusion has to be, therefore, that the safety culture in this new business must be closely related to that of the large-scale LNG rather than based upon the practices of the conventional marine fuels supply industry.

Physical Properties

This section looks at the physical properties of LNG and compares them with those of conventional marine fuels. The implications of the properties are discussed. The following are the properties addressed:

- Flash point
- Ignition energy
- Combustion characteristics
- Flammable cloud formation and dispersion
- Effects of spillage on steels used in ship construction
- Rapid phase transition (RPT)
- Rollover
- BLEVE
- Human Contact

To aid understanding, the composition of LNG is assumed to be:

Methane	87%–99%
Ethane	1%–10%
Propane	0%–3.5%
C4+	0%–1%
Nitrogen	0%–0.7%

And typical carriage conditions in the large-scale trade are:

Vapour pressure	1100 mbars (absolute)
Temperature	-159.5°C
Density	425–470 Kg/m3

The following table shows a comparison of the key combustion properties:

	Vaporised LNG (NG)	Diesel (DMA)
Flammable range in air	5–15%	0.5–5%
Flash Point	-175°C	>60°C
Self--ignition temperature	595°C	250–300°C
Ignition Energy	0.2 mJ	20 mJ
Vapour Density (air = 1)	0.55	>5

Discussion on Properties and Hazards

1. **Flash Point**

   This is the most significant property from the point of view of assessing hazards. Below the flash point, a fuel cannot generate a vapour cloud which supports combustion. The mixture is too lean. By regulation, conventional marine liquid fuels are not permitted to have a flash point less than 60°C (except for a special case for fuels for emergency generators and lifeboat engines which may have a flash point of 43°C). The normal storage, transport and delivery conditions of conventional marine fuels are less than 60°C and therefore a spill cannot create a flammable vapour cloud. From the flash point figures given above, any and every spill of LNG will rapidly generate a vapour cloud, some part of which will be in the flammable range. For conventional fuels, the risk of ignition from a remote source is therefore non-existent, whereas for any spill of LNG the risk of ignition is present. This is not to say that these conventional fuels are non-flammable, but to ignite spilled fuel requires direct contact with either a flame or other high temperature source (see 'Self-ignition temperature').

2. **Self-ignition Temperature**

   This is the temperature to which a flammable mixture must be heated for ignition to occur spontaneously, i.e. without any ignition source such as a spark or flame. Ignition will occur if the flammable mixture comes into contact with a surface at or above this temperature. This is not particularly relevant for spills in the open air but is relevant for releases in an engineroom. Engine exhaust manifolds and superheated stem pipes may be well above the temperature to ignite liquid fuels but are not normally at a temperature which would ignite natural gas (vapourised LNG). (This is not to say that such releases in an engineroom are safe—they can be ignited by other means; see next paragraph.)

3. **Ignition Energy**

   Flammable mixtures may also be ignited by a direct release of energy, such as an electrical spark or a spark generated by a dropped metallic object. For natural gas vapours, the ignition energy required is 100 times less than for a flammable mixture created from liquid marine fuels. Indeed, the electric spark needed to ignite a gas cloud can be so small as to be invisible to the naked eye. This is why, as part of the control mechanisms, control of sources of ignition is so important when dealing with LNG hazards. A particular case is that of guarding against stray current flows and static electricity in the transfer connection system. Guidance given in ISGOTT (2006) on the installation and use of insulation flanges in the system should be strictly adhered to. The strictures on the use of insulating flanges, and corresponding elimination of so-called bonding wires, apply equally to the case of a barge loading from a jetty and delivering to a customer's ship.

4. **Combustion Characteristics**

   Generally speaking, hydrocarbon liquids, including LNG, do not burn—it is the vapour given off from the liquids that combusts. The combustion characteristics of a vapour cloud from LNG are very different from those of conventional marine fuels. The main feature is that vapourised LNG burns with little smoke. A pool of conventional liquid fuels will burn vigorously, producing a very smoky flame with lots of soot. This shields the radiation from the flames, restricting the surface emissive power to a typical level of about 70 kW/m2. The natural gas fire, by contrast, has surface emissive powers about 4 times larger than this and is characterised by a very tall flame structure. This obviously has a major impact on the likelihood of the fire igniting other combustible materials and the likelihood of personnel suffering severe burns by radiant heat. The approach to firefighting becomes more one of fire hazard management than of extinguishing. The recommended approach is to isolate the source of gas and allow the fire to burn out, meanwhile using water spray/deluge systems to protect tanks and equipment from the high radiant heat.[1]

Fires in unconfined vapour clouds are not likely to lead to detonation, i.e. very high flame speeds and blast shock waves. The flame front speed in an unconfined vapour cloud is likely to be modest, about 2–3 m/s. Conversely, ignition of a vapour cloud in an enclosed space or heavily congested area can experience rapid acceleration of the flame front potentially leading to detonation. For this reason, great care must be taken about location of ventilation air intakes relative to potential spill points.

5. Vapour Dispersion Characteristics.

At ambient temperature the natural gas vapour cloud is lighter than air and will disperse buoyantly. The diesel fuel vapour cloud is, under ambient temperature conditions, always heavier than air and will hug the ground or water. (Note that to create this cloud, the bulk liquid temperature of the diesel fuel must be above 60°C.) When LNG is spilled, vapourisation commences instantly and proceeds rapidly. Initially the vapour is very cold, about -160°C, and is heavier than air so remains close to the surface. The low temperature freezes moisture out of the air, creating a highly visible white cloud which will travel with the wind. The vapour will warm up rapidly, taking heat mainly from the atmosphere and, when it gets to the range of -100°C to -80°C, it becomes buoyant. From various spill test programmes, it has been noted that the portion of the vapour cloud from spilled LNG within the flammable range is always smaller than the visible cloud limits.

6. Effects of spillage of LNG onto steel

Normal shipbuilding steel materials cannot withstand the effect of exposure to LNG at -160°C. The steels lose all of their inherent ductility and become brittle. The thermal stresses set up by the temperature gradient lead to instantaneous fracturing of the steel. Only a few litres of spilt LNG are sufficient to cause large fractures which will penetrate through deck plating and the attached stiffeners and secondary structure. A secondary hazard is that of the LNG flowing through the fractures into a space which may normally contain ignition sources or even, on a ferry, members of the general public. This hazard is unique to LNG and there is no comparable hazard for conventional liquid fuels.

7. Rapid Phase Transition (RPT)

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[1] 1 Ref “Liquefied Gas Fire Hazard Management” SIGTTO 2004.

This phenomenon is exactly what its name implies and is unique to situations where two liquids come into contact where the boiling point of one is far below the normal temperature of the other, i.e. LNG spilled onto water. When a liquid at its saturation temperature is heated slowly, the phase change from liquid to vapour will occur at a steady rate. If the heating is very rapid, owing to a large temperature difference between the hot and the cold liquid, it is possible for the cold liquid to become superheated as a meta-stableliquid up to a 'stability limit' (for LNG, this is about -100°C). When this stability limit is reached, rapid phase transition occurs. The excess energy stored in the superheated liquid is released instantaneously. The result has been described as a 'flameless explosion' or a 'physical explosion' because no combustion takes place. The energy release rate is orders of magnitude lower than that resulting from stoichiometric combustion of the same quantity spilled; nevertheless RPTs look and sound like explosions and can be potentially damaging. Note that RPTs cannot occur when a cryogenic liquid is spilled onto a hard surface. A phenomenon called 'film boiling' prevents direct contact between the liquid and the heat source and this limits the rate of heat transfer below that at which the liquid can become superheated. The phenomenon of RPT is not confined to the LNG industry but is a known issue in the steel making industry with water/molten iron interactions and in the nuclear industry with fuel/coolant interactions. As for the effects of spillage onto steel, there is no comparable hazard associated with the spillage of conventional liquid fuels.

8. Rollover

This phenomenon has occurred in large, fully-refrigerated LNG storage tanks. The circumstances that lead to rollover require the stratification of LNG layers of differing composition. These stratified layers, over time, become unstable. The consequence of rollover is a large amount of vapour generation from the liquid leading to a rapid rise in tank vapour pressure, possibly leading to uncontrolled release of vapour from relief valves. The normal operating procedures for small-scale LNG are likely to reduce the risk of this occurrence and the large margin between normal operating pressures and relief valve settings mean that uncontrolled release is also not likely. Whilst rollover cannot categorically be eliminated as a hazard in small-scale operations, it is considered a low risk. Should it occur, the likely symptom will be a rapid and unexplained rise in tank pressure.[2] There is no comparable hazard with conventional liquid fuels.

9. Boiling Liquid Expanding Vapour Explosion (BLEVE)

"Boiling Liquid Expanding Vapour Explosion" is the name for a particular type of catastrophic failure of a pressure vessel containing liquefied hydrocarbon gases. The sequence of events is that the pressure vessel is engulfed in flames and, even though the relief valves may work correctly and limit the pressure, the fire heats the exposed shell of the vessel above the internal liquid level to such an extent that it loses strength and fails. (Below the liquid level in the tank, the shell plating will remain substantially at the saturation temperature of the liquid; however as the fire progresses, the liquid boils and vaporises. The tank contents are expelled as vapour through the relief valve. The liquid

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[2] 2 Ref "Prevention of Rollover in LNG Ships" SIGTTO 2012

level drops exposing more of the upper shell to the fire.) When the BLEVE occurs, the vessel fragments into large sections and the contents are ejected violently into the air and rapidly deflagrate. The consequences are devastating, a combination of blast and fragmentation plus high thermal radiation from the rapid combustion of the tank contents. There have been a number of these incidents in pressurised LPG storage facilities and LPG transport vehicles (road and rail). There have been 2 recorded incidents with LNG road transport. The fact that, relative to LPG, there have been only two LNG BLEVEs is partly due to the differing scale of the businesses and partly due to the type of storage used (most LNG is stored at atmospheric pressure). A barge carrying LNG in a Type C tank would be low on the probability of suffering a BLEVE,not least because the tank insulation should provide additional protection in case of an engulfing fire, but the probability is not zero. Authorities and emergency responders need to be aware that BLEVEs can occur so that they can assess the risk. There is no comparable risk with conventional marine fuels.

10. Human Contact

The vapour from LNG is non-toxic. Some sources describe the vapour as slightly narcotic. However, LNG contact with human flesh causes immediate and severe tissue damage, similar to a severe burn. This is the result of the very low temperature and rapid vaporisation of LNG in contact with the skin. Whilst long exposure to diesel fuel may cause dermatological damage, it is nothing like the severity of that caused by contact with LNG.

Implications

Reduced to its simplest, the safety record of the large-scale LNG transportation industry is based upon the fact that the industry does not tolerate any spillage of LNG. The hazards described above can only occur if the LNG is spilt. It is therefore essential that all those involved directly or indirectly in the bunker chain fully understand the hazards and approach the issue with a similar zero-tolerance attitude towards spillage. They must also understand the methods to avoid any spillage and to manage the consequences of any spillage, which might occur. This extends to port authority staff and emergency responders.

In typical ports, there is a zoning system where hazardous cargoes, such as hydrocarbons, are handled in a restricted area away from general cargo and passenger operations. The introduction of LNG as a bunker fuel will lead to operations, that previously only took place in these restricted areas, now being conducted throughout the port area; hence the need for a high level of training and awareness amongst all port staff.

Safety Zones

Notwithstanding previous comments about not tolerating spills, one of the further layers or safety barriers found in the large-scale industry is the concept of a safety zone, sometimes described as , an ‘exclusion zone’. Within this zone, all ignition sources are controlled and only personnel directly involved in the operation are permitted. The concept here is that a spill is considered credible despite all efforts to prevent it by both design and operational procedures. To illustrate, in the large-scale industry the transfer process is considered the highest risk. An exclusion zone is established around the ship during loading or discharge. The size of the zone is determined from studies based on establishing the largest credible spill size consequent upon a single point failure and the furthest that a flammable cloud can travel in the worst conditions. This study is deterministic, i.e. probability of occurrence is not considered.

This approach could be applied to the LNG bunker supply situation. Careful studies would be needed to identify the largest credible spill from a single point failure. (For the large-scale, this is usually taken as the volume of liquid in one loading arm between the ships ESD valve and the shore ESD valve at the base of the loading arm.) The exact failure mechanism does not need defining, just a judgement that the resulting spill is credible. (Whilst larger volumes may be spilt in the event of multiple system failures, the probabilities of such multiple failures in a properly designed and maintained system are considered negligible.) The spill quantity so determined is then used as input for dispersion calculations. The equilibrium conditions of the LNG (i.e. the vapour pressure of the liquid) are also an important factor. The flammable cloud from a spill of LNG with a high vapour pressure is significantly larger than one from a similar spill quantity of LNG whose vapour pressure is substantially at atmospheric pressure. Representative physical arrangements of the bunker supply vessel and the receiving vessel are modelled. The calculations are performed in an iterative fashion, varying factors such as wind speed, air temperature, water temperature, humidity etc. to find the combination which leads to the furthest distance from the spill point that a flammable cloud can travel. That is then used to define the safety zone. From this, the dimensions of an exclusion zone can be defined. For the large scale, this is usually only done in two dimensions; for the small scale, three dimensional analysis should be considered. This is because the resulting flammable cloud could go above deck level.

Whilst this approach may seem rather complicated, it has become well established in the large-scale industry and some such rational approach must be developed for the small-scale industry. If such an approach is not adopted, the danger is that it will come down to an argument based on opinion which is impossible to validate.

A further aspect of this subject on exclusion zones relates to the question of loading/discharging cargo or passengers at the same time as conducting fuelling operations. A serious debate needs to be had but the logic seems to be that if the cargo operations or passengers have to be, or are likely to be, within the exclusion zone during LNG fuelling operations as determined above, then the operations cannot continue. Either the passengers have to be removed and cargo operations suspended, or the LNG fuelling does not take place. It is therefore critical that credible release scenarios, hazard analysis and exclusion zones be carefully evaluated when considering allowing cargo operations, freight or passenger, to take place at the same time as fuelling operations. Such evaluation process may lead to a redesign of equipment in order to minimise the size of the credible spill.

Training

This is a subject that has created much debate in the industry. For vessels supplying the LNG as fuel, it is difficult to support any argument for training the crew to a lower standard than currently codified in the ‘Dangerous Cargo Endorsement’ (DCE) requirements under IMO STCW for those serving on LPG and LNG vessels. There will undoubtedly be differences in detail, but the general level would seem to be a sensible guide. For the consumer vessels there is also much debate. The starting point would seem to be along the lines above, i.e. equivalent to a DCE, but there is a lot of resistance to this idea by some who consider this excessive. It would seem clear that there must be some training for crew on LNG-fuelled vessels and a careful analysis of the operational and maintenance requirements is necessary. It may be that some operations, e.g. draining and gas-freeing the fuel tanks for periodic inspection, and returning to service at 5 year intervals should be conducted by independent experts brought in to do the procedures. Thus, the vessel's staff would not be trained for this. This principle could be extended to routine maintenance of the control and safety equipment associated with the LNG storage. An extreme case may be where supplier takes full responsibility for filling the consumer vessels storage tanks. However, if the industry is going to follow this route, then, for safety standards to be maintained, there must be a high degree of standardisation of equipment and layout onboard LNG fuelled vessels.Coming to a pragmatic and practical conclusion to these debates is important as it is one of the high-level concerns that experienced LNG people have that large numbers of seafarers from a background that does not include handling hazardous materials, specifically liquefied gases, will suddenly be taking responsibility for LNG operations.

Conclusion

Small-scale LNG is poised to play an increasingly important role in the global energy mix, but the potential hazards associated with small scale LNG, especially in its use as a transportation fuel, are not yet widely understood. This paper has attempted to outline the major and specific hazards surrounding small scale LNG. It is critical, if the small-scale industry is to succeed, that these risks be understood and debates be resolved, in order to serve as a foundation for the development of safety codes, practices and procedures moving forward. The exemplary safety record of the large scale LNG segment suggests that when understood properly these hazards can be effectively managed and mitigated, and the small-scale sector now has an opportunity to insist on a similar safety culture and level of precautions in order to preserve the legacy of safe LNG operations.

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