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Guidance on Hazard and Safety Analyses of LPG Spills on Water

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Abstract

In 2004, at the request of the Department of Energy, Sandia National Laboratories (Sandia) prepared a report, “Guidance on the Risk and Safety Analysis of Large Liquefied Natural Gas (LNG) Spills Over Water”. That report provided a framework for assessing hazards and identifying approaches to minimize the consequences to people and property from an LNG spill over water. Because of increasing domestic U.S. supplies of natural gas and associated by products, such as liquefied propane gas (LPG), the United States Coast Guard requested that Sandia assess the general scale of possible hazards for a breach and spill of an LPG carrier.

Because of the broad range of LPG carrier types – refrigerated and pressurized, ships and barges, Sandia chose to focus this analysis on the larger LPG refrigerated systems. With cargo capacities ranging up to 100,000 m³, these types of ships can be expected to support potential increased LPG exports. Sandia assessed potential accidental and intentional threats, and based on LPG carrier configurations and designs, estimated potential breach sizes, spill rates and volumes, and conducted fire, vapor dispersion, and detonation hazard analyses. This report summarizes the analyses conducted, the expected range of potential hazards from an associated refrigerated LPG carrier spill over water, and risk management approaches to minimize consequences to people and property from such a spill.

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The authors received technical, programmatic, and editorial support on this project from a number of individuals and organizations outside Sandia National Laboratories. We would particularly like to express our thanks for their support and guidance in the technical evaluations and development of this report.

The U.S. Coast Guard was instrumental in providing background information on LPG ship and cargo tank designs for various types of vessels. Threat scenarios information was collected from several U.S. Coast Guard facilitated discussions at a range of port locations over the past five years and supplemented with discussions with national intelligence agency representatives over the past five years also.

The following individuals were especially helpful in supporting our efforts by providing LPG ship information and data, and reviewing our technical evaluations.

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NOMENCLATURE

BLEVE	boiling liquid expanding vapor explosion
CFD	computational fluid dynamics
CTH	Sandia shock physics modeling tool
dB	decibel
DOE	Department of Energy
FDS	Fire Dynamics Simulator
ft	feet
ft/s	feet per second
kW	kilowatt
kW/m ²	kilowatt per square meter
LNG	liquefied natural gas
LPG	liquefied propane gas
M	meters
m/sec	meters per second
Sandia	Sandia National Laboratories
UCVE	unconfined vapor explosion
USCG	United States Coast Guard

1. INTRODUCTION

In 2004 and 2008, Sandia provided reports that addressed hazard outcomes arising from spills from the smaller and larger class of Liquefied Natural Gas (LNG) tankers, respectively [1] [2]. Spills resulting from possible intentional events were the central focus of these reports, though accidental events were also considered. In these reports, potential threats were identified based on intelligence information, ship damage was assessed, evaluation of potential hazards arising from fire and vapor cloud dispersion was provided, and recommendations were given on potential counter measures and risk management approaches that could be utilized to minimize the impact of a potential large spill on property damage and public safety.

The objective of this report is to provide an assessment of the potential hazards and safety considerations of potential spills during the marine transport of Liquefied Petroleum Gas (LPG) carriers. The analyses were conducted in a similar spirit and intent as the past Sandia LNG hazard and safety reports. While LNG and LPG are similar in that they are gases that are liquefied to be more easily and economically delivered by ship, they differ significantly in their overall thermal and flammability properties, dispersion properties, and the construction and size of the shipping used in their marine transport. These differences change the risks of large breach events, size of spills, and the potential hazards from a spill.

In this study, the threats identified in earlier Sandia LNG reports have been revisited and updated over the past five years based on numerous discussions with port security groups across the U.S. in support of the USCG's Deep Water Port responsibilities. Information gained from simulations using Sandia's shock physics code, CTH, in the previous LNG work was utilized to identify breach sizes of representative LPG carriers from credible accidental and intentional events. It's important to note that the breach sizes identified are considered to be a best estimate, since detailed shock physics calculations for the LPG carriers were not performed in the current work due to the wide range of LPG ship and marine transport configurations that exist. This range includes large LPG refrigerated ships similar in size to typical LNG carries, to small pressurized LPG ships, and even smaller LPG barges.

Perhaps the strongest recommendation in the Sandia LNG reports were that site-specific analyses in the context of local risk protection goals to property and the public be conducted, rather than a single prescriptive hazard value. This is even more important when it comes to maritime LPG spills with the broad spectrum of shipping and locations that could be impacted. It is important to realize that the hazard zones reported in this report, like in our LNG reports, are to provide an understanding of the general scale of thermal and dispersion hazards for LPG. They are not meant to be used prescriptively, but instead used to identify when and where risk management and mitigation approaches are warranted and where they have the most benefit to the general public. Hazards and distances will vary depending upon the location and type of ship or facility under consideration, which are discussed in a range of detail in this report.

2. LPG SHIP DESIGNS

This section highlights the range in size, design, and operation of LPG maritime shipping. LPG shipping is much less homogeneous than current LNG shipping is in the U.S., and therefore highlights the complexity of establishing hazard, safety, and risk metrics. A comparison to LNG ships is also presented to help readers understand the reasons for differences in breach and spills relative to large LNG carriers.

2.1 Vessel Types

LPG is transported in numerous types of ship and cargo designs that can have an extensive range of vessel capacities. This is in contrast to LNG carriers which have basically two different containment system types, membrane and Moss, which can be grouped into generally four vessel capacities. As shown in Figure 1, the various LPG ship designs include a) fully pressurized, b) semi-refrigerated, c) semi-pressurized/fully refrigerated, or d) fully refrigerated carriers. Table 1 provides the characteristics of these different types of ships, while Table 2 shows the size of typical LNG ships. The LPG vessels can transport butane, propane, butadiene, propylene, or anhydrous ammonia. LPG is typically comprised of propane, butane, or a mixture of the two. For this work, propane is chosen for consideration since there is large-scale experimental data available for propane which can be used for validation. Since butane has similar combustion behavior as that of propane, the analysis should also be applicable to butane in understanding the scale of the hazards.

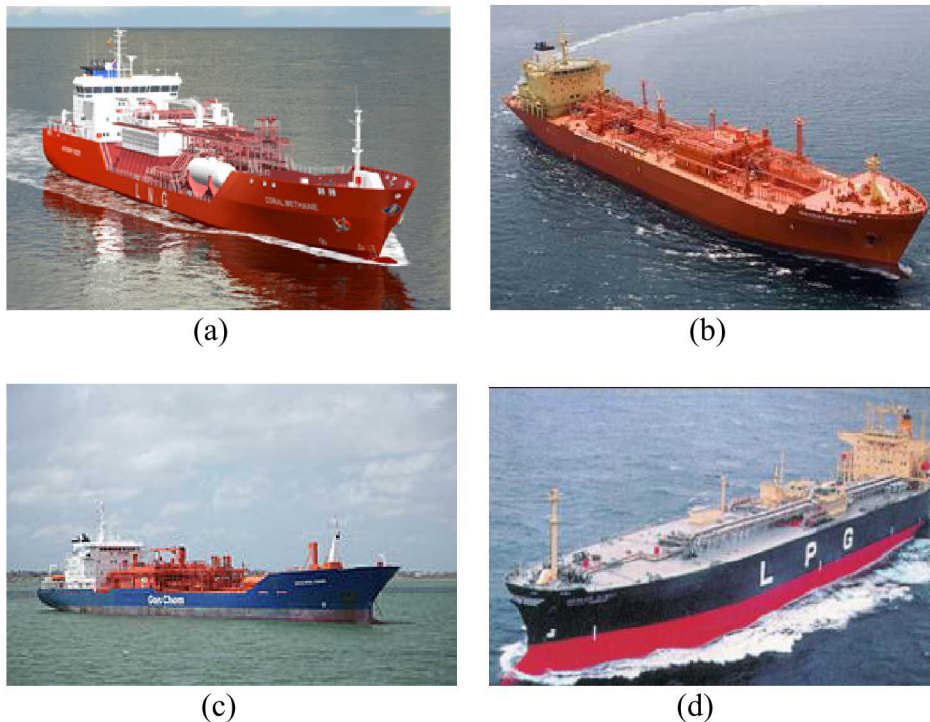


Figure 1: LPG vessel types: a) fully pressurized, b) semi-refrigerated c) semi-pressurized, and d) fully refrigerated.

Table 1: Characteristics of LPG vessel types

<i>Vessel type</i>	<i>Range of typical cargo capacities (m³)</i>	<i>Cargo containment system</i>	<i>Design pressure (barg)</i>	<i>Design temperature (°C)</i>	<i>Secondary barrier?</i>
fully pressurized	1,000 - 10,000	independent tank, type 'C'	up to 20	ambient	no
semi-refrigerated	3,000 - 30,000	independent tank, type 'C'	5 - 7	-10	no
semi-pressurized/ fully refrigerated	1,500 - 20,000	independent tank, type 'C'	5 - 7	-46	no
fully refrigerated	10,000 - 100,000	independent tank, type 'A'	0.5	-46	yes

Table 2: Characteristics of LNG vessel types

MEMBRANE DESIGNS				
	125,000 m³	155,000 m³	215,000 m³	265,000 m³
Tanks	4	4	5	5
Length (m)	283	288	315	345
Width (m)	44	44	50	55
Draft (m)	11.4	11.5	12	12
MOSS DESIGNS				
	125,000 m³	145,000 m³	200,000 m³	255,000 m³
Tanks	5	4	5	5
Length (m)	287	290	315	345
Width (m)	46	49	50	55
Draft (m)	11	11.4	12	12.5

The fully pressurized ships are the simplest of all LPG carriers with regards to its containment system and cargo handling equipment since insulation and re-liquefaction is not necessary. They use Type 'C' tanks which are pressure vessels fabricated of carbon steel with a typical design pressure of 17.5 barg (254 psig) which corresponds to the vapor pressure of propane at -45°C. These ships tend to be small since the tanks are extremely heavy. A secondary barrier is not required since the cargo tanks are pressure vessels.

The semi-refrigerated ships are similar to fully pressurized ships in that they use Type ‘C’ tanks, but have less tank thickness due to their reduced operating pressure. Refrigeration and tank insulation are required to have the cargo maintained at -10°C. The tanks can be cylindrical, conical or spherical in shape.

Semi-pressurized/fully refrigerated carriers will have insulated Type ‘C’ pressure vessel cargo tanks that are either spherical, bi-lobe or cylindrical, and can maintain the LPG at -46°C versus -10°C as compared to semi-refrigerated vessels. They also have re-liquefaction equipment and cargo heaters, allowing for flexibility in cargo-handling operations. They can transfer cargo either to or from a pressurized or refrigerated storage facility, and in this regard are the most flexible of all the ships.

The fully refrigerated carriers have self-supporting, independent prismatic Type ‘A’ cargo tanks that are insulated and constructed with low temperature steel and can transport the most cargo of all the vessel types. These ships require a secondary barrier that can contain a leak from the cargo tanks for a period of at least 15 days. The hull may act as a secondary barrier.

2.2 Cargo Containment Systems

LPG vessels have cargo containment systems that are comprised of completely self-supporting independent tanks that do not form part of the ship’s hull structure, and hence do not contribute to the hull strength. The International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk (IGC Code) defines three different types of independent tanks: Type ‘A’, Type ‘B’, and Type ‘C’.

Independent tanks of Type ‘A’, shown in Figure 2, require conventional internal stiffening and have a maximum allowable tank design pressure in the vapor space of 0.7 barg (10 psig). The tanks are externally insulated with foam and require a full secondary barrier capable of withstanding low temperatures and containing the whole tank volume at a defined angle of heel and may form part of the ship’s hull. The tank itself is considered the primary barrier. The hold spaces must be filled with inert gas to prevent a flammable environment in the event of a primary barrier leak. Typically these tanks will have a centerline bulkhead separating the tank into two tanks (Figure 2b).

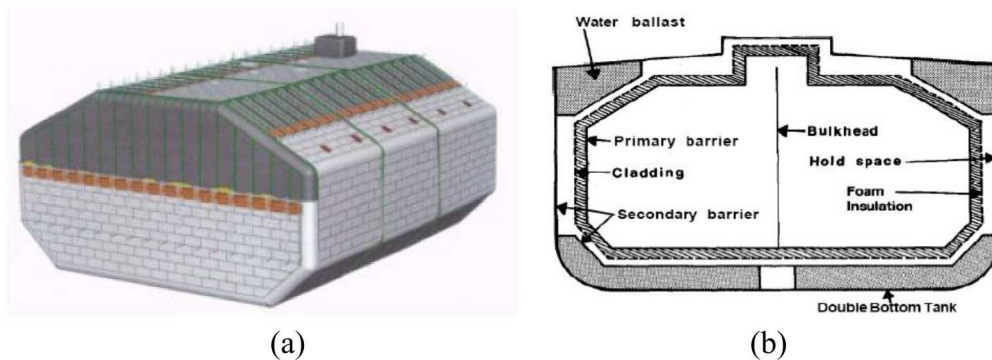


Figure 2: Type ‘A’ independent tank a) complete tank and b) tank cross section

Independent tanks of Type ‘B’ can be constructed of flat surfaces or may be spherical and are externally insulated with foam. Spherical tanks are typically used on LNG ships of Moss design. Type ‘B’ tanks undergo more detailed stress analysis that involves fatigue life and crack propagation behavior, than Type ‘A’ tanks undergo. Because of the enhanced design factors, a Type ‘B’ tank requires only a partial secondary barrier in the form of a drip tray that covers only the bottom of the hold. The maximum allowable tank design pressure in the vapor space is 0.7 barg (10 psig) and the cargo hold spaces typically contain dry air but may also be inerted.

Independent tanks of Type ‘C’ are typically spherical or cylindrical pressure vessels designed and built to conventional pressure vessel codes using accurate stress analysis (Figure 3a). They have a design pressure above 2 barg (29 psi) and may be vertically or horizontally mounted. A secondary barrier is not required and the hold space can be filled with either an inert gas or dry air. Bi-lobe tanks, which intersect two cylindrical tanks, are also used to better utilize the hull space, shown in Figure 3b.

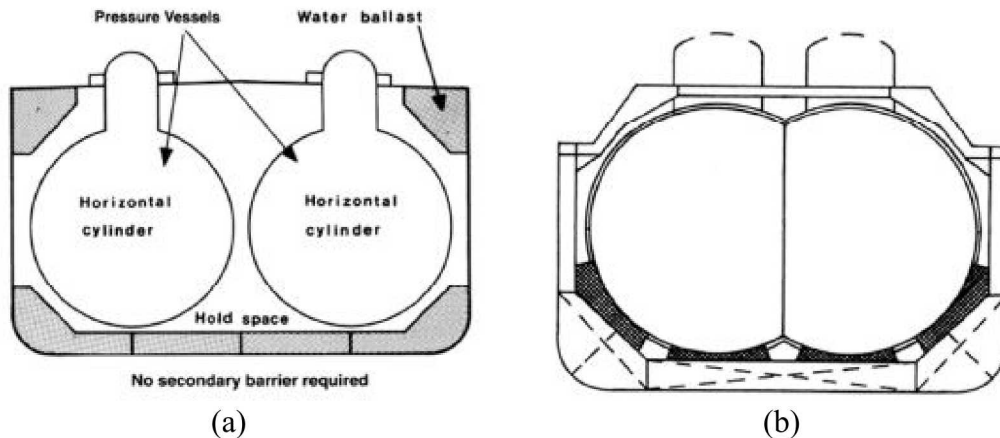


Figure 3: Type C independent tanks a) horizontal cylinders, and b) bi-lobe.

2.3 LPG Ship Structural Design

As highlighted in Figures 2 and 3, LPG ships are generally single hull vessels, but with essentially a double hull on the bottom. Since LPG is transported at no lower than -46°C and often at higher temperatures, the concerns of cryogenic damage from a spill are greatly minimized and therefore double hulls are not as critical. Pressurized LPG ships often have at least a partial double hull on some portion of the sides of the ships. The distance between the outer hull and the LPG cargo tanks in most cases is approximately 1.2 to 1.4 m, as opposed to about 2.0-2.4m on the large LNG ships. Most LPG ships have outer hulls with a series of closely spaced rib frame supporting the outer hull, rather than the box-type frame and scantling designs seen on large LNG ships. Therefore, refrigerated LPG ship structures will respond differently to the types of credible intentional and accidental events considered in maritime energy transport relative to refrigerated LNG ships. On the other hand, based on a survey of the various pressurized ships, pressurized LPG cargo tanks are structurally robust and subsequently very

resistant to many credible maritime breach threats. This suggests that LPG ship breach sizes and spills will be different than LNG ships.

3. ILLUSTRATIVE HISTORICAL ACCIDENTS

The intent of this section is to describe and discuss historical accidents that are examples of spill scenarios. Thus, a comprehensive survey is not provided, but rather illustrative cases are brought forth for discussion. The first incident involves an attack, the second involves a transfer operation, and the third involves grounding. The description of these incidents can be found in reference [3].

3.1 “Gaz Fountain” Missile Attack

The Gaz Fountain, a fully refrigerated LPG carrier with carrying capacity of 40,232 m³, was attacked during the Iraq/Iran war by an Iranian aircraft that fired three rocket propelled air-to-ground, armor-piercing missiles at the ship. Tank No. 1 was fully loaded with 10,840 m³ of propane. Tank No. 2 was half loaded with 7,420 m³ of butane and tank No. 3 was fully loaded with 12,780 m³ of butane. One of the missiles exploded on the main deck above tank No. 2 causing extensive damage to the deck, while the other two exploded above tank No. 3, one causing the tank to rupture and release butane, resulting in a large fire fueled by the butane on the main deck. The 29 crew members were able to escape without injury. The next day a salvage tug started cooling the main fire areas with powerful water jets. Various combinations of wooden plugs, canvas patches, cement boxes and sandbags were used to stop the gas leaks in the damaged deck and pipework. The hole in tank No. 3 could not be plugged and the hold space around the tank effectively became the cargo tank. A temporary gas vent was then rigged to control tank pressures.

Over a month later a ship-to- ship transfer was performed over the course of 4 days, saving 93% of the cargo, which is remarkable given that the refrigeration plant had failed and was not operating for almost a month. Loose fill perlite was the insulation used on this particular vessel. Adjacent tanks were not impacted.

This incident is notable since it demonstrates that the insulation used on the cargo tanks provides adequate thermal protection from a fire and that the ship’s steel does not undergo brittle fracture when exposed to LPG.

3.2 Transfer Operation Accident at Pajaritos Port

A major accident occurred at Pajaritos Port in Mexico during LPG cargo loading of a 57,000 m³ capacity refrigerated LPG carrier named the Ahkatun. Eleven ships, including five LPG carriers, were moored in Pajaritos at the time of the accident. Reports indicate that an LPG spill occurred from a cargo loading hose bursting. Flammable vapors then evolved engulfing a nearby tug/crew boat that provided an ignition source, thereby triggering an explosion and subsequent fire which completely destroyed the tug. Other ships in the port were trying to quickly depart in the confusion and two ships collided. The fire spread immediately to Ahkatun and two neighboring LPG ships. Both of these neighboring ships were damaged, one with major damage and the other

minor. The ship with major damage, capacity of 22,200 m³, was preparing to load ammonia and the other, with a 19,500 m³ capacity, was believed to be loading LPG. Accounts indicate that the leak was not turned off right away and was able to supply fuel to the fire for some time. The LPG in the tanks of the damaged ships did not ignite and remained intact throughout the incident. As a result of this accident, two people were killed and 15 people were injured.

This incident suggests the potential for transfer operation accidents and the significant hazards that can result. Even relatively minor spills, in comparison to the potential of a cargo tank, can result in a vapor cloud of significant hazard. It demonstrates that an LPG vapor cloud can be readily ignited from surrounding ignition sources. It also demonstrates the capability of the insulation to provide adequate thermal protection to adjacent cargo tanks.

3.3 Grounding of the “Sunrise”

The LPG pressure vessel ship, ‘Sunrise’, ran aground in the Philippines during a typhoon carrying approximately 800 m³ of butane. The cargo tanks were not damaged in the grounding, but the ship was stranded on some rocks preventing onshore off-loading, as well as a ship-to-ship transfer. Venting the cargo to the atmosphere was considered not an option due to safety and environmental impacts. The solution involved the design of a specialized burner that was set up offshore about 50 m away from the ship creating a flare lasting approximately two weeks. When the flaring was complete the ship had been stranded for about two months.

This incident highlights the potential for damage to an LPG ship with pressurized vessels. In the event that these tanks ruptured questions that arise are: What is the performance of the pressurized tanks when exposed to a fire? What is the mode of failure? How are adjacent tanks impacted? Can a spill rate be defined? The answer to these questions requires additional research and is not addressed in this report. They are raised here to provide awareness of the potential issues regarding pressurized vessels.

4. LPG SHIP THREAT, BREACH, AND SPILL ANALYSES

In the 2004 Sandia LNG report, a number of credible intentional and accidental events that could cause the breach of an LNG cargo tank were identified by law enforcement, security, and intelligence agencies for both on-shore and near-shore LNG terminals. Over the past 5 years the identified threats have been updated through interactions with a number of U.S. ports in support of the USCG off-shore LNG deep water port (DWP) program. This section discusses the threats and estimated governing breach and spill events for hazard analysis

4.1 General Threat Categories

Accidental events that should be considered include collisions with another ship, allisions with objects, or accidents involving LNG handling or transfer and processing equipment. Several intentional events have been identified including both insider and external attacks or hijackings involving a range of weapons, munitions, or explosives. Accidental and intentional events are always site-specific and in estimating appropriate breach sizes, factors that impact threat magnitude and impacts, such as vessel and port safety and security, safety equipment and operations, and terminal location and traffic should be considered. The threats identified from the Sandia LNG reports and updated based on the USCG DWP interactions were used to identify potential damage and breach sizes for LPG carriers.

The dynamics of a spill and the governing flow conditions vary depending upon the breach location. Three breach categories as determined by location have been identified as shown in Figure 4.

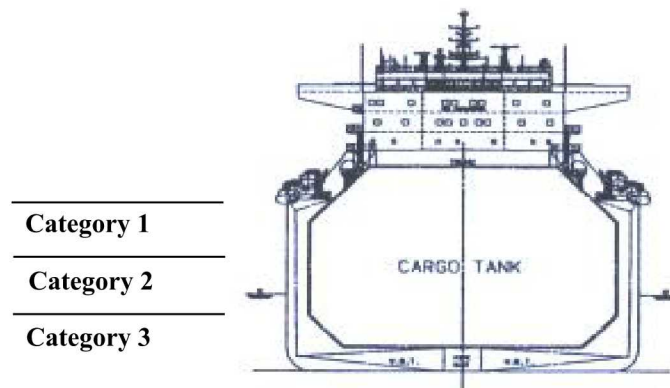


Figure 4: General LPG Ship Threat and Breach Categories

A breach in Category 1 can occur from a range of intentional events as well as some accidental events. For this category, the breach of a cargo tank is at a several meters above the water line. Thus, water flow into the LPG cargo tank will not occur. The flow through the hull and out onto

the water surface will be controlled by the LPG hydrostatic head, the breach size, and the distance to the outer hull. If the stream does not have sufficient velocity relative to the distance to the outer hull, then the LPG will spill into the interior of the ship, with minimal immediate hazards to the public and property.

For Category 2, the breach of an LPG carrier can either be at or near the water line. Accidental events such as collisions, allisions, as well as a few intentional events can cause a breach at this level. The spill dynamics can be complicated by the interaction of water flowing into the LPG ship and LPG flowing out of the breach in a cargo tank. The type of damage to the hull from the different large accidental and intentional breaching events as well as the dynamics of emptying a large tank make estimating LPG discharge rates for this category more complicated. A number of things can restrict the rate of LPG discharge. For example, a breaching event could cause petaling or irregular tearing of the ship hull and cargo tank. An additional consideration is creating a significantly lower pressure within the tank over time as the liquid drains which could result in additional damage to the tank.

For Category 3, the breach of an LPG vessel and cargo tank is several meters below the water line. The dynamics of this process is very complicated and there are many mechanisms to consider for this category such as water inflow, LPG outflow, LPG vaporization, and tank pressurization. A significant amount of water could enter the tank and solidify causing the LPG to vaporize, thereby increasing the pressure within the tank, and thus driving the outflow of LPG.

The aforementioned flow dynamic considerations indicate the complexity of predicting how much LPG will flow onto the water. Most analyses use the Bernoulli's equation to calculate flow rates with the orifice area multiplied by a factor, ranging from 0 to 1, termed the discharge coefficient. The discharge coefficient accounts for flow contraction due to orifice geometry, which effectively reduces the orifice area. For sharp-edged plates, discharge coefficients have been found to be around 0.6, while for optimized designed cornered orifices the discharge coefficient can approach 1 for very high speed flows. Due to the lack of experimental data on flow rates resulting from various breach scenarios, it is difficult to identify just one value for the discharge coefficient. Therefore, a range is generally considered by varying the discharge coefficients from 0.3 to 0.6 when applying the Bernoulli's equation. The lower range accounts for geometric irregularities of the breach and varying tank pressure.

4.2 Breach Evaluations and Breach Estimates

In this study, information gained from simulations using Sandia's shock physics code, CTH, in previous LNG work was utilized to identify breach sizes of representative LPG carriers for credible accidental and intentional events. The breach sizes identified were estimated from a series of two dimensional and three dimensional shock physics and finite element analyses and munitions effectiveness calculations of damage for single hull structures representative of LPG ships. These analyses cover the general hull and cargo tank thicknesses and separation distances for a wide range of LPG ship designs.

Table 3 provides a summary of the estimated nominal breach sizes for the estimated threats for the 80,000 m³ Type A LPG ships for several credible breach scenarios. These include accidents,

collisions, and a range of intentional events such as shoulder fired weapons, small explosive attacks, USS Cole type events, and other potential credible intentional events.

Table 3: Recommended Large LPG Ship Design Breach Sizes

Event	Cargo Tanks Breached	Breach Area (m²)
Accidental spill (collision, allision)	1	3
Near-shore waterway nominal intentional breach	1	7
Near-shore waterway multiple intentional breaches	2	7
Near-shore waterway maximum intentional breach	1	16

The breach sizes noted in Table 3 are generally larger than calculated for double hull LNG ships. This is due to the fact that large LPG ships are generally single hull designs and have smaller standoffs between their outer hulls and their cargo tanks, as discussed in Section 3. These design features lead to somewhat larger breach sizes for similar types of credible breach threats. The maximum spills for large LPG carriers are about half a tank volume, which is approximately 10,000 m³ for a single cargo tank breach associated with an 80,000 m³ class LPG ship.

As also noted in the previous discussions, the likelihood of either thermal or cryogenic damage to the LPG ship or other cargo tanks from an initial spill are minimal as shown by past events highlighted in Section 3. The initial evaluations and the current accident and threat data base suggest that cascading damage to other LPG cargo tanks is unlikely for spills on an LPG ship and that multi-tank spills do not need to be considered.

Analyses were also conducted on the smaller pressurized LPG ships. In reviewing ship and cargo tank structural drawings and details, they highlight the very robust nature of the pressurized cargo tanks to both accidental and intentional threats. This is again shown by the results of past events on pressurized LPG discussed in Section 3. Overall, many of the credible events considered for the smaller pressurized LPG ships provide very little damage, and the credible threats such as collisions, allisions, or attacks have little impact on the very robust cargo tanks. For these ships, a different set of accidental events, such as loading arm damage and spills would be more likely to cause a spill. The spill volumes and sizes would be small relative to the common accidental and intentional events generally evaluated. Therefore, loading arm spills of 3,000 -5,000 gallons would be more appropriate for evaluating safety hazards for these ship designs.

5. EVALUATION OF HAZARD ZONES

An LPG spill can result in various hazards that include a pool fire, fireball, torch fire, or flammable vapor cloud as listed in Table 4. Pressurized tanks pose additional hazards over insulated tanks such as boiling liquid expanding vapor explosions (BLEVE) and torch fires. For pressurized tank releases, the typical outcome will be a fireball, which can occur when rapid mixing between fuel and air results and the mixture is ignited. This results in a rapid release of heat that produces strong buoyancy forces causing the ignited mixture to quickly rise in the form of a fireball. Fireballs are short duration events, on the order of tens of seconds, but are still lethal within close proximity. Torch or jet fires result when LPG is released as a jet and an ignition source is immediately available. The flames are confined to a small local area in this case, but can result in additional hazards if the jet fire is impinging on an adjacent tank. BLEVEs can be initiated from an engulfing pool fire or torch fire. Due to heating, the pressure in the tank increases to a level where the tank ruptures explosively and a fireball and damaging projectiles result. In addition to fire hazards, other hazards can occur and include cryogenic contact and displacement of air resulting in asphyxiation.

For non-pressurized releases, the most likely outcome will be a pool fire if the LPG is immediately ignited. The duration of a pool fire will be governed by the duration of the spill. If the LPG is not immediately ignited upon release, vapors above the spill will rapidly form due to the heat transferred from the much warmer water. The vapors form a dense cloud that will disperse downwind from the spill site, staying along the ground. Since propane and butane have higher molecular weights than air, the cloud will persist even when warmed to the surrounding atmospheric temperature, and thus will not become buoyant. This persistence increases the odds of combustion related hazards and asphyxiation. In time, however, the cloud will become diluted due to turbulent mixing with air.

Regions in the cloud that are within the flammability limits, 2.1 – 9.6 % for propane, can be ignited if ignition sources are encountered (Table 5). The resulting fire is known as a vapor cloud fire or flash fire. The overall tendency of the fire will be to burn back to the spill site, but the propagation and nature of the fire can be affected by the wind. Experiments have shown that the wind can temporarily halt or reduce the speed of the burn front. Also, there can be regions where the cloud appears to be burning as a pool fire and others as a pre-mixed flame as it burns back to the spill. If the vapors propagate into congested industrial or urban areas, there is a potential not only for a flash fire and asphyxiation, but also explosions.

Explosions are classified as either a deflagration or detonation. Deflagration is a combustion front that progresses through an unburned fuel-air mixture at subsonic velocities, whereas, in a detonation the front progresses at supersonic velocities resulting in more damaging overpressures than a deflagration. With full or semi-confined conditions explosion will occur with LPG, usually in the form of a deflagration though detonation is possible, with flame speeds that result in damaging overpressures. An unconfined vapor cloud explosion (UVCE) is possible with LPG.

Table 4: Hazards associated with an LPG spill

Event	Hazard Description
Pool Fire (fire burning at the spill)	<ul style="list-style-type: none"> Casualties and/or injury to population and destruction of property from thermal radiation from fire
Ignited Flammable Vapor Cloud	<ul style="list-style-type: none"> Casualties and/or injury to population either within or nearby the propagating flame from a vapor cloud fire If confined or obstacles present, explosion with damaging overpressures to population and structures.
Boiling Liquid Expanding Vapor Explosions or BLEVE	<ul style="list-style-type: none"> Casualties and/or injury to population and destruction of property from flying shrapnel and overpressures Casualties and/or injury to population and destruction of property from fireball
Torch fire	<ul style="list-style-type: none"> Escalation of hazards by weakening nearby tanks from jet fire impingement
Cryogenic Contact	<ul style="list-style-type: none"> Tissue damage and possibly death from direct contact
Vapor cloud displacing air	<ul style="list-style-type: none"> Asphyxiation and lung damage

Table 5: Properties of propane, butane, and methane

Physical properties	Propane	Butane	Methane
Density of liquid at atm. pressure (kg/m ³)*	581	601	423
Density at boiling point and atm. pressure (kg/m ³)*	2.32	2.71	1.79
Specific Gravity relative to air	1.52	2.00	0.55
Specific Gravity relative to water	0.581	0.601	0.423
Liquid to vapor expansion	1:275	1:244	1:625
Normal boiling point (°C)(°F)*	-42 (-44)	0 (32)	-161.5 (-258.7)
Heat of vaporization (J/kg)	429,331	387,874	504,350
Flammability Limits (volume fraction in air, %)	2.1 – 9.5	1.8 – 8.4	5 – 15

*Taken from [4].

As provided in Table 6, fire events result in various thermal radiation damage levels which are a function of exposure time [5]. The fire hazard zone profile depends upon the fuel, size, duration, and type of fire event.

Table 6: Expected Damage for Various Thermal Radiation Levels

Exposure	Thermal Radiation Level (kW/m ²)
Typical radiant heat flux from the sun on a clear day.	1
Will cause pain in 15 – 20 seconds and injury. Second-degree burns after 30 seconds.	5
Significant chance of fatality for extended exposure. First degree burns in 10 seconds. Buildings made of cellulosic materials may suffer minor damage after prolonged exposure.	12.5
Extended exposure results in fatality; there is a chance of fatality for instantaneous exposure. Buildings that are made of cellulosic materials or not fire resistant will suffer damage after short exposures. Fire-resistant structures and metal may suffer damage after prolonged exposure	21.0
Process equipment and structural damage after 30 minute exposure. 100% lethality within 1 minute.	37.5

5.1 Dispersion

Several different types of models can be used to assess dispersion distances, varying in level of complexity. The level of complexity is determined by the degree of simplifying assumptions as applied to the governing fundamental equations. Empirical based or integral models simplify the equations sufficiently to a point where a closed form analytic solution is possible, at the expense of capturing significant physical mechanisms. The integral models also adjust parameters for a particular geometry, time and length scale, and thus have very limited predictive capability to other length and time scales and other geometries. The empirical based models can be useful for order of magnitude estimates and possibly to explore certain first order effects depending on the model.

Models that invoke the greatest level of complexity are CFD-based models. They also require simplification, but to a much lesser degree than integral models. For simple flows the full governing equations can be computationally solved in discretized form. For more dynamic and/or large scale turbulent flows, computational solution of the governing equations is not feasible with current computational capabilities due to the vast range of time and length scales. Thus, to overcome this difficulty, turbulence and sub-grid models have been utilized to reduce grid resolution requirements. With the use of turbulence and sub-grid models there has been impressive agreement with experimental data for many turbulent reacting and non-reacting flow configurations. Additionally, in the last several decades, computational capacity has dramatically increased, thus allowing for a greater number of significant physical mechanisms to be included in simulations and allowing for a larger range of time and length scales to be resolved. Thus, CFD based models have a much greater predictive capability than integral models. CFD codes are used in all areas of engineering. There are many problems that can be performed on a single

processor within hours or days depending on the application. Also, with hardware affordability a parallel system (from 10s to 100s of processors) is easily achieved by industry and academia. Additional discussion and listing of some integral and CFD models is provided in [1].

The code chosen to perform dispersion calculations in this work is the Fire Dynamics Simulator (FDS), available through the National Institute of Standards and Technology (NIST). This code was chosen since it is an open-source, publically available, Computational Fluid Dynamics (CFD) based code that has demonstrated reasonable predictive capabilities. It also has ample documentation, example cases, and internet user forums to facilitate learning. It has been tested against a rigorous suite of verification and validation problems as documented in NIST's verification and validation manuals [6] [7].

5.1.1 Validation

To gain confidence in the predictive capability of FDS for LPG dispersion, validation was performed comparing simulation and experimental results from dispersion tests for propane. The tests were conducted in the early 80s at Maplin Sands, England by the National Maritime Institute and were sponsored by Shell [52-55]. These tests were performed in order to obtain dispersion and thermal radiation data on 20 spills of LNG and 14 spills of propane onto water for instantaneous and continuous spills. Twenty-four continuous and ten instantaneous spills were performed in average wind speeds of 3.8 - 8.1 m/s (8.5-18 mph). Instantaneous spills were performed by rapidly sinking a barge loaded with LNG or propane. For the instantaneous spills, the spill volumes tested were 5-20 m³ (178-710 ft³), and for continuous spills, spill rates were 1.5-4 m³/min (53-141 ft³/min). A 300 m (984 ft) diameter dyke surrounded the spill point for containment.

One of the continuous spill dispersion tests for refrigerated propane, Trial 46, is chosen for comparison. The experimental conditions for this test are provided in Table 7. For the FDS simulation the conditions in Table 7 were specified as well as a variable wind speed representative of that recorded during the test as shown in Figure 5. A 15 m square pool and mass flux of 0.135 kg/m²s were specified. This pool area was estimated by visual records of the test and the mass flux value was chosen based on the reported total liquid volume released. Note that it's in close agreement with the value of 0.12 kg/m²s as reported by Blackmore, et al. [8] on the Maplin Sands tests, which was indicated as a lower bound among all the tests. The temperature of the liquid propane was specified as -42°C. The propane concentration contours shown in Figure 6 indicates the general shape of the cloud as elongated due to the relatively high wind speed. Figure 7 shows the experimental and simulated values of maximum arc-wise concentration values at various distances from the spill. The simulation predicts a LFL value of about 275 m versus the experimental value of 245±35 m, which is slightly over predictive of the average, but within experimental uncertainty.

Table 7: Experimental conditions for Maplin Sands dispersion test, Trial 46

Specifications	
spill type	continuous
mean spill rate	2.8 m ³ /min
liquid volume discharged	22.2 m ³
discharge period	7 min, 50 s
duration of steady spill	355 s
composition (% mole)	propane: 97.32 ethane: 1.05 iso-butane: 0.88 n-butane: 0.73 nitrogen: 0.02 methane: 0.01
mean wind speed	8.1 ± 1.1 m/s (at 10 m) 7.6 m/s (at 3 m) 7.05 m/s (at 1 m)
wind direction relative to array axis	-66 ± 7 degrees
air temperature	18.7 ± 0.2 °C
relative humidity	71%

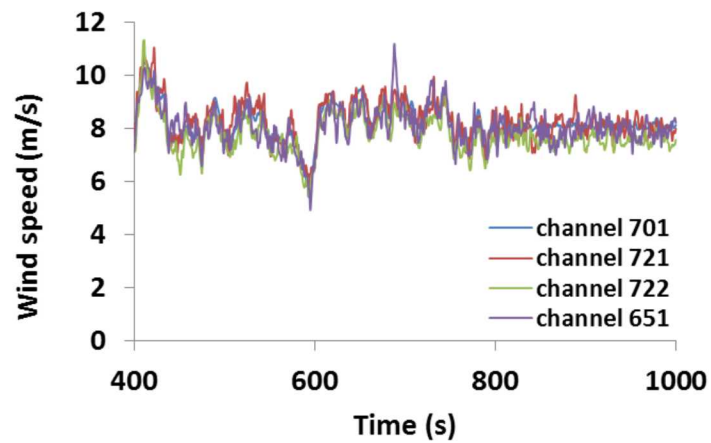


Figure 5: FDS wind speed profiles at various test channel locations, 10 m elevation.

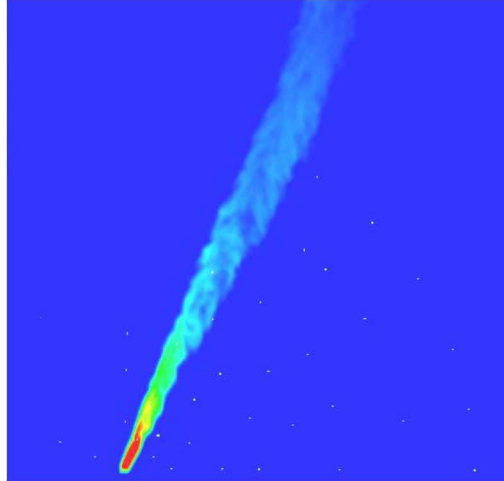


Figure 6: Propane concentration profiles from FDS simulation indicating elongated cloud.

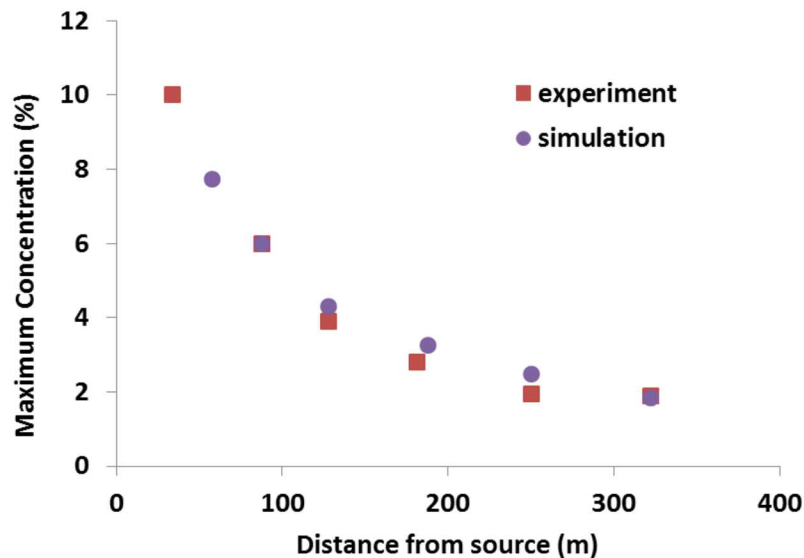


Figure 7: Comparison of simulated and experimental values of maximum arc-wise concentration as a function of distance from the spill

These results indicate that FDS can provide reasonable predictions for LPG dispersion, though this validation effort can be considered only partial. An extensive comparison regarding validation of FDS for dense gas dispersion has been conducted for LNG dispersion by Kohout [9]. In this work, comparison to 33 tests are provided, 31 of which pertain to LNG, the remaining Freon and nitrogen. Of the 31 cases, 13 were field trials, while the remaining were wind tunnel tests. The following excerpt provides the main conclusions from this comparison.

“For unobstructed trials, FDS generally over-predicts maximum arc-wise concentrations by a factor of 2 or less. However, there were still unobstructed trials where FDS under-predicts maximum arc-wise concentrations by approximately a factor of 2. Therefore, FDS should be used with a safety factor of 2 (i.e. $\frac{1}{2}$ LFL) for modeling LNG vapor dispersion in unobstructed flow fields. For obstructed and sloped trials, FDS generally under-predicts maximum arc-wise concentrations by a factor of 3 or less. Although there were obstructed trials where FDS under-predicts by more than a factor of 3, these trials were generally wind tunnel tests that included substances with denser vapor clouds than LNG vapor clouds and would have benefited from finer resolution of the grid near the boundary. Therefore, it is recommended that FDS be used with a safety factor of 3 (i.e. $\frac{1}{3}$ LFL) for modeling LNG vapor dispersion in sloped terrain or obstructed flow fields.” [9]

Thus, based on the above findings, distances to $\frac{1}{2}$ LFL are evaluated for the dispersion calculations pertinent to LPG carriers which are provided in the following section.

5.1.2 Dispersion Hazard Calculation

The release of a large volume of LPG without ignition has a much lower probability of occurrence than a pool fire. Since a large-scale dispersion event might occur, a calculation pertaining to the nominal case of a 7 m² hole in one tank was conducted. Stable atmospheric conditions were prescribed using a power-law profile. Specifications and results for the dispersions calculation are provided in Table 8 and Table 9, respectively. Grid refinement was not performed since it would require about 160 M elements for a factor of 2 reduction in cell width, which would be computationally prohibitive. Based upon the findings and recommendation by Kohout [9] regarding the use of FDS for dispersion prediction, the distance to $\frac{1}{2}$ LFL is evaluated. The results indicate that the dispersion distance to $\frac{1}{2}$ LFL is approximately 4,500 m and is reached 46 minutes after the start of the spill. The distance to LFL is provided for comparison and is approximately 2,600 m. The height of the cloud is approximately 20 m. Thus, the cloud has the potential to infiltrate structures below this height, with implications that explosions are possible if ignition sources are available. Propane is significantly more susceptible to explosion than methane [10].

A historical accident involving rail transport in Viareggio, Italy illustrates how the spillage of a relatively minor volume of LPG can lead to severe damage [11]. One of 14 rail cars was punctured after derailment, releasing about 110 m³ of LPG into a densely populated area (2000 persons/km²). The resulting vapor cloud propagated and infiltrated nearby buildings and houses which were an average of 10 m in height. Ignition of the cloud occurred approximately 100 to 300 seconds after the start of the spill. A flash fire and explosions resulted, killing 31 people. Evidence suggests that most deaths occurred due to the asphyxiation and thermal hazards from the flash fire. There were no indications of an unconfined vapor cloud explosion. Thus, as was pointed out with the Pajaritos Port transfer accident in section 3.1, the spillage of even small amounts of LPG can lead to significant hazards. Dispersion evaluation of relatively small amounts of spillage such as from loading arms should be performed for each site considered. The analysis should include any nearby infrastructure that can alter the dispersion path, as well as the evaluation of explosion potential.

Table 8: Specifications for dispersion calculation

hole size	7 m ²
number of tanks	1
pool diameter	391 m
wind speed (stable conditions)	2 m/s at 10 m, power exponent of 0.8
mass flux (kg/m ² s)	0.135
duration of release	361 s
size of mesh, (x, y, z)	10 km, 10 km, 120 m
smallest cell resolution* (x, y, z)	8 m, 8m, 4 m
CPU run time	~ 2 days
number of elements	20.5 M
number of processors	75

*encompassed vapor cloud

Table 9: Dispersion results

<i>criteria</i>	<i>maximum distance</i>	<i>reached at time after start of spill</i>	<i>maximum cloud height (1/2 LFL)</i>
LFL	2,600 m	33 min	20 m
½ LFL	4,500 m	46 min	

5.2 Thermal Hazard Calculations

In the 2004 and 2008 Sandia LNG reports, analyses were performed using a solid flame model. This approach is also used in this work. The solid flame approach models the surface of the flame with a simple, usually cylindrical geometry. The thermal radiation is uniformly emitted from this surface and the average radiant surface emissive power is based upon experimental data. The geometric view factor is modeled, which is the fraction of radiant energy that is received by an object's field of view. The attenuation of the thermal radiation by water vapor and carbon dioxide in the atmosphere is included in the model. In order to capture the tilting of the flame due to wind, a tilted cylindrical flame shape is typically used. Flame length, tilt and drag necessary to determine flame shape and view factors are based upon empirical correlations. Solid flame models are inaccurate at close distances to the fire due to the simplified geometry, but are accurate at distances beyond about a pool diameter. The disadvantage of these models is the inability to model more complex flame shapes such as those arising from irregular shaped pools or object interaction with the flame. If irregularly shaped pools and obstructions are present CFD-based codes can be used.

There are four parameters necessary to calculate thermal hazard distances using the solid flame model, namely the burn rate, flame height, surface emissive power (SEP), and transmissivity. The burn rate and flame height essentially affects the geometric aspects of the fire in that they determine the surface area applied for the solid flame model, whereas the SEP provides the power output from the idealized surface. The transmissivity accounts for the attenuation of radiation by absorption and scattering through the atmosphere. The transmissivity will decrease with increasing levels of relative humidity and atmospheric temperature. Experimental

measurement values for burn rate, flame height, and SEP for LPG pool fires on land and water are summarized in Table 10.

Table 10: Experimental values for LPG pool fires

<i>Terrain</i>	<i>pool diameter (m)</i>	<i>wind speed (m/s)</i>	<i>burn rate (kg/m²s)</i>	<i>flame height (m)</i>	<i>SEP (kW/m²)</i>
land [12]	20	6.6	0.13	47	48**
water [13]	25	7	0.31*	83	39**
	28	7	0.27*	85	46**

*Burn rate was calculated using the flame height correlation by Thomas.

**Determined by using a solid flame model where the fire is idealized as a tilted cylinder.

For the experiments on water, the average SEP from the two tests performed is 43 kW/m² (± 23 kW/m² sd). The variation in the measured SEP was due regions of the flame varying in degree of smoke coverage. For both tests, most of the flame was observed to be covered in smoke which will reduce the radiation received to an object external to the fire due to absorption. The burn rate was determined by the Thomas flame height correlation for the tests performed on water. The value calculated can vary by a factor of 2 depending on what flame height correlation is chosen. To calculate thermal hazard distances, the flame height correlation developed at Sandia will be used since it is applicable to very large pool fires. The correlation is of the following form:

$$H/D = 4.196Q^{*0.539} - 0.930.$$

where

$$Q^* = \frac{\dot{m}\Delta H}{\rho_a T_a c_{p_a} \sqrt{g} D^{5/2}} \quad (1)$$

\dot{m} is the fuel mass loss rate in units of kg/s, ΔH is the heat of combustion (46.35 MJ/kg for propane), and the thermal properties, ρ_a , C_{p_a} , and T_a are evaluated at ambient conditions. The uncertainty range can be represented by high and low correlations of similar form to eq (1). They are the following.

$$H/D = 3.623Q^{*0.539} - 0.837. \quad (\text{low range of uncertainty}) \quad (1a)$$

$$H/D = 4.828Q^{*0.539} - 1.023. \quad (\text{high range of uncertainty}) \quad (1b)$$

If the Sandia flame height correlation is used to determine the mass burn rate for the 28 m diameter pool fire test on water in Table 10, the predicted value is 0.145 kg/m²s versus 0.27 kg/m²s using the Thomas correlation. Since the burn rate is somewhat uncertain for LPG pool fires on water, a higher and lower mass burn rate will be considered for hazard evaluation,

namely, 0.145 kg/m²s and 0.29 kg/m²s. The average of this range, 0.218 kg/m²s, is used for the nominal value.

A transmissivity function developed by Wayne [14] for hydrocarbon fires is used in this work. The formula is applicable over the atmospheric temperature range of 253 – 313 K. The fire is assumed to be a blackbody at a temperature of 1500 K. Transmissivity values were shown to not vary appreciably with the assumed fire temperature over a range of a few hundred degrees. The level of uncertainty is estimated to be ±10%. The equation is of the following form.

$$\tau = 1.006 - 0.01171 \log_{10} X(H_2O) - 0.02368 (\log_{10} X(H_2O))^2 - 0.03188 \log_{10} X(CO_2) + 0.001164 (\log_{10} X(CO_2))^2 \quad (2)$$

with,

$$X(H_2O) = (R_H L P 2.8865 \times 10^2) / T$$

$$X(CO_2) = 273 L / T$$

X(H₂O) and X(CO₂) are the amount of H₂O and CO₂ along a path length, L (m). R_H is the relative humidity (0 – 1.0) and P is the saturated water vapor pressure in mm of mercury at the atmospheric temperature T (K). The saturated water vapor pressure can be determined from the Antoine formula where the coefficients are from Stull [15] applicable over the temperature range 255.8 – 373 K.

$$\log_{10} P = 4.65430 - \frac{1435.264}{T - 64.848} \quad (3)$$

The pressure, P, must be converted from bar to mm mercury by multiplying eq. (3) by 750.061. An atmospheric temperature of 273 K and relative humidity of 5% is used for the calculations since lower temperatures and humidity levels provide higher transmissivity values. Though this relative humidity value may be too low for most locations, it was chosen to provide more conservative thermal hazard distances.

As was done in the 2004 and 2008 Sandia reports on LNG, nominal fire modeling parameters along with variations around the nominal case were used to calculate the thermal hazards. The variations are the range of uncertainties as noted above for each parameter. Due to the non-site specific nature of the analysis, the effect of wind tilting the flame was not included.

To determine the size of a pool fire, the amount of LPG draining over time from a breached tank, as well as the spreading of LPG on water must be calculated. The spilling and spreading of LPG onto water can be classified as a multi-phase, multi-component problem. Most simplified models for the draining of LPG from a tank apply the Bernoulli's equation which neglects the effect of viscosity. Bernoulli's equation is a good approximation for large ratios of tank cross sectional to orifice areas (~100 or greater) since viscous effects will be negligible. The Bernoulli's equation, which was used for this analysis, can provide a reasonable approximation for the rate of LPG

flowing out of a tank with the intent of providing the general scale of the range of hazards from these events.

Once spilled onto the water, the shape and size of a spreading LPG pool can be affected by several factors: wind, waves, currents, and object interaction. Despite these complexities, in order to obtain an estimate of pool size, a steady mass balance can be utilized in which the mass flux of LPG flowing into the pool is balanced by the mass flux being evaporated or burned. The results presented in this analysis used such an approximation. The pool will grow and then eventually shrink and break up after reaching a maximum diameter. The results presented pertain to the maximum pool diameter during spreading assuming an average flow rate from the tank. This approach was also used in the 2004 and 2008 Sandia LNG reports.

The volume spilled and the tank height above the water line, as well as the density assumed for the liquid propane, are provided in Table 11. The results using a range of parameter values as discussed above are provided in Table 12.

Table 11: Specifications used in thermal hazard calculations

Density of liquid propane	581 kg/m ³
Tank height above waterline	9 m
Volume spilled	10,000 m ³

Table 12: Distances to a heat flux level of 5 kW/m² for different parameter values

hole size (m ²)	Number of tanks	SEP (kW/m ²)	burn rate (x 10 ⁻⁴ m/s)	pool diameter (m)	flame height to diameter ratio	duration of spill (min)	distance to 5 kW/m ² (m)
7*	1	43	3.75	308	1.65	6	519
7**	1	43	3.75	218	1.91	12	383
7	1	20	3.75	308	1.65	6	297
7	1	66	3.75	308	1.65	6	676
7†	1	43	3.75	308	1.39	6	499
7††	1	43	3.75	308	1.95	6	537
7	1	43	2.5	377	1.65	6	561
7	1	43	5.0	267	1.65	6	479
7	1	43	3.75	308	1.65	6	481
7+	1	43	3.75	308	1.65	6	552
7++	2	43	3.75	435	1.65	6	698
16	1	43	3.75	465	1.65	2.6	738
average							535

*nominal case

**discharge coefficient of 0.3 is used instead of 0.6 as described in section 4

†flame height to diameter ratio using equation 1a

†† flame height to diameter ratio using equation 1b

+transmissivity (eq. 2) reduced by 10%

⁺⁺transmissivity (eq. 2) increased by 10%

The heat flux level of 37.5 kW/m² is not listed since this level is achieved at a distance essentially adjacent to the fire, indicating that structural damage would occur only with fire engulfment and not when an object is external to the fire. The average distance to a heat flux level of 5 kW/m² is approximately 535 m, with a range of 297 – 738 m. The distance will vary depending upon the ship design and the location for a particular site under consideration. As emphasized in the 2004 and 2008 Sandia LNG reports, site specific analysis should be conducted.

6. SUMMARY

The following summarizes the recommended breach sizes and results regarding hazard zones from an LPG dispersion event and pool fire. These hazard zones are intended to provide an understanding of the general scale of thermal and dispersion hazards for an LPG release and are not meant to be used prescriptively. Hazards and distances will vary depending upon the location and type of ship or facility under consideration and are discussed in this report.

It is recommended that site-specific analyses in the context of local risk protection goals to property and the public be conducted, rather than a single prescriptive hazard value. This is even more important when it comes to maritime LPG spills with the broad spectrum of shipping and locations that could be impacted.

In summary, the recommended breach sizes for large LPG ships are provided in Table 13.

Table 13: Recommended Large LPG Ship Design Breach Sizes

Event	Cargo Tanks Breached	Breach Area (m ²)
Accidental spill (collision, allision)	1	3
Near-shore waterway nominal intentional breach	1	7
Near-shore waterway multiple intentional breaches	2	7
Near-shore waterway maximum intentional breach	1	16

The CFD code, FDS was used to perform dispersion calculations with specifications provided in Table 14 and results provided in Table 15.

Table 14: Specifications for dispersion calculation

hole size	7 m ²
number of tanks	1
pool diameter	391 m
wind speed (stable conditions)	2 m/s at 10 m, power exponent of 0.8
mass flux (kg/m ² s)	0.135
duration of release	361 s
size of mesh, (x, y, z)	10 km, 10 km, 120 m
smallest cell resolution* (x, y, z)	8 m, 8m, 4 m
CPU run time	~ 2 days
number of elements	20.5 M
number of processors	75

Table 15: Dispersion results

<i>criteria</i>	<i>maximum distance</i>	<i>reached at time after start of spill</i>	<i>maximum cloud height (1/2 LFL)</i>
LFL	2,600 m	33 min	20 m
½ LFL	4,500 m	46 min	

Thermal hazard zones resulting from an LPG pool fire was also assessed with specifications provided in Table 16 and the results provided in Table 17.

Table 16: Specifications used in thermal hazard calculations

Density of liquid propane	581 kg/m ³
Tank height above waterline	9 m
Volume spilled	10,000 m ³

Table 17: Distances to a heat flux level of 5 kW/m² for different parameter values

hole size (m ²)	Number of tanks	SEP (kW/m ²)	burn rate (x 10 ⁻⁴ m/s)	pool diameter (m)	flame height to diameter ratio	duration of spill (min)	distance to 5 kW/m ² (m)
7*	1	43	3.75	308	1.65	6	519
7**	1	43	3.75	218	1.91	12	383
7	1	20	3.75	308	1.65	6	297
7	1	66	3.75	308	1.65	6	676
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7	1	43	3.75	308	1.65	6	481
7+	1	43	3.75	308	1.65	6	552
7++	2	43	3.75	435	1.65	6	698
16	1	43	3.75	465	1.65	2.6	738
average							535

*nominal case

**discharge coefficient of 0.3 is used instead of 0.6 as described in section 4

†flame height to diameter ratio using equation 1a

†† flame height to diameter ratio using equation 1b

+transmissivity (eq. 2) reduced by 10%

++transmissivity (eq. 2) increased by 10%

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