Safety and Security of Liquefied Natural Gas

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Abstract: LNG has been transported and used safely in the U.S. and worldwide for roughly 40 years. The U.S. has three types of LNG facilities: LNG export, LNG import and LNG peaking facilities. The U.S. has the largest number of LNG facilities in the world, scattered throughout the country and located near population centers where natural gas is needed. The LNG industry has an excellent safety record. This strong safety record is a result of several factors. First, the industry has technically and operationally evolved to ensure safe and secure operations. Technical and operational advances include everything from the engineering that underlies LNG facilities to operational procedures to technical competency of personnel. Second, the physical and chemical properties of LNG are such that risks and hazards are well understood and incorporated into technology and operations. Third the standards, codes and regulations that apply to the LNG industry further ensure safety.

I. INTRODUCTION

The physical and chemical properties of LNG necessitate these safety measures. LNG is odorless, non-toxic, non-corrosive and less dense than water. LNG vapors (primarily methane) are harder to ignite than other types of flammable liquid fuels. Above approximately 163 k, LNG vapor is lighter than air. If LNG spills on the ground or on water and the resulting flammable mixture of vapor and air does not encounter an ignition source, it will warm, rise and dissipate into the atmosphere. Because of these properties, the potential hazards associated with LNG include heat from ignited LNG vapors and direct exposure of skin or equipment to a cryogenic (extremely cold) substance. LNG vapor can be an asphyxiant. This is also true of vapors of other liquid fuels stored or used in confined places without oxygen. There is a very low probability of release of LNG during normal industry operations due to the safety systems that are in place. Unexpected large releases of LNG, such as might be associated with acts of terrorism, bear special consideration although the consequences may well be similar to a catastrophic failure. In the case of a catastrophic failure, emergency fire detection and protection would be used, and the danger to the public would be reduced or eliminated by the separation distances of the facility design. LNG operations are industrial activities, but safety and security designs and protocols help to minimize even the most common kinds of industrial and occupational incidents that might be expected. LNG contains virtually no sulfur; therefore the combustion of re-gasified LNG used as fuel has lower emissions of air contaminants than other fossil fuels. In crude oil producing countries, as a general move towards lessening the environmental impact of oil production, a larger percentage of the associated natural gas is being converted to LNG instead of being flared. In many instances, this choice reduces the environmental impact of the continuous flaring of large quantities of natural gas, while also capturing this valuable resource for economic use. Thus, LNG development can have significant environmental and economic benefits.

II. LNG PROPERTIES AND POTENTIAL HAZARDS

To consider whether LNG is a hazard, we must understand the properties of LNG and the conditions required in order for specific potential hazards to occur. Natural gas produced from the wellhead consists of methane, ethane, propane and heavier hydrocarbons, plus small quantities of nitrogen, helium, carbon dioxide, sulfur compounds and water. LNG is liquefied natural gas. The liquefaction process first requires pre-treatment of the natural gas stream to remove impurities such as water, nitrogen, carbon dioxide, hydrogen sulfide and other sulfur compounds. By removing these impurities, solids cannot be formed as the gas is refrigerated. The product then also meets the quality specifications of LNG end users. The pretreated natural gas becomes liquefied at a temperature of approximately 111 k and is then ready for storage and shipping. LNG takes up only 1/600th of the volume required for comparable amount of natural gas at room temperature and normal atmospheric pressure. Because the LNG is an extremely cold liquid formed through refrigeration, it is not stored under pressure. The common misperception of LNG as a pressurized substance has perhaps led to an erroneous understanding of its danger. LNG is a clear, non-corrosive, non-toxic, cryogenic liquid at normal atmospheric pressure. It is odorless; in fact, odorants must be added to methane before it is distributed by local gas utilities for end users to enable detection of natural gas leaks from hot-water heaters and other natural gas appliances. Natural gas (methane) is not toxic. However, as with any gaseous material
besides air and oxygen, natural gas that is vaporized from LNG can cause asphyxiation due to lack of oxygen if a concentration of gas develops in an unventilated, confined area. The density of LNG is about 420 kg/m³, compared to the density of water, which is about 1000 kg/m³. Thus, LNG, if spilled on water, floats on top and vaporizes rapidly because it is lighter than water. Vapors released from LNG as it returns to a gas phase, if not properly and safely managed, can become flammable but explosive only under certain well-known conditions. Yet safety and security measures contained in the engineering design and technologies and in the operating procedures of LNG facilities greatly reduce these potential dangers. The flammability range is the range between the minimum and maximum concentrations of vapor (percent by volume) in which air and LNG vapors form a flammable mixture that can be ignited and burn. Figure below indicates that the upper flammability limit and lower flammability limit of methane, the dominant component of LNG vapor, are 5 % and 15 % by volume, respectively. When fuel concentration exceeds its upper flammability limit, it cannot burn because too little oxygen is present. This situation exists, for example, in a closed, secure storage tank where the vapor concentration is approximately 100 percent methane. When fuel concentration is below the lower flammability limit, it cannot burn because too little methane is present. An example is leakage of small quantities of LNG in a well-ventilated area. In this situation, the LNG vapor will rapidly mix with air and dissipate to less than 5 percent concentration.

A comparison of the properties of LNG to those of other liquid fuels, as shown in Table below, also indicates that the Lower Flammability Limit of LNG is generally higher than other fuels. That is, more LNG vapors would be needed (in a given area) to ignite as compared to LPG or gasoline.

The auto-ignition temperature is the lowest temperature at which a flammable gas vapor will ignite spontaneously, without a source of ignition, after several minutes of exposure to sources of heat. Temperatures higher than the auto-ignition temperature will cause ignition after a shorter exposure time. With very high temperatures, and within the flammability range, ignition can be virtually instantaneous.

**Important points:**

1. The primary component of natural gas is methane (CH₄); the shortest and lightest hydrocarbon molecule.
2. The gross heat of combustion of one normal cubic meter of commercial quality natural gas is around 39 MJ (~10.8 KWh)
3. The price of natural gas varies greatly depending on the location and type of consumer, but as of 2007 a price of $7 per 1000 cubic feet is typical in United States. One cubic foot of natural gas produces about 1.086 MJ.

4. Natural gas is a major source of electricity generation and the use of gas turbines and steam turbines. The world’s largest gas field is in Qatar, estimated to have 25 trillion cubic meters (900 trillion cubic feet) of gas in place.

**TABLE: COMPARISONS OF PROPERTIES OF LIQUID FUELS**

<table>
<thead>
<tr>
<th>Properties</th>
<th>LNG</th>
<th>LPG</th>
<th>Gasoline</th>
<th>Fuel oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toxic</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Flammable vapour</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Forms vapour clouds</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Asphyxiant</td>
<td>Yes, but in a vapour cloud</td>
<td>Same as LNG</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Extreme cold temperature</td>
<td>Yes</td>
<td>Yes, if refrigerated</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Other health hazards</td>
<td>None</td>
<td>None</td>
<td>Eye irritant, Narcosis, Nausea, Others</td>
<td>Same as Gasoline</td>
</tr>
<tr>
<td>Flash point (k)</td>
<td>85</td>
<td>168</td>
<td>227</td>
<td>333</td>
</tr>
</tbody>
</table>
For methane vapors derived from LNG, with a fuel-air mixture of about 10 percent methane in air (about the middle of the 5-15 % flammability limit) and atmospheric pressure, the auto-ignition temperature is above 813 k. This extremely high temperature requires a strong source of thermal radiation, heat or hot surface. If LNG is spilled on the ground or on water and the resulting flammable gas vapor does not encounter an ignition source (a flame or spark or a source of heat of 111 k or greater), the vapor will generally dissipate into the atmosphere, and no fire will take place.

When compared to other liquid fuels, LNG vapor (methane) requires the highest temperature for auto-ignition, as shown in the Table.

**TABLE: AUTO-IGNITION TEMPERATURES OF LIQUID FUELS**

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Auto-ignition temperature, k</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNG (Primarily methane)</td>
<td>813</td>
</tr>
<tr>
<td>LPG</td>
<td>723-783</td>
</tr>
<tr>
<td>Ethanol</td>
<td>695</td>
</tr>
<tr>
<td>Methanol</td>
<td>736</td>
</tr>
<tr>
<td>Gasoline</td>
<td>530</td>
</tr>
<tr>
<td>Diesel fuel</td>
<td>588</td>
</tr>
</tbody>
</table>

In summary, LNG is an extremely cold, non-toxic, non-corrosive substance that is transferred and stored at atmospheric pressure. It is refrigerated, rather than pressurized, which enables LNG to be an effective, economical method of transporting large volumes of natural gas over long distances. LNG itself poses little danger as long as it is contained within storage tanks, piping, and equipment designed for use at LNG cryogenic conditions. However, vapors resulting from LNG as a result of an uncontrolled release can be hazardous, within the constraints of the key properties of LNG and LNG vapors – flammability range and in contact with a source of ignition.

**TYPES OF LNG HAZARDS**
Explosion:
An explosion happens when a substance rapidly changes its chemical state – i.e., is ignited – or is uncontrollably released from a pressurized state. For an uncontrolled release to happen, there must be a structural failure – i.e., something must puncture the container or the container must break from the inside. LNG tanks store the liquid at an extremely low temperature, about 111 k, so no pressure is required to maintain its liquid state. Sophisticated containment systems prevent ignition sources from coming in contact with the liquid. Since LNG is stored at atmospheric pressure – i.e., not pressurized – a crack or puncture of the container will not create an immediate explosion.

Vapor Clouds:
As LNG leaves a temperature-controlled container, it begins to warm up, returning the liquid to a gas. Initially, the gas is colder and heavier than the surrounding air. It creates a fog – a vapor cloud – above the released liquid. As the gas warms up, it mixes with the surrounding air and begins to disperse.

The vapor cloud will only ignite if it encounters an ignition source while concentrated within its flammability range. Safety devices and operational procedures are intended to minimize the probability of a release and subsequent vapor cloud having an affect outside the facility boundary.

Freezing Liquid:
If LNG is released, direct human contact with the cryogenic liquid will freeze the point of contact. Containment systems surrounding an LNG storage tank, thus, are designed to contain up to 110 percent of the tank’s contents. Containment systems also separate the tank from other equipment. Moreover, all facility personnel must wear gloves, face masks and other protective clothing as a protection from the freezing liquid when entering potentially hazardous areas. This potential hazard is restricted within the facility boundaries and does not affect neighboring communities.

Rollover: When LNG supplies of multiple densities are loaded into a tank one at a time, they do not mix at first. Instead, they layer themselves in unstable strata within the tank. After a period of time, these strata may spontaneously rollover to stabilize the liquid in the tank. As the lower LNG layer is heated by normal heat leak, it changes density until it finally becomes lighter than the upper layer. At that point, a liquid rollover would occur with a sudden vaporization of LNG that may be too large to be released through the normal tank pressure release valves. At some point, the excess pressure can result in cracks or other structural failures in the tank. To prevent stratification, operators unloading an LNG ship measure the density of the cargo and, if necessary, adjust their unloading procedures accordingly. LNG tanks have rollover protection systems, which include distributed temperature sensors and pump-around mixing systems.

FIG: VAPOUR CLOUD
Rapid Phase Transition:
When enough LNG is spilled on water at a very fast rate, a rapid phase transition, or RPT, occurs. Heat is transferred from the water to the LNG, causing the LNG to instantly convert from its liquid phase to its gaseous phase. A large amount of energy is released during this rapid transition between phases and physical explosion can occur. While there is no combustion, this physical explosion can be hazardous to any nearby person or buildings.

Spill: Spill on water may result in to rapid phase transition
- Looks like a fog.
- Lighter than air once above 167 k
- Leaves no residue on land or water after its disperse.

Difference between LNG, CNG, NGL, LPG, and GTL.

It is important to understand the difference between Liquefied Natural Gas (LNG), Compressed Natural Gas (CNG), Natural Gas Liquids (NGL), Liquefied Petroleum Gas (LPG), and Gas to Liquids (GTL). Figure shows the difference in typical composition of these products.
LNG is made up of mostly methane. The liquefaction process requires the removal of the non-methane components like carbon dioxide, water, butane, pentane and heavier components from the produced natural gas. CNG is natural gas that is pressurized and stored in welding bottle-like tanks at pressures up to 3,600 psig. Typically, CNG is the same composition as pipeline quality natural gas. NGLs are made up mostly of molecules that are heavier than methane like ethane, propane, butane. LPG is a mixture of propane and butane in a liquid state at room temperatures. GTL refers to the conversion of natural gas to products like methanol, dimethyl ether (DME), middle distillates (diesel and jet fuel), specialty chemicals and waxes.

![Diagram showing typical compositions of LNG, NGLs, CNG, GTL, & LPG]

**FIGURE: TYPICAL COMPOSITIONS OF LNG, NGLS, CNG, GTL, & LPG**

### III. CONCLUSION

The principal constituents of natural gas, methane, ethane, and propane, are not considered to be toxic. The American Conference of Governmental Industrial Hygienists (ACGIH) considers those gases as simple asphyxiants, which are a health risk simply because they can displace oxygen in a closed environment. The Occupational Safety and Health Administration (OSHA) has set a time-weighted average (TWA) personal exposure limit (PEL) of 1,000 ppm for propane. A number of the minor constituents of natural gas have ACGIH listed threshold limit values (TLVs), including butane - 800 ppm, pentane - 600 ppm, hexane - 50 ppm, and heptane - 400 ppm. The effective TLV for an average natural gas composition, considering all of these limits, is about 10,500 ppm. There are no significant environmental hazards associated with the accidental discharge of LNG.

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