KISH P & I LOSS PREVENTION CIRCULAR KPI-LP-09-2012
(General Guidelines about Liquefied Gas Cargoes)

<The following are extracts from ISGOTT and other internationally reliable sources>

►Bulk liquefied gas cargoes :

The liquefied gases which are normally carried in bulk are hydrocarbon gases used as fuels or as feed stocks for chemical processing and chemical gases used as intermediates in the production of fertilizers, explosives, plastics or synthetics. The more common gases are LPGs, such as propane, butane, propylene, butylene, anhydrous ammonia, ethylene, vinyl chloride monomer (VCM) and butadiene.

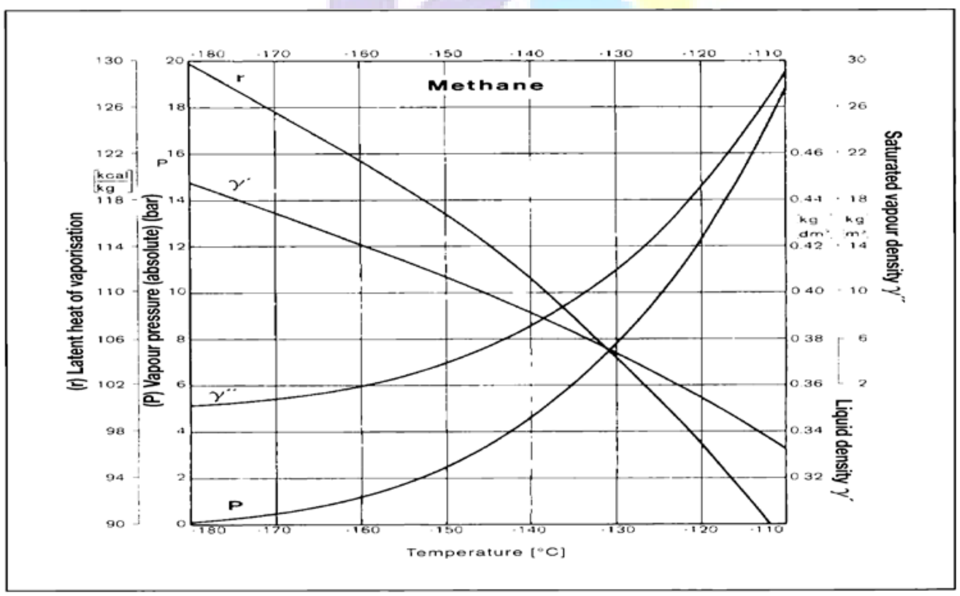
LNG is also transported extensively in dedicated ships, LNG being a mixture of methane, ethane, propane and butane with methane as the main component.

►Gas properties :

Liquefied gases are vapours at normal ambient temperatures and pressures. The atmospheric boiling points of the common gases are given as follows:

LPG Propane -42.3°C / Butane -0.5°C / LPG propylene -47.7°C / Butylenes -6.1°C

Ammonia -33.4°C / Ethylene -103.9°C / VCM -13.8°C / LNG -161.5°C.



Methane characteristics

-True Vapour Pressure : All crude oils and the usual petroleum products are essentially mixtures of a wide range of hydrocarbon compounds (i.e. chemical compounds of hydrogen and carbon). The boiling points of these compounds range from -162ºC (methane) to well in excess of +400ºC, and the volatility of any particular mixture of compounds depends primarily on the quantities of the more volatile constituents (i.e. those with a lower boiling point).

The volatility (i.e. the tendency of a crude oil or petroleum product to produce gas) is characterised by the vapour pressure. When a petroleum mixture is transferred to a gas free tank or container it commences to vaporise, that is, it liberates gas into the space above it. There is also a tendency for this gas to re-dissolve in the liquid, and equilibrium is ultimately reached with a certain amount of gas evenly distributed throughout the space. The pressure exerted by this gas is called the *equilibrium vapour pressure* of the liquid, usually referred to simply as the *vapour pressure*.

The vapour pressure of a pure compound depends only upon its temperature. The vapour pressure of a mixture depends on its temperature, constituents and the volume of the gas space in which vaporisation occurs; that is, it depends upon the ratio of gas to liquid by volume.

The True Vapour Pressure (TVP), or bubble point vapour pressure, is the pressure exerted by the gas produced from a mixture when the gas and liquid are in equilibrium at the prevailing temperature. It is the highest vapour pressure which is possible at any specified temperature.

As the temperature of a petroleum mixture increases, its TVP also increases. If the TVP exceeds atmospheric pressure the liquid commences to boil.

The TVP of a petroleum mixture provides a good indication of its ability to give rise to gas. Unfortunately, it is a property which is extremely difficult to measure, although it can be calculated from a detailed knowledge of the composition of the liquid.

- Reid Vapour Pressure :The Reid Vapour Pressure (RVP) test is a simple and generally used method for measuring the volatility of petroleum liquids. It is conducted in a standard apparatus and in a closely defined way.

A sample of the liquid is introduced into the test container at atmospheric pressure, so that the volume of the liquid is one fifth of the total internal volume of the container. The container is sealed and immersed in a water bath where it is heated to 37.8ºC. After the container has been shaken to bring about equilibrium conditions rapidly, the rise in pressure due to vaporisation is read on an attached pressure gauge. This pressure gauge reading gives a close approximation, in bars, to the vapour pressure of the liquid at 37.8ºC.

RVP is useful for comparing the volatilities of a wide range of petroleum liquids in a general way. It is, however, of little value in itself as a means of estimating the likely gas evolution in specific situations, mainly because the measurement is made at the standard temperature of 37.8ºC and at a fixed gas/liquid ratio. For this purpose, TVP is much more

useful and in the case of products, reliable correlations exist for deriving TVP from the more-readily measured Reid Vapour Pressure and temperature.

The carriage of gases in the liquid phase can only be achieved by lowering the temperature or increasing the pressure or a combination of both low temperatures and increased pressures.

The carriage condition is classified as either: ‘fully refrigerated’ (at approximately atmospheric pressure) or ‘semi-refrigerated’ (at approximately 0 to -10°C and medium pressure) and fully pressurized (at ambient temperature and high pressures).

LNG and ethylene are normally always carried in the fully refrigerated condition – they cannot be liquefied by increasing the pressure alone – while the LPGs, ammonia, VCM and butadiene can be liquefied by lowering the temperature or increasing the pressure. This permits them to be carried in the fully refrigerated, or the semi-refrigerated or the fully pressurized condition. The IMO/IGC Code provides standards for 'gas tankers' and identifies the types of tanks which must be employed for the carriage of liquefied gases as:

- Integral tanks – tanks which form part of the ships hull
- Membrane – non-self-supporting, completely supported by insulation
- Semi-membrane – non-self-supporting and partly supported by insulation
- Independent tanks – self-supporting tanks not forming part of the ships hull, independent tanks being subdivided into Types A, B and C.

Integral membrane and semi-membrane tanks are designed primarily with plane surfaces. Of the independent tanks, both A and B can either be constructed of plane surfaces or of bodies of revolution, Type C is always constructed of bodies of revolution.

►Dangerous space knowledge :

One of the main operational features of working on 'gas carriers' is the awareness of personnel to what is and what is not a gas-dangerous space. This is given by the following definition:

- ***A gas-dangerous space***, or zone is a space in the cargo area which is not arranged or equipped in an approved manner to ensure that its atmosphere is at all times maintained in a gas – safe condition.

– Further: an enclosed space outside the cargo area through which any piping containing liquid or gaseous products passes, or within which such piping terminates, unless approved arrangements are installed to prevent any escape of product vapour into the atmosphere of that space.

– Also: a cargo containment system and cargo piping.

– And: a hold space where cargo is carried in a cargo containment system requiring a secondary barrier; a space separated from a hold space described above by a single gas-tight steel boundary; or a cargo pump room and cargo compressor room; or a zone on the open deck, or semi-enclosed space on the open deck, within 3 m of any cargo tank outlet, gas or vapour outlet, cargo pipe flange or cargo valve or of entrances and ventilation openings to cargo pump rooms and cargo compressor rooms.

– The open deck over the cargo area and 3 m forward and aft of the cargo area on the open deck up to a height of 2.4 m above the weather deck.

– A zone within 2.4 m of the outer surface of a cargo containment system where such surface is exposed to the weather; an enclosed or semi-enclosed space in which pipes containing products are located.

A space which contains gas-detection equipment complying with Regulation 13.6.5 of the IGC Code and space-utilizing boil-off gas as fuel and complying with Chapter 16 are not considered gas-dangerous spaces in this context.

– A compartment for cargo hoses; or an enclosed or semi-enclosed space having a direct opening into any gas-dangerous space or zone.

- ***A Gas-Safe space is defined by a space other than a gas-dangerous space.***

►Headspace Flammability :

Gas detectors such as explosimeters have been used to check that enclosed spaces are gas free and they are entirely suited to this purpose. They are also used to measure the "flammability" of headspaces in terms of percentage of the lower flammability limit (LFL). Such detectors rely on a calibration carried out

normally on a single hydrocarbon, such as methane, which may have LFL characteristics that are far removed from the hydrocarbons actually present in the headspace. When using an explosimeter to assess the degree of hazard in non-inerted residual fuel oil tank headspaces, it is recommended that the instrument is calibrated with a pentane/air or hexane/air mixture. This will result in a more conservative estimate of the flammability but the readings should still not be regarded as providing a precise measurement of the vapour space condition.
When taking measurements, the manufacturer operating instructions for the instrument should be closely followed and the instrument calibration should be frequently checked as oxidation catalyst detectors (pellisters) are likely to be susceptible to poisoning when exposed to residual fuel oil vapours.
In view of the problems associated with obtaining accurate measurements of the flammability of residual fuel tank headspaces using readily available portable equipment, the measured % LFL only broadly ranks fuels in terms of relative hazard. Care should therefore be exercised in interpretation of the figures obtained by such gas detectors.

►Main safety aspects for Cargo operations :
Three main safety aspects should be borne in mind when handling liquefied gases are:
1-Flammability of the cargo and the need to avoid the formation of explosive mixtures at all times,
2. Toxicity of the cargo ,
3. Low temperature of the cargo which could cause serious damage to the ships hull.

	Cargo vapour in air			Toxic effects of vapour or liquid	
Substance	Flammable	Toxic	Typical TLV-TWA (ppm)	Corrosive/ Irritant	Effects on Nervous System
Methane	Yes	—	A	No	—
Ethane	Yes	—	A	No	Yes
Propane	Yes	—	A	No	Yes
Butane	Yes	—	600	No	Yes
Ethylene	Yes	—	A	No	Yes
Propylene	Yes	—	A	No	Yes
Butylene	Yes	—	800	No	Yes
Isoprene	Yes	—	No Data	—	Yes
Butadiene	Yes	Yes	10	Yes	Yes
Ammonia	Limited	Yes	25	Very	—
Vinyl chloride	Yes	Yes	5	Yes	Yes
Ethylene oxide	Yes	Yes	10	Very	Yes
Propylene oxide	Yes	Yes	50	Very	Yes
Chlorine	No	Yes	25	Very	Very

Example for various effects of cargo vapours & Threshold Limit Values

►Various Stages in Cargo Operation:
-Drying : Once a vessel is ordered to receive a cargo of LNG following overhaul or delivery trials, all traces of water must be removed from the tanks. If this is not done, operating problems due to freezing may result. The dew point of IG or air in equipment must be low enough to prevent condensation of water vapour when in contact with the cold surfaces. Purging with dry gas refrigerated driers and dosing with methanol are not uncommon techniques for removing moisture.
-Inerting : Once cargo tanks and associated equipment are suitably dried, air must be removed from the cargo system before loading to prevent the formation of explosive mixtures and also to prevent product contamination. Either IG from the ship's IG generator or a nitrogen supply from shore may be used.

IG from a shipboard IG generator is of a relatively low purity content in comparison with 'pure' nitrogen from a shoreside supply and usually will contain up to 15% CO_2 and 0.5% O_2. This can lead to contamination problems with cargoes, such as ammonia, butadiene, etc. To prevent explosive mixture formation, the oxygen content of the tank must be reduced to 6% for hydrocarbon gases and 12% for ammonia using IG or nitrogen.
-Purging :When the cargo tanks are suitably inerted, cargo vapours may be introduced to purge the tank of inerts. If the inerts are not completely purged from the tank, then operating problems will be encountered in the re-liquefaction plant operations. IG is incondensable and can therefore lead to high pressure in the plant condenser with associated difficulties. The cargo vapours are introduced either at the top or bottom of the tank depending on the density of the gas, and the vapour IG mixture is either vented through the vapour return to the shore flare stack or, where local port regulations allow, to the ship's vent stack.

►**Special Precautions with Very High Vapour Pressure Cargoes :**
Consideration should be given to the need for special precautions during loading when the True Vapour Pressure (TVP) of the cargo is expected to exceed the following:
-☐For natural gasoline type cargoes (e.g. pentanes plus): 0.75 bar
-☐For crude oils, with or without added gas: 1.0 bar.
For some intermediate cargoes, for example, flash stabilised condensates, some distillation overhead products, and crude oils with abnormally low methane and ethane contents, TVP limits may lie between these two values.
When cargo temperature, crude oil stabilisation conditions and Reid Vapour Pressures are known, true vapour pressures can be calculated for checking with the above criteria.
The terminal should supply the necessary information.

Precautions, which should be applied, may include:
1. ☐Permitting only closed loading methods.
2. Avoiding loading when the wind speed is less than 5 knots.
3. ☐The use of very low initial flow rates into tanks.
4. The use of very low topping off rates.
5. ☐Avoiding a partial vacuum in the loading line.
6. Avoiding loading hot oil which has been lying in shore lines exposed to the sun. If this is unavoidable, this oil should be loaded to tanks which vent well clear of the superstructure (e.g. forward tanks).
7. Providing additional supervision to see that gas dispersion is monitored and to ensure compliance with all safety requirements.
8. ☐Monitoring inert gas main pressure where this gives an indication of the cargo tank pressure.