LNG HEAVIES – ADDRESSING OPERATIONAL CHALLENGES ONBOARD SHIPS

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Introduction

Liquefied Natural Gas (LNG) plays an essential role in the global energy market, offering a cleaner alternative to coal and oil. Key LNG producers include countries like Qatar, Australia, the United States and Russia, which dominate global LNG exports. With LNG production steadily increasing and new export terminals being built, the LNG carrier fleet has expanded significantly to meet growing demand. According to recent data, there are 772 LNG carriers in operation and an additional 373 on order.

LNG ships encounter various operational challenges, many of which are closely tied to the quality of the LNG cargo. Impurities, including heavier hydrocarbons (often referred as **heavies or C6 plus**) and high nitrogen (N2) content, can affect the performance of LNG vessels and lead to delays and other operational issues during the voyage.

The production of LNG involves several stages, starting with the extraction of natural gas from underground reserves. This raw gas undergoes preprocessing to remove impurities such as water, carbon dioxide, and hydrogen sulphide, as well as heavier hydrocarbons, such as ethane, propane, and butane. Older LNG Plants typically use conventional methods, such as scrub columns or expansion and condensation schemes, to remove heavier hydrocarbons from the natural gas stream. These traditional techniques are effective in processing feed gases with higher concentrations of heavier hydrocarbons. However, they may not be as efficient when handling lean feed gases, which contain low concentrations of heavy hydrocarbons. This limitation can lead to operational challenges, including freezing in cryogenic systems and issues with the final product, as these heavier components are not effectively separated.

Liquified Natural Gas (LNG) – Composition And Physical Properties

LNG is primarily composed of methane (C1), with small percentages of heavier hydrocarbons such as ethane (C2), propane (C3), butane (C4), and occasionally nitrogen. The physical properties of LNG, including its solubility and temperature behaviour, are highly dependent on its composition. At temperatures around -162°C, methane and other light hydrocarbons (C1 to C5) are highly soluble in the liquid phase. However, as the carbon chain length increases beyond C5, such as with hydrocarbons in the C6 to C14 range, their solubility in LNG decreases. These heavier hydrocarbons can solidify under the extremely low temperatures found in LNG systems, potentially causing operational issues. The formation of solids or the presence of heavier hydrocarbons can lead to freezing in cryogenic systems, blockages in pipelines or pumps, and operational challenges in LNG processing and storage. The effective handling of these heavier hydrocarbons is crucial to prevent damage to equipment and ensure smooth operations in LNG Plants and during transportation.

Location	Methane (%)	Ethane (%)	Propane (%)	Butane (%)	Pentane and heavier (%)	Nitrogen (%)
US	94.9	2.5	0.2	0.06	0.04	1.6
Qatar	89.5	5.3	2.0	0.8	0.03	1.8
West Africa	90.4	4.3	2.8	1.1	0.02	0.9
Australia	93.5	3.2	1.2	0.7	0.03	1.0
Range	87 ~ 96	1.8 ~ 6	0.1 ~ 5	<1.5	<0.1	0.5 ~ 6

Table 1 - Composition of typical LNG cargoes[1].

Example – A concentration of 0.04 mol% (or 400 ppm) of heavies in an LNG cargo of 100,000 tonnes would result in 40 tonnes of heavies in the cargo.

1 As per the Union Gas Material Safety Data Sheet and the Cargo Operation Manual from Hudong Zhonghua Shipbuilding Group, the above composition is provided without any guarantee.

LNG Cargo – Ageing

Ageing, or weathering, of LNG cargo refers to the gradual alteration of its composition during storage and transit. This process primarily involves the evaporation of lighter hydrocarbons, such as methane and nitrogen, leading to a concentration of heavier components like ethane, propane, butane and others. As a result, the energy content per unit volume may decrease, and the density of the remaining LNG increases.

During long ballast voyages, the ageing process becomes more pronounced, especially on LNG-fuelled vessels. The absence of a full cargo load leads to higher boil-off gas (BOG) generation because of increased heat ingress. To mitigate potential operational issues arising from this, strategic heel management procedures are implemented. These procedures include:

- Precise calculations of the heel quantity to be retained, especially for vessels with Dual Fuel Engines;
- Careful distribution of heel across the cargo tanks, with heel distributed in all tanks, below sloshing limits;
- Continuous monitoring of tank temperatures and pressures, with an Average Tank Temperatures (ATR) maintained around -125°C during the voyage;
- Diligent planning for cargo tank conditioning prior arrival loading ports, to achieve an ATR below -155°C.

LNG Cargo – Sampling and Analysis

Online Gas Chromatography (GC)

The most widely used testing method by loading and discharging terminals is *Online Gas Chromatography* (GC), which enables continuous, real-time analysis of gas streams. In this method, either a Flame Ionization Detector (FID) or a Thermal Conductivity Detector (TCD) is employed to measure and analyse the gas composition.

The results from the Online GC testing are compared against established Standards, such as International Organisation for Standardization (ISO) 6974 and Gas Processors Association (GPA) 2261. These Standards are widely adopted for LNG cargoes to ensure compliance with specifications for quality, energy content, and safe handling. ISO 6974 is globally recognised, while GPA 2261 is specific to North America. It is crucial that the Certificate of Quality (COQ) from this testing is provided to the vessel after both loading and discharging.

Operational Issues due to LNG Heavies

BOG is typically composed of light hydrocarbons, but over time, heavier hydrocarbons may accumulate in the gas mixture. These heavier hydrocarbons (such as Pentane, Hexane, and Nonane) have higher freezing points compared to lighter components like methane or ethane, which causes them to solidify under the low temperatures in the refrigeration system. For instance, Pentane freezes at around -129.7 °C, while Hexane freezes at approximately -95.3 °C.

Figure 1 - Cargo manifold strainer 60 mesh size – partially clogged.

The following operational issues may be encountered:

- Cargo Manifold Strainer clogging during loading or discharging;
- Clogging of BOG Compressors inlet filters or demisters in partial reliquefication/ reliquefication system (PRS – FRS);
- BOG strainers on the Cold Box;
- Clogging of Fuel Gas Pump strainers.
- Challenges with cargo tank cooling after extended ballast voyages.

In case LNG heavies enter the BOG stream or Cold Box, a Warm-up of BOG loop by N2 may be required. This procedure generally takes about 16 to 18 hours to complete, and equipment manufacturers typically provide detailed instructions for performing this operation.

Onboard Troubleshooting and Fault Diagnosis

When addressing operational issues such as filter clogging or increased back pressure, it is essential to inspect the internal components of the vessel's machinery to identify potential sources of moisture ingress or other forms of contamination. Key areas to examine include:

- Inert Gas Generator - Verify the dew point and calibrate if necessary;
- Nitrogen Generator - Verify the dew point and calibrate if necessary;
- LNG Vaporiser – Check for internal leaks;
- BOG Compressor cooling water system – Check for internal leaks;
- Cargo and condensate lines purging after maintenance – Review purging requirements and procedure;
- Increasing the filter mesh size may be considered in consultation with equipment manufacturers and Charterers, but it is not the preferred option.

Once the possibility of moisture ingress is ruled out, it is advisable to collect both a cargo sample and a strainer residue sample for extended analysis. Additionally, it is recommended that the vessel be equipped with 'Gastec Detector Tubes' 120L (for n-Hexane) or an equivalent device to test the gas onboard.

Extended Analysis

Recommended Tests – Gas Chemical Composition Test as per GPA 2286 Standards

A gas sample must be collected for this purpose. The LNG sampling procedure is outlined in Section 6 of the GIINL – LNG Custody Transfer Handbook. Typically, samples are collected using electrical or steam sampling vaporisers installed onboard, where the LNG is vaporised and collected in a small gas cylinder for analysis. If the vessel is not equipped with a sampling vaporiser, samples can be taken from the cargo tank dome or the BOG compressor outlet. In such cases, a thorough risk assessment must be conducted to ensure both safety and the accuracy of the sample collection, minimising any potential hazards associated with these alternative methods.

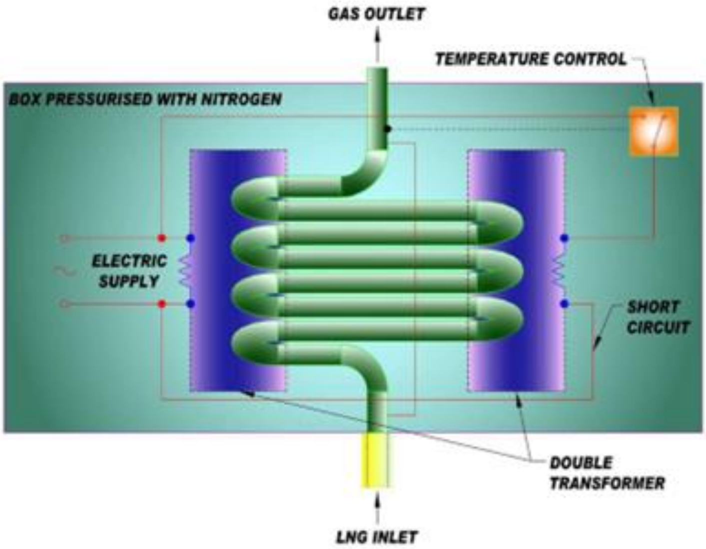

Figure 3 - Electrical LNG sampling vaporiser.

GPA 2286 is a method designed for the extended analysis of LNG and similar gaseous mixtures. It specifically addresses gas sampling and chromatographic procedures to determine the detailed composition of the gas, including both light hydrocarbons (such as methane, ethane, and propane) and heavier hydrocarbons. This Standard plays a crucial role in providing an accurate chemical composition of LNG, enabling operators to assess the quality and energy content of the gas. GPA 2286 is particularly valuable in contexts where the composition of heavier hydrocarbons needs to be precisely measured, ensuring compliance with industry regulations and contractual requirements during LNG production, transport, and storage. This test can give concentrations of compounds even below, 0.01 mol% (or less than 100 ppm) which a standard Gas chromatography might not be able to give.

<u>Recommended Tests for Strainer Residue Samples</u>

The strainer residue sample will consist of a mixture of aqueous and organic phases (in liquid form). The testing laboratory will separate the organic phase and perform the following tests.

Chemical Composition Test as per GPA 2286 Standards

Similar to the test for Cargo vapor (gas), this test will be done to see the chemical composition of the liquid sample.

GCMS (Gas Chromatography-Mass Spectrometry) Qualitative Screening

GCMS combines the separation capabilities of gas chromatography with the identification power of mass spectrometry. This method effectively detects and quantifies volatile and semi-volatile organic compounds within LNG samples, including both light and heavy hydrocarbons. During analysis, the sample is vaporised and transported through a chromatographic column by an inert gas. As compounds elute, they are ionised and fragmented in the mass spectrometer, producing unique spectra that facilitate precise identification and quantification.

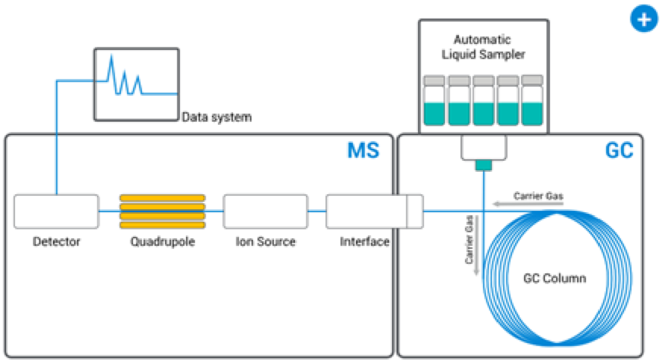

Figure 4 – Gas Chromatography-Mass Spectrometry.

Scanning Electron Microscope SEM – EDX Analysis

SEM is a type of electron microscope that provides detailed, high-resolution images of the surface of a sample by scanning it with a focused beam of electrons for analysing the microstructure of materials, including metals, polymers, and ceramics.

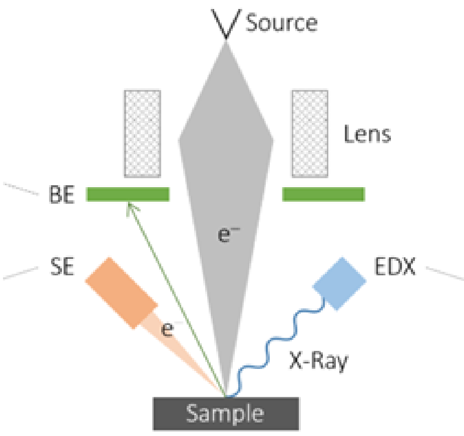

Figure 5 – Scanning Electron Microscope SEM – EDX.

Commercial Impacts and Safeguards

In conclusion, the presence of heavier hydrocarbons (LNG heavies) in LNG cargoes presents significant operational challenges. These include potential clogging of equipment, reduced cooling efficiency, and complications during LNG transfer operations. Such challenges can lead to delays in cooling down and during cargo operations, as well as potential issues during the voyage for LNG-fuelled vessels.

In 2021, Baltic and International Maritime Council (BIMCO) has developed a suite of LNG fuel clauses for Time Charterparties to address various operational aspects of LNG-fuelled vessels. These clauses cover LNG fuel quality, delivery and redelivery procedures, gas-freeing, and cool-down operations. However, there isn't a specific BIMCO clause that directly addresses LNG ships carrying LNG with high heavy hydrocarbon concentrations.

The existing BIMCO LNG Fuel Quality Clause for Time Charterparties focuses on ensuring that the LNG supplied meets certain quality standards, such as methane content, heating value, and the presence of corrosive contaminants. This clause aims to prevent issues related to fuel quality but does not specifically address the challenges posed by heavy hydrocarbon concentrations in LNG.

For situations involving LNG with high heavy hydrocarbon concentrations, it may be necessary to include bespoke clauses in the Charterparty Agreement. These custom clauses would outline the responsibilities of both Owners and Charterers concerning the handling, treatment, and potential offloading of heavy hydrocarbons to ensure safe and efficient operations.

References

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For further information or assistance on any related matter, please feel free to reach out to Brookes Bell. We will be happy to assist.