The key is accuracy

Dr Matthew Hammond, EffecTech, UK, outlines the difficulties that come with measuring LNG, detailing how the calibration of spectroscopic instruments helps to make gas measurement more accurate.

LNG is traded on the basis of total energy, which requires the volume of LNG as well as calorific value (CV) and density, both of which are calculated from the LNG composition. Traditionally, composition is measured by vaporising a sample of LNG and subsequent analysis by gas chromatography (GC).

The vaporiser must be set up correctly otherwise the LNG sample could fractionate, resulting in a change in composition, leading to errors in the measured composition and physical properties, including CV and density. These errors propagate through to the calculation of total energy, meaning increased financial risk for both buyers and sellers. Spectroscopic methods have emerged as an attractive alternative to vaporiser-GC systems, as they measure the LNG composition directly without the need to sample and vaporise. However, in order to calibrate these instruments, traceable calibration artefacts that are representative of LNG are required.

EffecTech has developed and validated an LNG production facility which produces LNG of known composition with defined uncertainty that is traceable to the SI unit of amount of substance, the mole. This facility has been used to calibrate a variety of optical instruments whose measurements are now traceable through ISO 17025 accredited methods.

Table 1. EN 12838 criteria for select physical properties

Property	EN 12838 criteria	Calculation
Gross calorific value (GCV), continuous (kJ/kg)	9	
Gross calorific value (GCV), intermittent (kJ/kg)	54	ISO 6976[6]
Gas density (kg/m^3)	3 X 10^{-4}	
Liquid density (kg/m^3)	0.15	ISO 6578[7]

Table 2. EffecTech's ISO 17025 scope of accreditation for LNG analyser calibrations

	Reference gas range (%mol/mol)	
Component	**Minimum**	**Maximum**
nitrogen	0.1	1.8
methane	79.0	100.0
ethane	0.1	14.0
propane	0.02	4.0
iso-butane	0.02	1.3
n-butane	0.02	1.3
iso-pentane	0.01	0.16
n-pentane	0.01	0.16

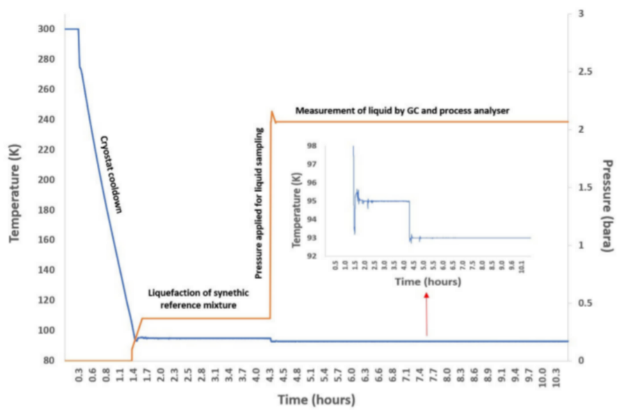

Figure 1. Temperature and pressure profile for condensation.

Background

Around the world, more and more countries are adopting net zero emissions targets, and natural gas is projected to play a significant role in reducing emissions. Natural gas is seen as a suitable alternative to coal or oil during the transition to renewable energy sources due to the lower emissions relative to coal and oil.

LNG is natural gas which has been processed and liquefied by cooling to -160˚C. The resulting liquid occupies 600 times less volume than the natural gas and is therefore economically viable for transportation via ships. This opens up the natural gas market, allowing gas to be traded between areas where pipelines are not feasible. Global LNG trade volumes have grown y/y since the early 1970s. LNG trade grew marginally to 360 million t in 2020, despite the COVID-19 pandemic, and demand is projected to grow to approximately 700 million t by 2040.[1]

LNG is typically vaporised again and injected into gas transmission networks for use in heating, industry, and power generation. More recently, LNG has been used as a transport fuel as a replacement for marine fuel oil in cruise ships and ferries, or replacing diesel in heavy goods vehicles (HGVs).

Like natural gas, LNG is traded on the basis of total energy, calculated from volume (flow metering), CV, and density (both determined from composition). Natural gas composition is typically measured by sample analysis using GC. Chromatography is a well-established technique, and instruments can be maintained and calibrated easily. Current best practice for LNG composition measurement for custody transfer applications requires vaporising a sample of LNG and analysing the sample using GC.[2] Whilst the performance of the instrument itself can easily be assessed, the vaporiser must be set up correctly to ensure a representative sample is delivered to the instrument. The LNG sample must remain in the liquid phase right up to the vaporiser. If too much heat enters the sample line and/or sample subcooling is insufficient, pre-vaporisation can occur and the sample can fractionate. This means the vaporised sample may not be representative of the LNG stream, leading to errors in the measurement which propagate to the calculated physical properties including CV and density, which are used to calculate total energy. The vaporiser can therefore lead to increased financial risk in LNG custody transfer if improperly set up.

Recently, spectroscopic analysers have emerged as an alternative solution to vaporiser-GC systems. The 2021 edition of the *LNG Custody Transfer Handbook* describes some of the recent testing into Raman spectroscopy for LNG composition measurement.[2] The advantage of these instruments is that they offer fast response times and in situ composition measurement, avoiding the need to sample and vaporise the LNG. However, as spectroscopy is not a primary measurement, calibration of these instruments is required to ensure they are sufficiently accurate. Calibration requires traceable reference liquids which resemble the LNG process stream to be measured by the instrument i.e., similar composition and physical state (temperature, pressure). EffecTech has developed a facility in which cryogenic reference liquids can be realised and used to calibrate direct measurement analysers for LNG, providing traceability and measurement confidence to end users. EffecTech is accredited to ISO 17025 for the calibration of LNG analysers by the United Kingdom Accreditation Service (UKAS).

Calibration of spectroscopic instruments for LNG measurement

EffecTech specialises in gas measurement, and provides high-quality, traceable calibration gases with the lowest commercially available uncertainties. EffecTech is accredited by UKAS against the requirements of ISO 17025 for calibration and ISO 17034 for reference materials.[3] The calibration gases are prepared accurately by gravimetry whereby pure components are weighed individually before being added to the gas cylinder. Once all of the components have been added, the cylinder is homogenised and the composition is calculated and the mixture verified by analysis as required by ISO 6142.[4] The newly prepared mixture is then calibrated using GC with traceable gases from National Measurement Institutes (NMIs) to establish traceability to the mole, the SI unit of amount of substance according to ISO 6143.[5]

In order to calibrate LNG analysers, a cryogenic reference liquid with known composition is required. EffecTech has developed a facility for liquefying calibration gases in a bespoke cryostat which accepts optical probes used by spectrometers. Cooling is provided by liquid nitrogen heat exchangers and the system is vacuum insulated to minimise heat influx from the surroundings. The liquid temperature can be controlled by adjusting liquid nitrogen flow and heating elements in the sample cell. The sample cell temperature is set to below the bubble point of the gas mixture in order to condense the gas as it is transferred into the cryostat.

A primary reference gas mixture (PRGM) is used, as these have the lowest commercially available uncertainties in amount fraction. Normally, the temperature is set to between 90 and 110 K to provide enough subcooling and ensure all components remain in the liquid phase. Approximately 450 g of gas is condensed, resulting in 1 l of liquid. Once condensed, the temperature can be maintained within 0.1 K of the target temperature (Figure 1).

The liquid composition must be verified analytically to ensure the composition has not changed during the condensation process. To do this, a small amount of liquid is sampled and vaporised then analysed using GC. However, as the liquid is subcooled, the vapour pressure is less than ambient pressure, therefore helium is used to pressurise the sample to approximately 1.5 bara. This forces liquid through the sample system. Helium is used as it is relatively insoluble in LNG and is also used as the carrier gas in the GC so does not interfere with the measurement.

Data is collected from the spectrometer, normally over an extended period, to assess repeatability and accuracy. Data can be collected over a range of temperatures and pressures, if required, as some customers have varying operating conditions. The average composition measured by the instrument is compared to the verified liquid composition. Additionally, various physical properties calculated by the instrument are compared to the physical properties of the reference liquid against the requirements of EN 12838 detailed in Table 1.[6] This standard describes the testing requirements for LNG, sampling systems involving vaporisation of a sample. A certificate of calibration is produced which shows the difference in composition and CV.

Seven mixtures covering a range of LNG compositions have been verified using the above methods, proving the cryostat is a good facility for producing accurate, stable, and traceable reference liquids for calibrating LNG analysers. The range of components to which EffecTech is accredited to ISO 17025 is shown in Table 2. The composition can be tailored to match the LNG composition that the instrument is expected to see during operation.

Summary

Since its inception, a range of different spectroscopic instruments designed for in situ LNG measurement have been calibrated using the cryostat, providing traceability and measurement confidence to end users. The facility is also ideal for providing representative data to OEMs for development of chemometric models. In the future, a new portable cryostat could be designed which can be taken to site and used to calibrate instruments without having to send them to EffecTech's laboratory. **LNG**

References

1. Royal Dutch Shell, 'Shell LNG Outlook', 2021.
2. GIIGNL, *LNG Custody Transfer Handbook*, 6th Edition, 2021.
3. ISO 17025:2005 General requirements for the competence of testing and calibration laboratories.
4. ISO 6142:2001 Gas analysis – Preparation of calibration gas mixtures – Gravimetric method.
5. ISO 6143:2001 Gas analysis – Determination of composition and checking of calibration gas mixtures – Comparison methods.
6. EN 12838:2000 Installations and equipment for LNG – Suitability testing of LNG sampling systems.
7. ISO 6976:1995 Natural Gas – Calculation of calorific values, density, relative density, and Wobbe Index from composition.
8. ISO 6578:1991 Refrigerated hydrocarbon liquids – Static measurement – Calculation procedure.