UK company outlines details of world's first facility to produce reference liquids for LNG

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Traditionally the heating value of LNG is determined by sampling a stream, vapourising the LNG without introducing fractionation or enrichment, measuring the resulting composition by gas chromatography and collecting a retained sample from the same stream as a backup.

In recent years optical methods employing chemometric models have been developed to measure the cryogenic LNG directly without vapourisation. Using this approach may provide some improvement in the reliability of on-line calorific value measurements and a significant reduction in operational costs. The downside to the optical methods is the lack of traceable calibration artefacts covering the composition range of LNGs passing through the metering point.

EffecTech has developed and validated a production facility which produces LNG of known composition with defined uncertainty which is traceable to the SI unit of amount of substance, called the mole.

This facility can be used to calibrate instruments in LNG against a traceable LNG standard. Shell Global Solutions has already been a main user of the facility, initiating value-adding research and development for its LNG business.

Background

LNG is a hot topic in the world's energy vision for the future. At a temperature of minus 163°C the volume of natural gas reduces by more than 600 times to form a liquid which can be transported by ship to almost any port around the globe.

LNG is being used more and more in small-scale and mid-scale facilities around the world where the source of the gas is too far from the end user to be transported by conventional pipeline.

There are many advantages to having this clean high-energy density liquid at ambient pressures, and the vision is not only to use LNG to power industry but also to power the next generation of clean-fuel burning commercial vehicles without the need for high-pressure containers.

The physical properties of LNG are important in the production, transportation and combustion of the fuel and also for commercial billing.

The issues

The energy content of a cargo of LNG is derived from the volume of liquid, the calorific value of the liquid and the density of the liquid and these final two parameters are calculated from the LNG's composition.

Unfortunately, LNG is a cryogenic liquid and unlike natural gas does not lend itself easily to direct measurement.

In most cases, the LNG liquid is vapourised and measured as a gas; it is this vapourisation step which has the potential to cause measurement problems.

Vapourising a cryogenic hydrocarbon liquid is the same as vapourising any hydrocarbon liquid mixture. Fractionation and enrichment processes occur on the application of heat.

These processes are a benefit when refining crude oil. However, these same processes are a problem when a representative sample of the LNG is needed in the gas phase.

The main issue with LNG is that the more volatile components are preferentially vapourised, making the sample unrepresentative of the bulk LNG.

Measuring an unrepresentative sample will lead to an incorrect measurement of the LNG and of the actual cargo.

Vapouriser efficiency and the knock-on effect on composition measurements have always caused concern within the LNG industry and as a consequence, some manufacturers have developed instruments to measure LNG without the need for vapourisation.

Direct *in situ* measurements using spectroscopic techniques have been claimed to be the answer but herein lies the problem. Spectroscopy is not a primary measurement; it requires calibration but currently there are no traceable calibration artefacts for cryogenic LNG composition measurements.

The solution

EffecTech, a specialist gas calibration company based in the UK, has developed a facility for the production of cryogenic reference liquids in the laboratory.

These reference liquids with known composition can be used to calibrate instruments measuring LNG directly and thus removing the vapourisation step completely, improving traceability, accuracy and reducing uncertainty.

EffecTech specialises in the production of traceable calibration gases in cylinders and is accredited by UKAS (United Kingdom Accreditation Service) against the requirements of ISO 17025[i].

The calibration gases can be prepared very accurately by weighing individual pure components into the gas cylinder in accordance with ISO 6142[ii].

Once all of the components have been added, the cylinder is mixed, the composition is calculated and the mixture verified by analysis. The newly prepared mixture is calibrated in accordance with ISO 6143[iii] using gas chromatography with traceable gases from National Measurement Institutes (NMIs). This establishes traceability to the mole, the SI unit of amount of substance.

Once calibrated, the synthetic gas mixture is carefully transferred from the gas cylinder into a bespoke cryostat where the gas mixture is cooled using liquid nitrogen.

The specially designed cryostat uses vacuum technology to provide efficient thermal insulation from the external environment.

Heating elements in the LNG cell inside the cryostat, in combination with adjustable liquid nitrogen flow through heat exchangers around the cell, allow the temperature of the produced LNG to be carefully controlled.

The cryostat temperature is set to a value below the dew-point of the gas to initiate the condensation process.

The cryostat can easily maintain the LNG temperature anywhere between 80 K and the boiling point of the mixture to within 1 Kelvin, hence there is plenty of sub-cooling available to prevent vapourisation of the LNG inside the sampling system of the cryostat.

Once a sufficient amount of LNG is condensed in the cryostat, a continuous but small sample of the LNG is taken from the cryostat and is vapourised.

The composition of the re-vapourised gas is compared to the composition of the gas taken directly from the reference gas cylinder, i.e. with the gas which has not been condensed in the cryostat.

This step is to ensure all of the components have been quantitatively condensed into hydrocarbon liquid inside the cryostat.

Comparisons of the reference gas composition and the analysis results from the re-vapourised LNG are made between seven different mixtures covering a wide

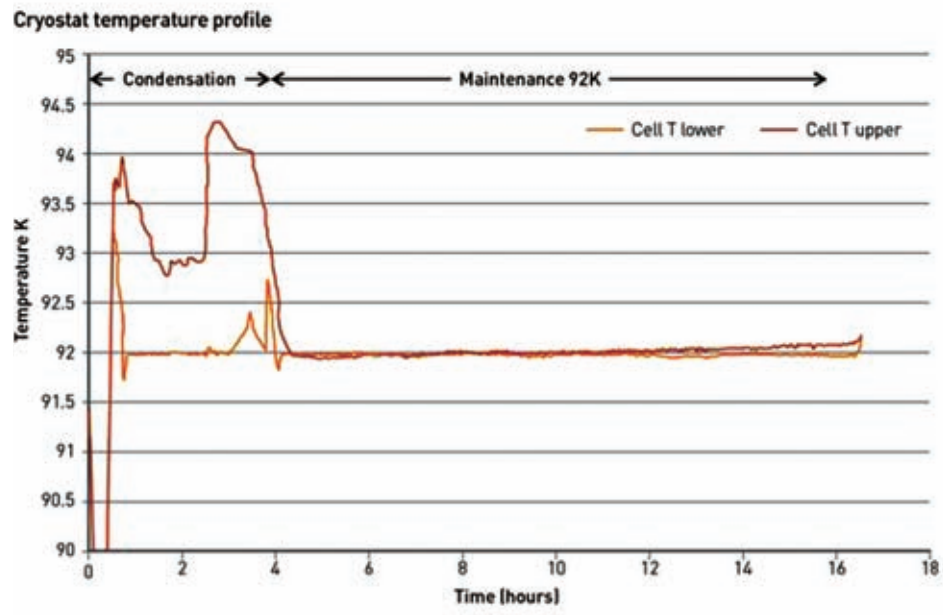

Figure 1: Cryostat temperature profile during condensation and maintenance at 92 K

TABLE 1. REFERENCE LNG COMPOSITION RANGES PRODUCED IN THE CRYOSTAT		
Component	Minimum	Maximum
	(%mol/mol)	
nitrogen	0.1	1.5
methane	79.6	99.3
ethane	0.1	14
propane	0.1	4
iso-butane	0.08	1.3
n-butane	0.08	1.1
iso-pentane	0.03	0.15
n-pentane	0.02	0.15

Table 1. Reference LNG composition ranges produced in the cryostat

range of LNG compositions (methane as low as 79 % mol/mol). See Table.

All seven gases have been condensed in the cryostat and in all cases the component En ratios were less than 1, showing the gas and re-vapourised LNG were statistically the same composition.

Gross heating value (ISO 6976)[iv], gas density (ISO 6976) and LNG density (ISO 6578)[v] differences between the gas and re-vapourised LNG were less than 9 $KJ.kg^{-1}$, 3 x $10^{-4}kg.m^{-3}$ and 0.15 $kg.m^{-3}$ respectively which satisfies the requirements of EN 12838[vi].

Results from the measurements of re-vapourised LNG reference liquids showed that the cryostat is an excellent facility for the production of accurate, well defined LNG reference liquids which remain stable for many hours.

The components that can be condensed in the cryostat are not limited to hydrocarbons; they can, in principle, be any compound which can be introduced into the reference gas cylinder and be fully mixed with the matrix gas.

The future

The LNG calibration facility can provide traceable calibrations for instrumentation design to make in situ measurements of LNG at cryogenic temperatures.

Instruments measuring composition and using this to calculate physical properties, or those measuring physical properties directly, can be calibrated in the correct matrix and at the normal operating temperature found in the field.

The first performance evaluation has already been carried out on a spectrometer used for direct continuous LNG composition measurements.

The existing chemometric model can be assessed and updated if necessary with a new model which can provide more accurate measurements directly traceable to the mole. ■

EffecTech is a specialist gas company based in the UK, India and Qatar focusing on the measurements of natural gas, LNG and other fuel gases. The company holds several accreditations from UKAS for calibration, testing, inspection and proficiency testing.