FAIR’S FAIR – THE ROLE OF GAS CHROMATOGRAPHY IN GLOBALLY HARMONISED LNG TRADING

Since the 2011 tsunami crashed ashore in Japan and disabled the Fukushima Daiichi nuclear reactor, the demand for liquefied natural gas (LNG) in Japan has grown tremendously.

Where supply and demand are closely located, the dominant method of natural gas transportation is by pipeline. In Asia, LNG transportation by ocean-going tankers is more common. At present, the major sources of LNG for the Asian market are Qatar and Australia.

A major boost to the trade of LNG between Australia and north Asia took place in May of 2019 when the Prelude floating liquified natural gas (FLNG) facility shipped its first cargo of LNG from its location in the Browse Basin off the coast of Western Australia.

Dry and sweet

When natural gas rises from the ocean bed, the methane is laden with heavier hydrocarbons, carbon dioxide, moisture, hydrogen sulphide and mercury. A primary function of the FLNG facility is to separate and liquefy the hydrocarbons into LNG, natural gas liquids (NGL) and condensate and remove the undesirable components such as hydrogen sulphide (H2S), which would corrode the process equipment.

Carbon dioxide is also removed because it would solidify at the extremely low temperatures in the LNG liquefaction process and block the equipment. Hydrogen sulphide and carbon dioxide are removed in an amine sweetening unit. The gas must also be dried using glycol dehydration, since moisture would also freeze during gas liquefaction.

Mercury is removed in molecular sieves to avoid condensation in the liquefaction train, which would damage the heat exchangers and cause gas leaks through the formation of amalgams. Mercury removal also minimises toxic pollutant emissions when the natural gas is burned.

Quality gases to measure gas quality

Precise measurement of the composition of the gas arriving at the FLNG facility is required to assess the status of the sub-sea gas field and also prepares the gas purification and liquefaction operations for the task in hand. Sophisticated laboratory analysers, such as a gas chromatograph fitted with a flame-ionisation detector (GC-FID) are ideal to determine the raw gas stream composition.

Operation of such an instrument relies on high purity specialty gases. A carrier gas of helium or hydrogen is required to move the sample through the chromatography column where the various chemicals are separated. High purity hydrogen and synthetic air are also required to create the flame that is used to detect the chemicals as they are eluted from the gas chromatography column.

Gas cylinders or generators?

In a land-based laboratory, cylinder gas supplies are practical. However, delivering cylinders to a floating LNG platform presents a major challenge. For this reason, generation of the required gases in-situ is desirable. Heinz P. Schmidlin, Sales & Marketing Manager at the Gas Generator Division of VICI AG International confirms the point: “the simple choice that analytical instrumentation users have is either to make or buy their high purity gases”.

Growth of hydrogen as a carrier gas in chromatography has been strong in recent decades, partly driven by the increasing scarcity of helium and occasional supply interruptions. Schmidlin adds that “whether it’s a bench-top generator for the laboratory or a 19-inch rack-mounted unit for process control applications, we offer instrumentation engineers and scientists the ability to be more independent”.

High purity gas generators are optimised to produce 5.0 grade or 6.0 grade hydrogen and an equivalent grade of purified air. These are self-contained tool-kits for creating the gases required to run a GC-FID setup. With an eye on safety, Schmidlin says that “our VICI generators are always on the look-out for leaks and will automatically stop hydrogen production if an excessive flow is detected. And all our hydrogen generators are equipped with USB ports for seamless integration into distributed control systems”.

Instrumentation gases and high precision gas mixtures

The carrier gas and detector gases run through the GC continuously and are consumed in relatively large quantities. This is one reason that the delivery of these gases in cylinders to an offshore FLNG facility would be expensive and impractical. On the other hand, calibration gas mixtures are used intermittently and in small quantities. So, a single specialty gas cylinder might last several years.

Calibration gas mixtures containing H2S are required to calibrate the process control instrumentation that monitors the Amine sour gas sweeting unit. The preparation of gas mixtures that contain corrosive components, such as H2S, requires careful attention to the type of cylinder that is used to contain the gas mixture.

Alan Watkins, Executive General Manager at the industrial, medical and specialty gases producer Coregas explains the technicalities: "steel cylinders are suitable for high purity chromatography gases, such as helium, hydrogen and synthetic air. However, they are not compatible with calibration gas mixtures that contain low concentrations of reactive components such as H2S. For these mixtures, aluminium cylinders are required.

"Some aluminium alloys have a high strength to weight ratio which makes them ideal for medical gases applications where light weight and portability are essential. However, the elevated copper content in these alloys renders them unsuitable for highly sensitive specialty gas mixtures. For these mixtures we use a different aluminium alloy. Rigorous preparation of the internal surface of the cylinder is accomplished using techniques such as: chemical polishing; sequential vacuum, bake and purge cycles and saturation conditioning. It sounds complicated, but at Coregas it's our bread and butter".

Quality assured

When a calibration gas mixture is used off-shore for a period of several years, it must be certified with a shelf-life for this duration. One of the advantages of the recently introduced ISO17034:2016 accreditation for reference materials is that it guarantees the stability and homogeneity of gas mixtures over their defined shelf-life.

To achieve this accreditation, the reference material producer must demonstrate that their products and manufacturing processes comply to the most stringent requirements. Watkins of Coregas confirms what this means for his team: "our lab has been ISO Guide 34 accredited for many years and we have been one of Australia's leading producers of accredited specialty gas mixtures at Yennora, close to Sydney, in recent decades. The successful transition from the Guide 34 to ISO17034:2016 that we made in 2018 with certification by the National Association of Testing Authorities, Australia (NATA) means that we can continue to occupy our position at the top of the metrological pyramid in the Asia-Pacific region".

Fair trade for precious natural resources

The monthly value of Japan, South Korea and China's LNG imports can often touch the US$10 billion mark, making the importance of accurate measurement of the gas quality for invoicing during custody transfer clear. A tiny inaccuracy could have a financial impact of millions of dollars and harmonisation of measurement is essential to ensure fair trade. These are the drivers for the use of internationally traceable, accredited gas mixtures when calibrating the instrumentation used to measure the quality of the LNG.

The analysers used in this application are generally gas chromatographs which are used to monitor the energy value of the LNG as it is loaded onto the ships and unloaded into the land-based LNG terminals where it is stored. Since these instruments are located on board ship, they have specific requirements for vibration tolerance in addition to the need to operate at a wide range of ambient temperatures.

Steve Lakey, Global Product Manager for GC Products at ABB in the United States puts the problem into context: "this is not the highly controlled laboratory environment of bench-mounted gas chromatographs, it is the high seas where tropical hurricanes roar. At ABB we have made certain that our NGC 8200 series of process gas chromatographs can withstand ambient temperatures from -18ºC up to 55ºC. That's certainly compatible with the intensity of the Australian climate. Furthermore, with Class 1, Division 1 explosion proof rating, they are suitable for LNG tanker and FLNG applications.

"The NGC 8200 range is also highly versatile. Changing the GC module within the instrument is a simple 15-minute job, after which you can simply download the relevant software for the new application and the job is done. This means that the initial investment can be paid off several times over with low cost modifications to difference service".

When it comes to accuracy, modern process gas chromatographs can match many of their laboratory-based cousins.
Lakey continues: "the NGC 8200 measurement accuracy is extremely good at 0.1% and that's a big deal in this business – we need to count every cent when we are trading these precious natural resources".

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