LNG: adapting to a more strategic role calls for effective quality analysis

Traditional methods of measuring calorific value and contaminant levels are complex and costly. New analyzer technologies provide easier alternatives.

By Alan Garza, Sam Miller and Scott Sutherland at Endress+Hauser

Disruptions of global hydrocarbon supply chains this year have increased the importance of liquefied natural gas (LNG), causing larger numbers of buyers and sellers to consider it for satisfying energy demand. For some, this is unfamiliar territory, and it requires gaining a greater knowledge of the technologies and practices involved, as billions of dollars will be changing hands.

One major aspect of LNG custody transfer involves basic questions of gas purity and energy content to ensure the product can be added to local distribution networks without issues. In this article, we will examine analyzer technologies to evaluate LNG through its production chain and verify its suitability for pipeline use.

Under normal conditions, LNG is often sweeter and has fewer contaminants than locally produced sales gas available in most parts of the world. This is because feed gas goes through extensive amine and molecular sieve treatment to remove contaminants that cause problems during the liquefaction process, such as hydrogen sulfide (H_2S), carbon dioxide (CO_2), and water (H_2O) (Figure 1 — see page 2).

Additionally, higher hydrocarbons must also be removed since they precipitate at the temperatures involved. Nonetheless, it is possible to create off-spec LNG as these contaminants can still be present and various diluents may remain, reducing calorific value and affecting the Wobbe Index.

At this pretreatment stage, the contaminant levels involved normally call for tunable diode laser absorption spectroscopy (TDLAS) analyzers (Figure 2 — see page 3) at transfer points between the stages to verify each step of the process.

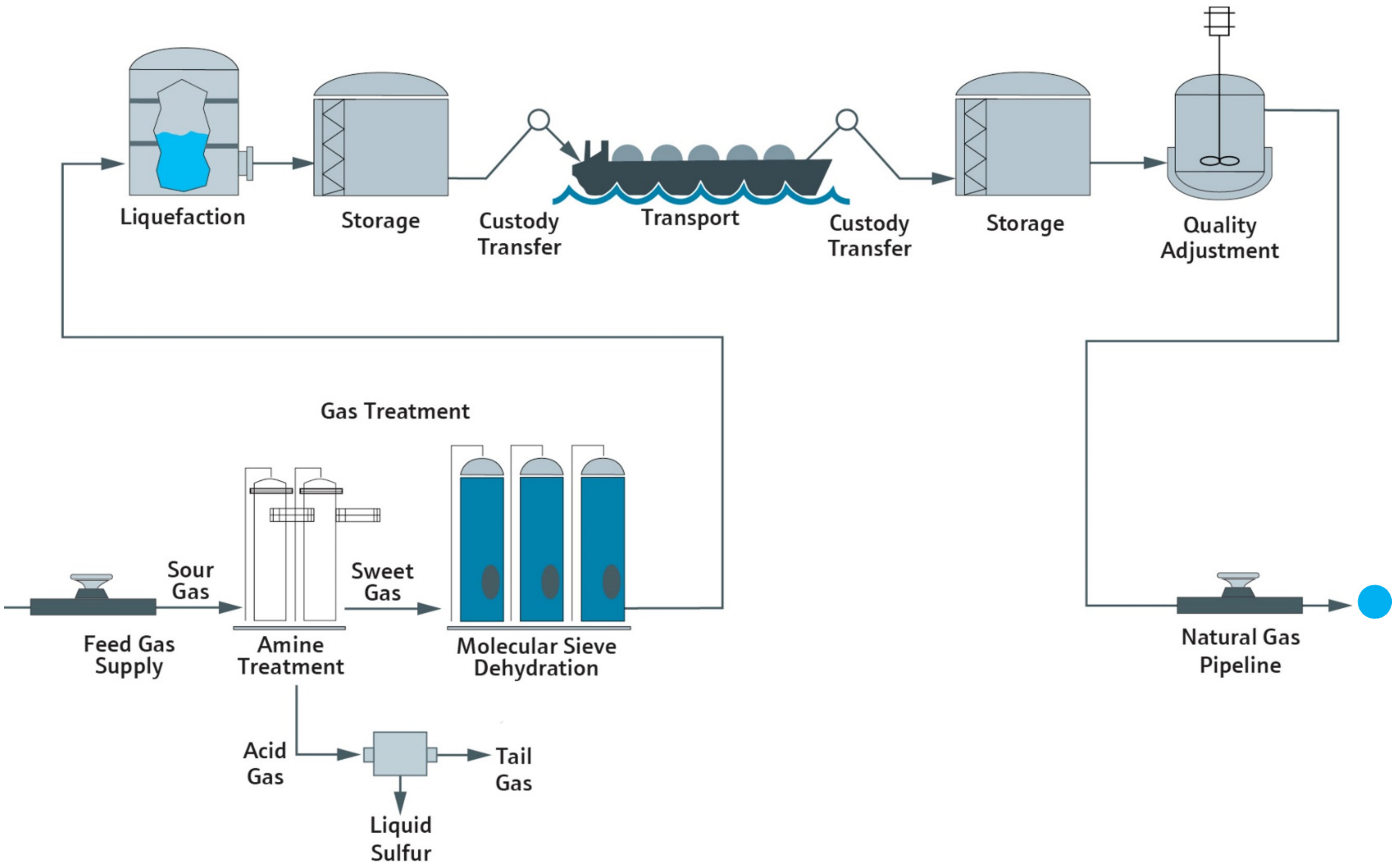
High-resolution TDLAS analyzers provide selective and specific on-line measurements of hydrogen sulfide, carbon dioxide and water in LNG feed gas.

Laser and detector components are isolated and protected from the process gas and entrained contaminants, thereby avoiding fouling and corrosion, while ensuring stable long-term operation and accurate measurements in the field. Fast response to increases in water concentration can trigger timely alerts when there is a breakthrough in molecular sieve adsorbent beds. Once pretreatment is complete, gas moves to liquefaction and on to the transport mechanism.

In the transport stream

Once natural gas pretreatment is complete, it moves to the liquefaction stage, after which it is bunkered onto a ship for its primary journey. Once it arrives at a shoreside receiving terminal, it transfers to storage tanks for regasification before entering consumption pipelines. Some may be loaded to trucks and railcars while still in liquid form.

By the time any of this natural gas reaches an ultimate customer, it can change ownership multiple times, passing through custody transfer facilities at each handoff point. Various loads with potentially differing characteristics get mixed into the process, so there is no assurance all loads are necessarily on-spec. LNG also changes while in transport as it boils off its light components, with these escaping into the tank or other enclosure. This alters the overall composition, and depending on the elapsed time and storage conditions, can significantly modify the calorific value of the load. Given the typical LNG tanker load value of $50 million USD or more, a change of even 1% is worth $500,000 USD.



Description	Measured Component	Typical Range
Molecular Sieve Dryer Outlet	H_2O	0 – 10 ppm_v
Receiving Terminal	H_2O	0 – 10 ppm_v
Amine Treatment Unit Outlet	CO_2	0 – 100 ppm_v
Amine Treatment Unit Inlet	CO_2	0 – 500 ppm_v
Amine Treatment Unit Outlet	H_2S	0 – 10 ppm_v
Amine Treatment Unit Inlet	H_2S	0 – 500 ppm_v

Figure 1: Natural gas must be treated before liquefaction to remove contaminants that can precipitate at cryogenic temperatures or damage equipment.

Each time LNG passes through a custody transfer point, the new owner must verify its composition and calorific value characteristics to avoid paying for lost value or passing off-spec product into the larger supply chain. This analysis does not need to be as stringent as during pretreatment processes, but basic contaminant levels and calorific value must be verified. The challenge is finding an analyzer technology suited to the application.

Gas chromatography

The traditional method for analyzing natural gas after the pre-treatment stage is with gas chromatography (GC). Various models are available that can quantify the relevant components with the required precision and calculate the calorific value and Wobbe Index. A typical GC takes a sample of the natural gas, mixes it with an inert carrier gas, and pushes it through a packed column enclosed in an oven.

Figure 2: The Endress+Hauser JT33 TDLAS gas analyzer uses a differential spectroscopy technique to quantify low ppb to ppm levels of H_2S in the outlet gas stream of an amine treatment unit.

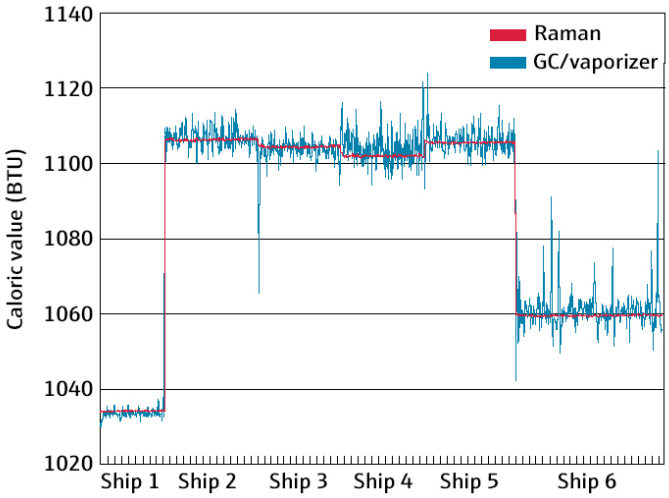


Figure 3: Variability with the sample vaporizer results in erratic BTU readings from the GC

During the time in the column, the gases separate and exit individually, passing through a detector that measures the amount of each. Some models use multiple columns for a higher degree of separation.

Operationally, GCs tend to be complex. First, they depend on a sampling system to deliver gas to the analyzer. This requires tubing and valving over a limited distance, so the analyzer must be near the source. GCs often require a shelter, though some models can be installed in the open in forgiving environments. Second, GCs require a supply of consumables in the form of carrier gas and test gases for calibration, so there is an ongoing cost.

Third, while GCs can perform this analysis routinely with sufficient precision, there is a weaker link in the analysis chain. An LNG sample must pass through a vaporizer to phase change the sample into a gaseous form suitable for GC analysis. The vaporizer stage is often more problematic than the analyzer itself, and in day-to-day operation, the vaporizer may not always provide a truly representative sample of the LNG, resulting in an inaccurate picture of the product's characteristics.

The task of the vaporizer is especially tricky because of the compositional complexity of natural gas. It must completely vaporize the sample without performing what is effectively a fractional distillation action. All the components do not vaporize simultaneously, so the vaporizer must ensure it does not lose the lighter fractions or stop the process while some of the heavier fractions remain partially liquified.

The vaporizer must operate in a very narrow range that is easily disrupted by changes in LNG flow, pressure, or temperature. This makes it especially difficult to extract truly representative samples while the process is undergoing startup and shutdown actions. For reliable performance, vaporizers require time to stabilize, which may be longer than an actual loading procedure. Making matters trickier, most loading procedures begin and end with empty pipes, extending the time required to stabilize the vaporizer. Typical instability is visible as a noisy reading with random high and low spikes (Figure 3), even when the supply being analyzed is very homogenous.

The overall sampling system—covering extraction, vaporization, and transport to the GC—is highly complex, and all elements must work together to prevent pre-vaporization, incomplete vaporization, or sample loss. This requires careful design, installation, and maintenance through all steps, with precise temperature control. Given the procedure's difficulties, the motivation for simple and reliable alternative mechanisms is understandable.

Because natural gas is burned in gaseous form, it may seem counterintuitive to suggest evaluating its characteristics in liquid form, but its chemical composition and calorific value are not dependent on its phase. It may also seem counterintuitive to suggest using an analyzer at cryogenic temperatures. The solution is Raman spectroscopy, which can be applied to analyze natural gas whether in gas or liquid form.

Raman spectroscopy

A variety of gas and liquid analysis technologies have been developed around the ability of lasers to produce highly specific wavelengths of light. Various molecules are affected by this radiation at specific wavelengths, in characteristic and measurable ways, making it possible to detect and quantify chemical components of interest.

One method is Raman spectroscopy, which uses a laser to produce light of visible or near-infrared wavelengths. When

various molecules pass through this light, the light's energy causes molecular bonds, such as the bond between two hydrogen atoms, to vibrate. This vibration creates a scattering effect, casting the laser light into different wavelengths.

What started as a single laser-generated color now becomes its own rainbow spectrum because each molecule in the sample produces a signal at a unique wavelength, and the relative intensity indicates the sample's molecular concentration. A Raman analyzer looks for these specific wavelengths and intensities to create a chemical profile of the sample.

When this concept is applied to LNG analysis, a probe is inserted into the pipe to analyze the flowing liquid or gas (Figure 4).

The probe is inserted into the flowing LNG stream, either directly or via a bypass loop. Laser light is emitted from the end of the probe into the LNG sample, and the scattered Raman light is collected back through the same probe tip. The collected Raman light travels through a second fiber optic cable, then enters a detector in the analyzer, where the resulting individual wavelengths are identified and quantified. All electronic components are housed inside the analyzer enclosure (Figure 5).

This approach has several critical advantages when compared to GC analysis:

- The probe inserts directly into the LNG stream, so it takes the reading in situ, with the moving liquid constantly refreshing the sample.
- Measuring LNG in situ means there is no vaporizer, and no sample lines, valves, heaters, or regulators. This results in more stable measurements from a Raman analyzer, without the noise and spikes characteristic of vaporizer variability.
- The Rxn-41 cryogenic probe can handle pressures up to 213.7 barg (3,100 psig) for C276 alloy or 158.6 barg (2,300 psig) for hybrid metal combo, and temperatures as low as -196°C (-320.8° F) for both material options.
- The laser and detector are housed within the analyzer, and the light is carried to and from the probe via fiber optic cables over distances up to 500 meters. The probe itself contains only the optical system, and is rated for installations in Class 1, Division 1 and Zone 0 hazardous areas.
- A single analyzer can support up to four probes, so readings can be taken at multiple locations in the process stream.
- Output from the probe changes in real time, and the analyzer can take a snapshot of the composition in less than 10 seconds, with no delay between readings.

Compositional measurements with Raman spectroscopy can be used to calculate Wobbe Index or calorific value, according to ISO and GPA Midstream Association standards such as GPA2172-09/GPA2145-2009, GPA2172-09/GPA2145-2016, and ISO6976-1995E, ISO6976-2016.

The Raman analyzer can detect most natural gas components down to 200 ppm, so is not suited for trace analysis of LNG contaminants, such as hydrogen sulfide or carbon dioxide, down to regulatory levels. For practicality, LNG pretreatment typically reduces contaminant levels well below specified thresholds. Instead, the calorific value is the more critical

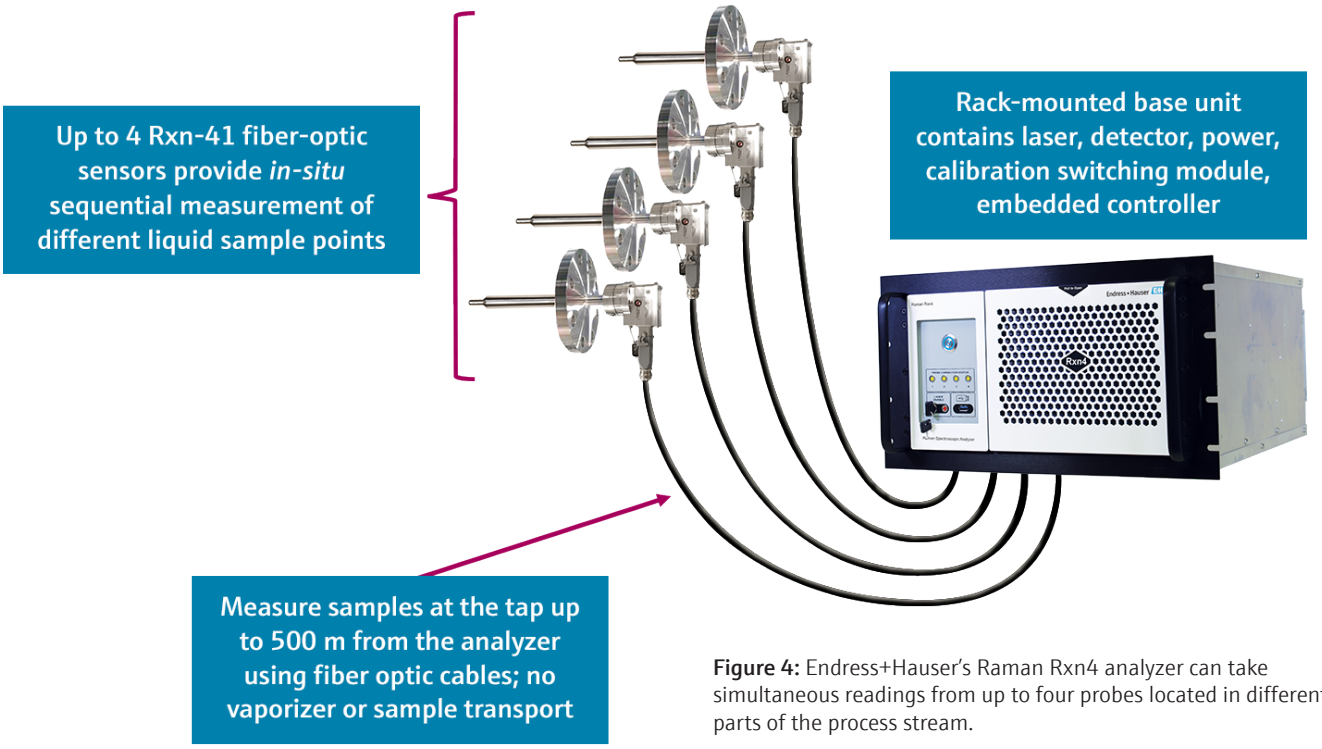


Figure 4: Endress+Hauser's Raman Rxn4 analyzer can take simultaneous readings from up to four probes located in different parts of the process stream.

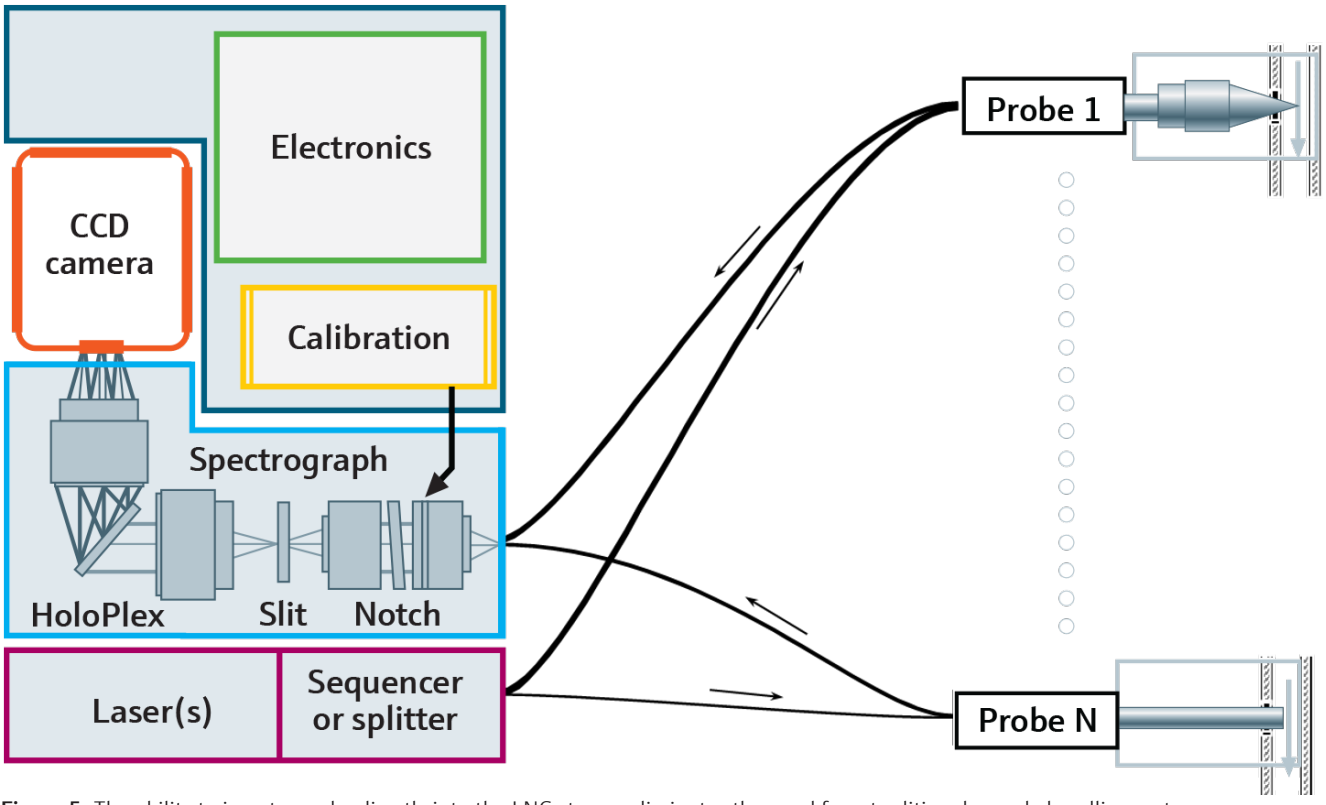


Figure 5: The ability to insert a probe directly into the LNG stream eliminates the need for a traditional sample handling system.

measurement, which Raman analyzers can handle within the required ranges. In the event it is necessary to measure lower contaminant levels, a GC is a better solution.

Analyzer calibration

All analyzers require periodic calibration, but the frequency and complexity of the calibration process varies. GCs used for LNG terminal service typically require daily calibration, performed by feeding a pre-measured test gas into the analyzer. This is not normally an arduous process, but it requires consumables and taking the analyzer off-line. Though calibration can maintain GC measurement accuracy, it does not solve the larger issue with the vaporizer and sampling system. GCs can provide highly precise analysis, but if a sample is not representative of the LNG composition, the underlying problem remains unsolved.

Raman analyzers also require calibration, but the mechanisms for measurement are very stable, so they can typically operate up to two years without calibration. Because their probes are inserted directly into an LNG stream, most calibration requires process shutdown for probe removal, which can be performed during planned facility maintenance cycles. Mounting mechanisms are available in certain applications which enable online probe removal while LNG is flowing.

Analyzer validation can be performed using a surrogate liquid sample. If the validation result indicates a calibration is required, standard calibration tools are available for field calibration of the analyzer to ensure it is brought back to factory specifications. The calibration procedure tests the entire analyzer, including the probe, fiber cables, and the full analyzer.

Importance of analysis

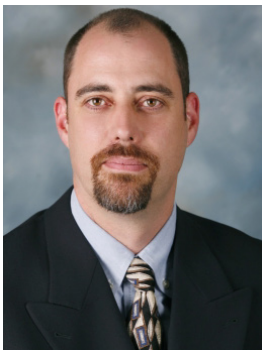
Billions of dollars' worth of LNG moves around the world every day, and it comes from a variety of sources, each with unique characteristics. While pretreatment removes some of the variability, even slight changes in calorific value can change the value of a single load by hundreds of thousands of dollars.

Analyzer technologies available today can ensure natural gas is fully processed prior to liquefaction, and then identify when it suffers value loss during extended time in transit. New techniques provide greater measurement accuracy and reliability, combined with lower lifetime costs and maintenance, and receiving terminals should consider all available measurement options.

All figures courtesy of Endress+Hauser.

About the authors

Alan Garza is the Product Marketing Manager for the Advanced Analysis product lines at Endress+Hauser. He began his career at Endress+Hauser as a rotational engineer where he developed multiple instrumentation technologies. Alan was also part of the Inside sales team where he championed gas analytics and developed as an applications engineer. His background also includes business development and operations management. Alan holds a BS in Mechanical Engineering Technology from the University of Houston.



Sam Miller is the Head of Technical Marketing, TDLAS/QF at Endress+Hauser Optical Analysis. He has more than 20 years of experience in oil and gas markets and in the development of laser-based products. Sam is a member of the ASTM D03 standards committee and participates in numerous natural gas conferences including AGA, ISA Analytical Division Symposium, and various international hydrocarbon measurement organizations. Sam holds a BS degree from California Polytechnic University, Pomona and received an MBA with honors from the University of California, Irvine.

Dr. Scott Sutherland is the Product Manager at Endress+Hauser Optical Analysis. He is responsible for Raman analyzers, including the Raman Rxn5 and its applications in the oil and gas and chemical industries, including ammonia and methanol production, hydrogen generation, and synthetic natural gas. Scott has BS degrees in physics and chemistry and a PhD in analytical chemistry. He has spent more than 32 years designing Raman analyzers and developing Raman solutions for General Electric, Thermo Electron, Photon Systems, Bruker Optics and Endress+Hauser in the areas of law enforcement, forensics, pharmaceuticals, hazardous materials and process gas analysis.

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