Getting a Hydrogen Signal in Natural Gas

How to safely control the injection of H_2 in natural gas.

By Cory Marcon, Endress+Hauser

The growth of renewable sources of electricity, such as wind and solar, have been unprecedented. At times, the supply of renewable energy is not aligned with the consumption. This is a common occurrence because electricity demand from the grid typically peaks during the summer between 5–7 p.m., whereas solar energy peaks between 11 a.m.–3 p.m. Similarly, wind energy typically peaks in the hours around midday. These factors are exacerbated in some areas, such as Southern California, where peak summer power demand occurs on hazy days with minimal wind.

One way to store power from renewable sources is in the form of hydrogen generated by electrolysis, where excess electricity can be channeled into an on-site installation that breaks water into its components hydrogen and oxygen. This process is often referred to as Green Hydrogen, as there are no carbon emissions.

Hydrogen in a net-zero world

As the world looks for ways to use less carbon, hydrogen (particularly green hydrogen) is growing in importance as an alternative:

- It can be converted to heat and electricity very efficiently by fuel cells or (less efficiently) gas turbines.
- It can replace carbon-intensive processes, such as direct-reduction ironmaking rather than conventional blast furnaces.
- Hydrogen produced via electrolysis from renewable electricity can replace hydrogen produced by reforming natural gas, eliminating the resulting carbon dioxide.

Where hydrogen is not necessary as a feedstock for the facility's processes or fed to a fuel cell, it can be blended into the local natural gas supply. This can be used for on-site consumption or it can be sent out to the surrounding natural gas distribution. Every incremental amount of hydrogen injected into a natural gas fuel system or pipeline abates some amount of methane, and therefore CO_2. This relationship is non-linear (Figure 1).

Hydrogen is highly combustible, but its effects when blended with natural gas are complicated. Measured by mass, pure hydrogen has enormous heat value, well beyond any other fuel gas, simply because there are so many diatomic (H_2) molecules per unit of weight. But for most practical applications, energy is a function of volume. Hydrogen has a volumetric heating value approximately one-third that of methane due to its low density.

As a result, there are limits imposed by gas producers and pipeline companies on the permissible volume to avoid reducing overall heat value too greatly. Users such as gas turbine operators are particularly concerned about this since

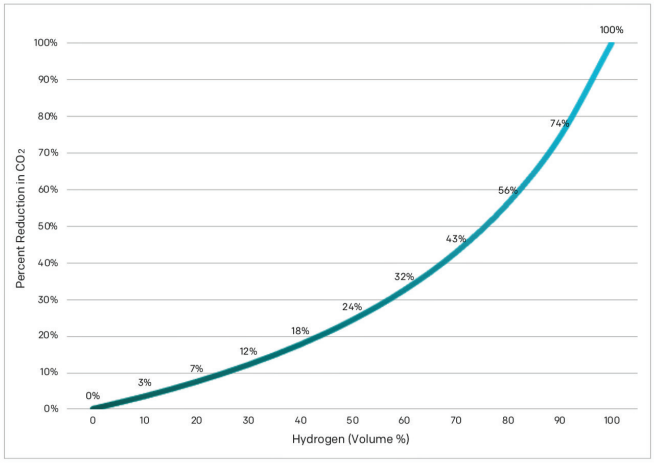

Figure 1: Blending green hydrogen with natural gas reduces the overall carbon footprint. Source: Earthjustice

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diluting heat value has a direct effect on a turbine's horsepower output. Hydrogen can therefore impact equipment performance.

Maximum blending amounts are also influenced by safety concerns. They vary based on the situation, but generally for pipeline gas, hydrogen content can't exceed 20%. For dry, low-NOx (DLN) gas turbines, 50% is the general threshold, with simple combustion turbines, aero-derivatives, and gas engines having fewer limitations. For a 20% and 50% blend, the amount of carbon reduction is 7% and 24%, respectively, as shown in Figure 1. The various application limits mitigate potential safety issues related to embrittlement due to corrosion of carbon steel pipelines and hydrogen's increased flame speed subjecting gas fuel nozzles to higher temperatures.

These performance and safety limitations leave everyone involved in the discussion—producers, pipelines, and consumers—with reason to know just how much hydrogen has been mixed into the stream. The question is, how should this value be measured?

Analyzing natural gas to understand composition

The need to determine what is mixed into a pipeline often referred to as sales gas, is nothing new. While natural gas is generally thought of as methane, it is actually a mix of up to a dozen chemical components (Figure 2). Pure hydrogen is not normally found in well gas since it tends to react with sulfur to form hydrogen sulfide.

Heavier hydrocarbons increase the overall heat value, while ballast gases (carbon dioxide, nitrogen, etc.) reduce it. Gas producers usually extract heavy hydrocarbons since they can cause the gas to exceed pipeline heating value specifications and can be sold separately at a higher value. If left in the pipeline, they can cause problems downstream if present at sufficient concentrations to condense at low temperatures and form liquid slugs. The same can happen with water. All this to say, natural gas producers, pipelines, and industrial consumers have a variety of reasons for needing to know gas composition in varying degrees of detail, including the amount of hydrogen blended in. Generating this information requires the right type of analyzer.

Typical Compostition of Natural Gas		
Methane	CH_4	70–90%
Ethane	C_2H_6	0-20%
Propane	C_3H_8	
Butane	C_4H_{10}	
Carbone Dioxide	CO_2	0-8%
Oxygen	O_2	0-0.2%
Nitrogen	N_2	0-5%
Hydrogen sulfide	H_2S	0-5%
Rare gases	Ar, He, Ne, Xe	trace

Figure 2: NaturalGas.org lists the components typically found in natural gas. Hydrogen is atypical and not listed.

Technologies for analyzing natural gas

There are five primary technologies (Figure 3) for analyzing natural gas, each with its own strengths and considerations.

For applications that require a deep and detailed analysis of natural gas composition, a mass spectrometer or gas chromatograph analyzer are the primary choices. Other technologies with faster response, such as a calorimeter, are often used to provide a quick analysis of the Wobbe index or heating value of the gas.

Mass spectrometers provide fast responses and have good accuracy, but are not typically supplied in an enclosure ready for mounting in plant areas. Expensive system integration is therefore required, especially in hazardous areas, along with complex sample conditioning systems to significantly reduce process pressure and temperatures for analysis.

Gas chromatographs are the most common choice, especially due to the history of this technology in billing applications, but high hydrogen content will require a special design, using argon as the carrier gas instead of helium. Additionally, gas chromatographs offer a granular compositional analysis, but produce slow response times of about four to six minutes for each sample stream. In some cases, this is too long, particularly where safety and performance considerations rely on quick feedback from the gas stream.

Infrared and near-infrared analyzers aren't suited for hydrogen blending applications due to their inability to speciate and quantify hydrogen with the necessary speed and accuracy. They can measure various other components, but where hydrogen is the primary concern, they should not be the choice as they cannot reliably measure Btu when there is a fluctuation of H_2 content in the gas.

Residual O_2 burn can be used to reliably measure Btu, even with the presence of H_2, but this technology cannot provide a true compositional measurement.

Instruments using these technologies are often designed with one common characteristic: the actual analysis is performed inside the analyzer housing, meaning that the gas sample must be pumped through a length of tubing, and then conditioned in some way to prepare it for analysis. When finished, the system must flush itself, or flare the sample gas, to prepare for the next round. This adds time before the measurement can be provided, along with complexity, operating expense and emissions.

Raman spectroscopy: advanced optical analysis technology

In the last 50 years, a variety of gas analyzer technologies have been developed around the ability of lasers to produce highly specific wavelengths of light across a wide spectrum. Various gases affect this radiation or are affected by the

	Mass Spectrometer	Gas Chromatograph	Infrared or Near IR	Residual O2 Burn	Raman Spectroscopy
Analyzer Housing	GP (optional ATEX IP 65 available)	NEMA 4X (IP 56)	IP 64 (NEMA 4/4X equivalent)	IP65 (NEMA 4X/6 equivalent)	Painted steel (316L stainless steel optional), IP56
Gas Sampling	In Analyzer	In Analyzer	In Analyzer	In Analyzer	At sample tap via optical probe
Gas Return	Typically Flared	Typically Flared	Typically Flared	Typically Flared	Emission Free. Return to gas stream.
H2 Compatible	Yes	Yes	No (Interf. of O2, H2, He must be < 0.1 mol%)	Yes	Yes
BTU & Density	Yes	Yes	Yes	Yes	Yes
Composition (for blending)	Yes	Yes	Yes, but limited (HCs, combined CH only)	No	Yes
Pressure & Temp of Process Gas at Probe/Analyzer	< 36 psig, < 392 °F	< 15 – 2 psig, must be dry, no condensate (< 0.1 ppm) or particulate (< 1 µm), < 176 °F	Between 21.76 psig and 43.51 psig; Up to 131 °F	Up to 72.5 psi; Up to 300 °F	Up to 1000 psia; Up to 302 °F
Instrument Air Required?	Yes, for ATEX (4-8 barg)	No, but carrier gas (He, H2, Ar, or N2 @ 50 cc/min)	No	Yes	Yes, in Hazardous Areas
T90 at the Sensor	< 7 seconds per stream	360-400 sec, depending on composition	< 10 s, 90% Step Response	< 10 s	10-15 s
Response time from the Tap	< 7 s – Gas Transport and Sample Conditioning Time	360-400 s – Gas Transport and Sample Conditioning Time	< 10 s – Gas Transport and Sample Conditioning Time	< 10 s + Gas Transport and Sample Conditioning Time	~ 10-15 s + Speed of light
Analyzer Channels (multiple fuel channels simultaneously)	1 (Inlet Sw can add multi-channel sequencer (12-0 samples).	1	1	1	Up to 4
Calibration Interval	Application dependent.	Application dependent.	Weekly (or line). Annual (Full Service)	Automatic; Plus routine maintenance	Validate as necessary, during Outages

Figure 3: Different analyzer technologies are available for analyzing the chemical composition of natural gas.

radiation, in characteristic and measurable ways, making it possible to detect and quantify gases of interest.

Raman spectroscopy is one such technique. It utilizes laser radiation to produce light in the visible or near-infrared wavelength regions to excite the vibrational modes of different gases in the sample. The resulting scattered radiation changes color based on the type of chemicals in the gas. A Raman analyzer measures these scattered colors to determine the components in the gas, and the intensity of each color to determine component concentrations.

What started out as a single laser-generated color now becomes its own rainbow since different gases in the sample produce specific wavelength spikes indicating their presence, and the relative intensity indicates relative concentration. The analyzer looks for these specific spikes to create a chemical profile of the gas.

When this concept is applied to an industrialized analyzer (Figure 4), it uses a probe inserted into the gas stream that allows the gas to flow through a passage.

Perpendicular to the gas passage is a miniature optical system. The green laser light shines through a lens and across the passage (Figure 5), where it strikes a reflector and passes back through the passage a second time. It now enters a detector where the resulting individual wavelengths are identified and quantified by the analyzer.

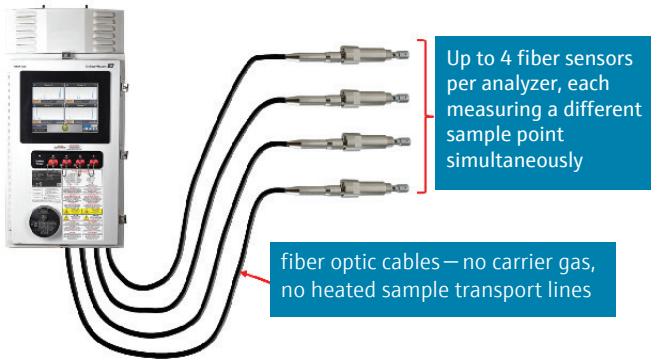


Figure 4: Endress+Hauser's Raman Rxn5 analyzer can take simultaneous readings from up to four probes located in different parts of the process stream.

This approach has several critical advantages over the other technologies discussed earlier:

- The probe is located remotely from the analyzer, so no sample is transported to the analyzer, enhancing operator safety.
- The probe can handle pressures up to 70 bar (1,000 psi) and temperatures to 148°C (300°F), with higher temperature solutions available.
- Output from the probe changes in real-time, and the analyzer can take a snapshot in 15 to 30 seconds.

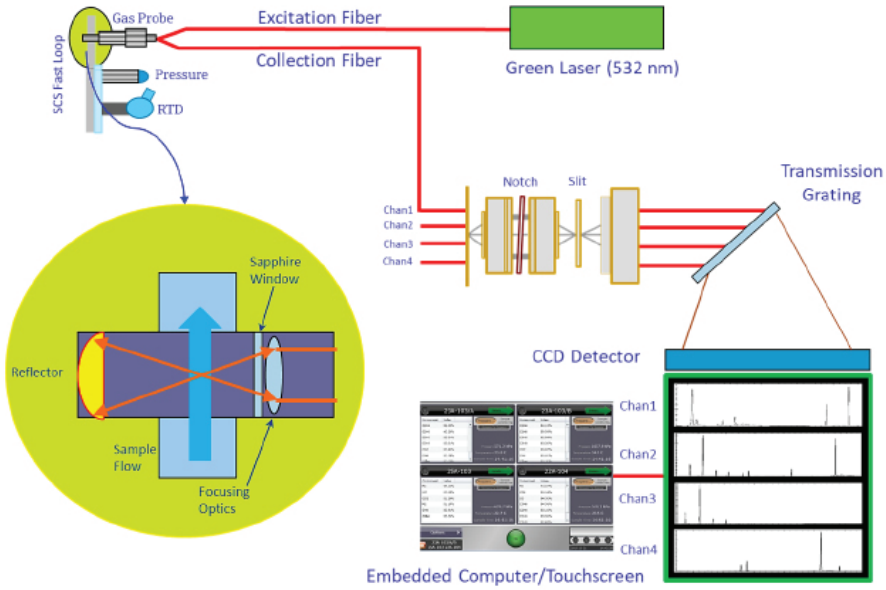


Figure 5: The ability to connect a gas probe to the analyzer using fiberoptic cables eliminates the need for sample transport to the analyzer. The probes can be designed to handle samples at or near process pressures and temperatures

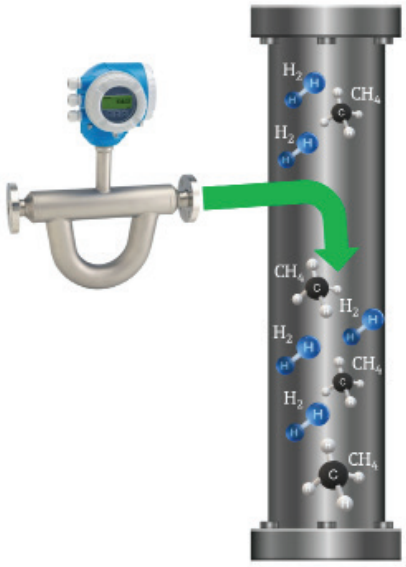


Figure 6: Measuring just the volume of hydrogen blended can't determine the final mix ratio.

- The laser and detector are housed within the analyzer and the light is carried to and from the probe via fiberoptic cables over distances up to 50 meters (165 ft.) or 150 meters (492 ft.), with response times closer to 60 seconds. The probe is designed for installation in Class 1, Division 1, or Zone 0 environments.
- A single analyzer can support up to four probes, reading each simultaneously, so readings can be taken at multiple locations in the process stream for feedforward and feedback control loops.
- In addition to hydrogen content, a Raman analyzer can also handle many of the commonly measured natural gas components.

Compositional measurements with Raman spectroscopy can be used to derive Wobbe index or heating value, according to ISO and GPA Midstream Association standards such as:

- GPA2172-09/GPA2145-2009
- GPA2172-09/GPA2145-2016
- ISO6976-1995E, ISO6976-2016

Creating a hydrogen signal

At present, the blending limit for hydrogen into pipeline gas is capped at 20% for the reasons discussed earlier. However, since so much of the energy industry is currently in transition, there is little reason to believe this is a permanent limit.

But for the time being, let's consider the case of a facility with a sizeable photovoltaic array which often finds itself with a surplus of power for much of the day. The facility installs a modest electrolyzer with the intent of feeding the hydrogen it produces into the local gas pipeline. If the facility can measure the volume of pipeline gas moving through the local system, it can program its blending unit to feed in hydrogen such that it will not exceed 20% by volume.

By using an Endress+Hauser Proline Promass Coriolis flowmeter (Figure 6), it is a simple matter to measure, and ultimately control, the flow of hydrogen into the pipeline appropriately.

This works conceptually but with the assumption that no other gas blender is already adding hydrogen somewhere upstream. If the pipeline is already carrying 10% hydrogen, our hypothetical facility can't add 20%. Additionally, it can't tell if the present content is changing as different blenders go online and offline.

Similarly, a gas turbine must operate differently for Low Heating Value (LHV) conditions during start-up so knowing the composition of the incoming fuel from the gas pipeline is critical, especially if there is additional H_2 injection downstream within the fuel system of the power plant.

To address these and other issues, a Raman analyzer can be used to create a real-time signal indicating hydrogen content, which can then be used for regulating blending rates, monitoring Btu / Wobbe Index, or adjusting air-to-fuel mixture for combustion optimization. When used in a closed-loop control strategy, the system can respond automatically to changing conditions.

Key to an effective natural gas blending strategy

For facilities producing green hydrogen, natural gas blending is often the most practical way to capture its value. The challenge becomes determining the best mechanism for controlling the injection rate to avoid exceeding local limits. As described earlier, controlling blending rates based solely on volume was not effective because without a means to measure how much hydrogen is already in the pipeline, adding more could push content over the limit.

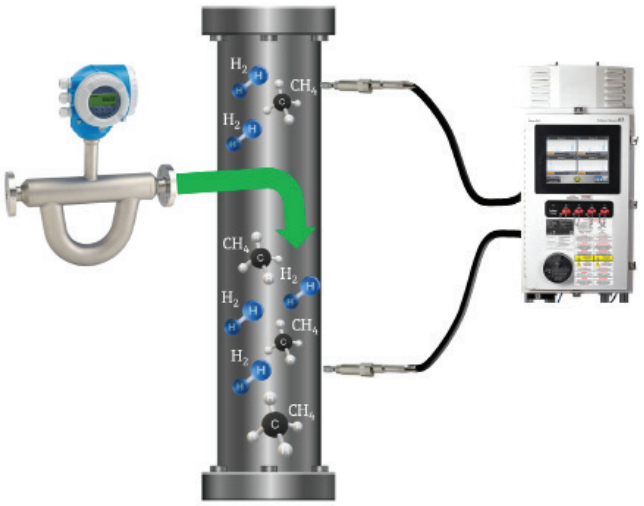


Figure 7: A Raman analyzer that supports multiple probes gives it the ability to measure hydrogen before and after injection.

While a Raman analyzer is exceptionally well suited for controlling and monitoring H_2 injection, there is a broader system context.

At scale, with dozens of hydrogen injections stations in a gas distribution network across multiple service providers, it may be necessary to know how much hydrogen is already in the pipeline. Measuring the gas composition at the entry point is the obvious choice since it determines how much capacity remains for additional injection.

For totalization and throttling flow rates, an Endress+Hauser Proline Promass Coriolis flowmeter is ideal for this purpose. It provides options to consolidate data, such as total hydrogen flow, in the cloud for real-time transparency to stakeholders or shareholders alike. This can be complicated if the pipeline flow rate is not known at the point of injection since the injection rate must reflect the overall flow rate, as well as hydrogen content. For verification, safety, and tracking, the use of a second hydrogen measurement, downstream from the injection point can prove that the gas is still within defined limits (Figure 7).

With up to four-channel availability and fiber optic lengths up to 150 m, a Raman analyzer can also monitor hydrogen composition over a long length of pipeline (Figure 8) after being injected. This data can be used to monitor the mixing quality or be used to corroborate predictive models of how H_2 will behave in the gas grid at scale. This is especially useful for gas utilities looking to meet renewable gas portfolio standards in their distribution networks, without compromising safety or quality for their customers and other stakeholders.

Fortunately, the entire injection process can be automated and packaged as a single skid (Figure 9), sized to reflect the incoming hydrogen (or syngas) supply. Built around a Raman analyzer, the skid's automation and instrumentation system determines the maximum injection flow to offload the greatest amount of hydrogen, or to optimize the mix to match the requirements of a gas turbine or other combustion process. This way it can serve internal or external needs as the application demands.

H_2 Injection and Blending systems can be designed with or without a PLC, and instrumented to accommodate application-specific control, monitoring and safety strategies for H_2 injection in natural gas. The result is a bespoke system based on the project's H_2 injection rates or unique requirements based on regional compliance or custody transfer standards.

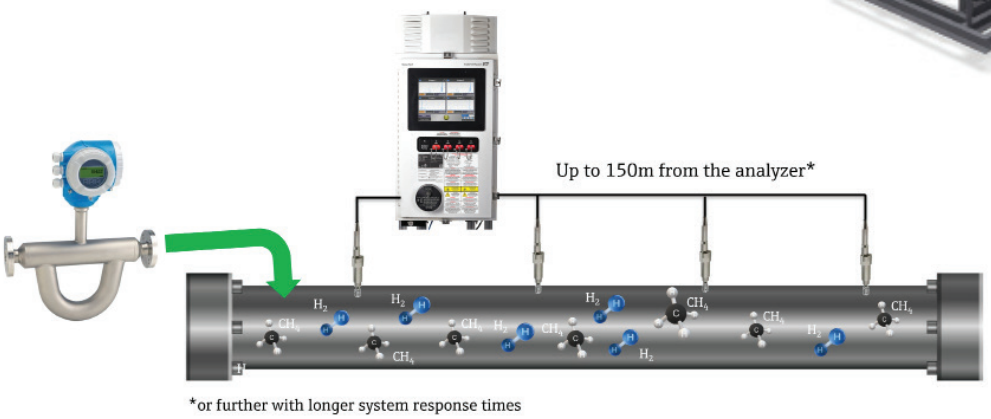


Figure 8: Using multiple Raman probes over a long length of pipeline can help determine how hydrogen mixes into the flow after injection.

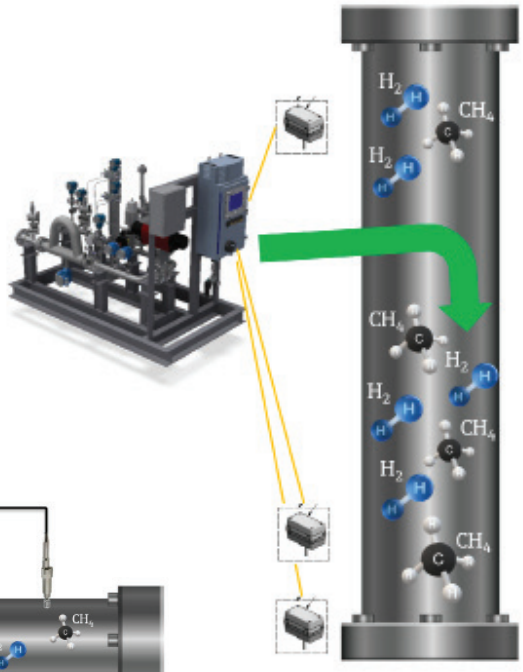
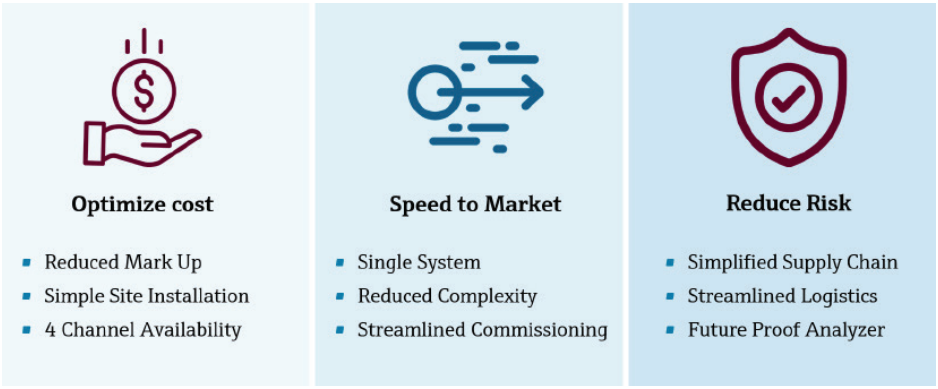


Figure 9: All the necessary components for an injection station can be assembled onto a single skid.

When combining Raman spectroscopy with a comprehensive control strategy, companies can maximize the injection hydrogen into fuel systems and pipelines without compromising safety or efficiency, ultimately reducing overall carbon emissions.



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About the Author

Cory Marcon is the Power & Energy Industry Manager for Endress+Hauser, responsible for the overall business development and growth of the company position related to the traditional power generation and the energy transition. Cory is a 2012 graduate of McGill University with a decade of experience in all forms of energy from solar to wind to gas.

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