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H_2 EQUIPMENT AND SERVICES

Ensure H_2 purity with modern gas analyzers

D. GUYMER, Emerson, Cumbernauld, Scotland

As the world grapples with decarbonization and alternative power supplies to reduce global greenhouse gas (GHG) emissions, more ways to condition, store and distribute energy from new fuel sources are needed. To that end, hydrogen (H_2) gas applications play a major role in global sustainability initiatives.

While batteries are being used to harness and store power in small- and mid-scale applications, they are not ideal for larger applications due to cost, weight and other factors. Even when used to power electric vehicles (EVs)—perhaps the most predominant mid-scale example—they present several drawbacks.

Although the primary metal contained in modern lithium-ion cells is readily available with no near-term shortage in sight, other battery components come with negative environmental and societal repercussions, especially in some developing countries where the minerals are harvested. Additionally, batteries are subject to degradation, losing around 2.3%/yr of capacity, and to power loss of about 1% of capacity per week, depending on the application.[1]

With EVs, grid capacity and charging infrastructure pose limitations, especially in long-distance transport, where frequent and time-consuming recharging is required. Furthermore, charging technology is only available in limited locales.

H_2 provides a more viable answer to the energy storage problem because:

- It is not subject to degradation or noticeable energy leaks
- It has a very high energy density of 35,000 watts/kilogram (kg), while lithium-ion batteries have a density of just 200 watts/kg
- It can supplement natural gas to power homes and industry using existing power generation infrastructure
- It is easily transported
- H_2 fuel cell-powered vehicles are refueled at a similar speed to those with internal combustion engines
- Burning H_2 produces only water as a byproduct, absent of carbon dioxide (CO_2), nitrous oxide (NOx) or GHGs.

Sourcing H_2. H_2 is produced by many paths, classified as a color by the eco-friendliness of its production process and can be designated as gray, blue, turquoise or green (**FIG. 1**).

Gray H_2 is produced via steam methane reforming (SMR) of natural gas, oil, coal or another hydrocarbon according to one of these chemical formulas (Eq. 1):

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (1)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

or

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$$

SMR is the most common process for producing H_2 today; however, it has the drawback of releasing carbon monoxide (CO) or CO_2 into the atmosphere, which reduces environmental benefits gained by consuming the H_2 later in its lifecycle. Blue H_2 solves the issue of carbon release, using the same SMR chemical processes but capturing and storing the waste carbon byproducts to prevent release into the atmosphere.

Like gray and blue H_2, turquoise H_2 also uses methane (CH_4) as a feedstock—but the process is driven by heat produced with electricity rather than through the combustion of fossil fuels—in a process known as CH_4 pyrolysis.

Like blue and gray H_2 production, CH_4 pyrolysis produces H_2 and carbon, but unlike SMR, the carbon byproduct is generated as a solid instead of a gas. As a result, there is no requirement for carbon capture, and storage is greatly simplified.

Green H_2 is the most environmentally friendly form, produced via renewable energy-powered water electrolysis. Chemically, the process is (Eq. 2):

$$2H_2O \leftrightarrow 2H_2 + O_2 \quad (2)$$

With electrolysis, no carbon or other pollutants are produced. However, transforming water into its di-elemental constituents requires more energy than generating H_2 from fossil fuels. For this reason, a small percentage of the H_2 produced today is green H_2.

Regardless of the source, H_2 purity is a necessary consideration for every application. The International Standard Organization's (ISO's) 14687 standard was created to correlate applications and uses with required H_2 purity.

Ensuring H_2 purity with ISO 14687. ISO 14687 specifies the quality tolerances for H_2 fuel, primarily focused on stationary, vehicular and proton exchange membrane (PEM) fuel cell uses. Depending on the application, each gas grade defines an acceptable impurity allowance (**TABLE 1**).

Grades A–C comprise direct burning applications, requiring measurement of impurities that pose environmental risks when released. Grades D and E cover power generation through fuel cell applications, primarily concerned with impurities that can poison the cell. The acceptable impurities are broken down into allowable contaminants in **TABLE 2.**

As the tables show, the acceptable purity and contaminants vary considerably by application.

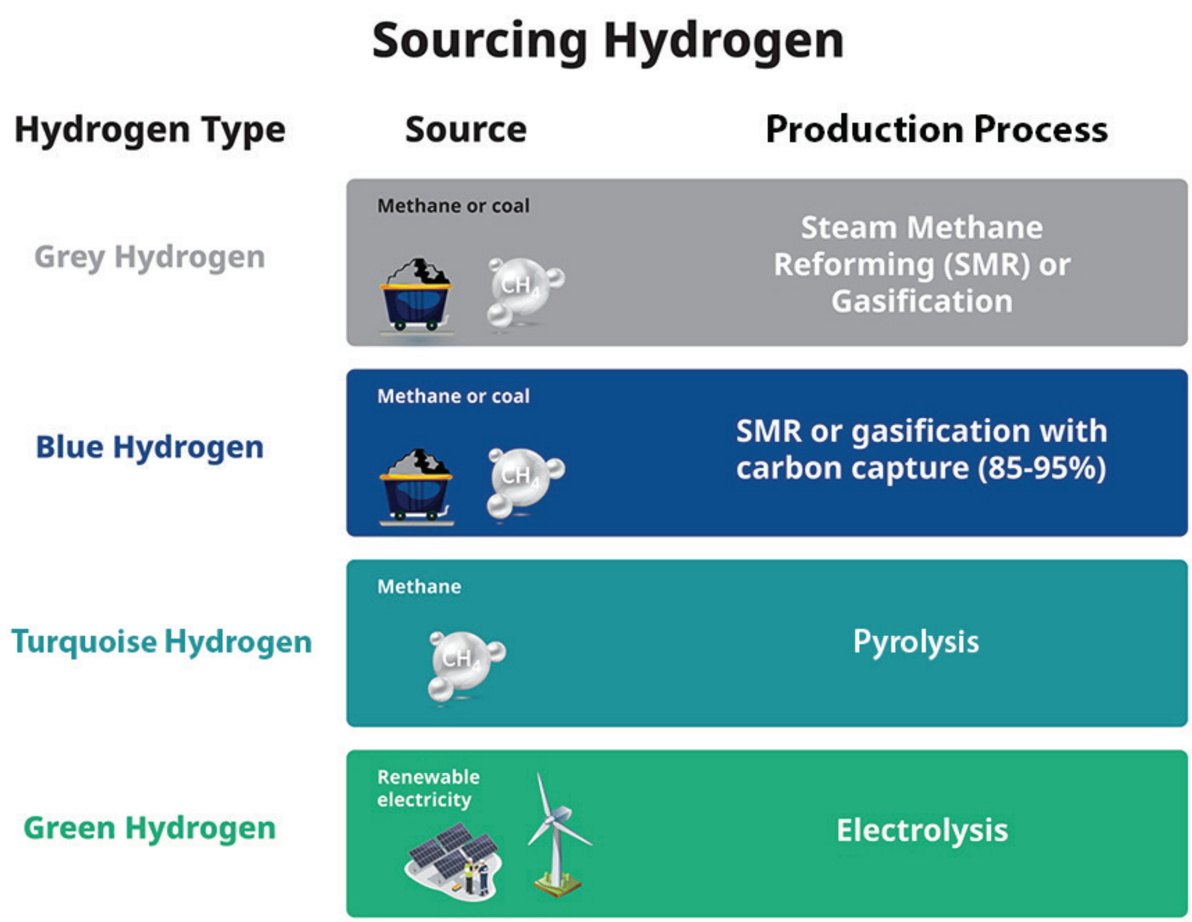

FIG. 1. The sources, processes and classifications of H_2.

Measuring H_2 purity. The two main modern ways of measuring H_2 purity are gas chromatography (GC) and continuous gas analysis. GC relies on a thermal conductivity, flame ionization or micro flame photometric detector. Thermal conductivity detectors are mainly used to measure inert gases and most hydrocarbons, while flame ionization detectors are adept at measuring trace hydrocarbons, and micro flame photometric detectors specialize in measuring low-level sulfur species.

However, a GC analyzer cannot individually measure argon and oxygen when both are present, has a high detectable lower-range value for water—which does not comply with ISO 14687—and requires a relatively long response time, measured in minutes. When any of these requirements need to be met, continuous gas analyzers provide better options.

There are several continuous gas analysis technologies on the market, including laser absorption spectrometry analyzers [e.g., quantum cascade laser (QCL) technology], non-dispersive infrared and ultra-violet photometers, thermal conductivity detectors, electrochemical sensors and paramagnetic oxygen detectors.

QCL analyzers measure components using mid-range infrared spectroscopy and tunable diode laser spectroscopy to make low-ppm measurements over a host of molecules. Modern continuous gas analyzers are configurable to provide a wide range of measurements. However, GC analyzers provide lower detection limits than continuous gas analyzers for inert gases. The following examples demonstrate how GCs and continuous analyzers can be applied to measure H_2 purity.

TABLE 1. Required H_2 purity by grade, with example applications

Grade	% H_2	Example Application
A	98	Transport internal combustion engines
B	99.9	Industrial power generation
C	99.995	Aircraft ground support systems
D	99.97	PEM fuel cells for road vehicles
E – category 1	50	
E – category 2	50	PEM power generation
E – category 3	99.9	

TABLE 2. Allowable contaminant levels by H_2 grades A–E

<table>
<tr><th></th><th colspan="7">Grade (accepted contaminants in ppm)</th></tr>
<tr><th>Contaminant</th><th>A</th><th>B</th><th>C</th><th>D</th><th>E (cat1)</th><th>E (cat2)</th><th>E (cat3)</th></tr>
<tr><td>Water (H_2O)</td><td>NC</td><td>NC</td><td rowspan="4">9</td><td>5</td><td>NC</td><td>NC</td><td>NC</td></tr>
<tr><td>THC (non-CH_4)</td><td rowspan="2">100</td><td rowspan="2">NC</td><td>2</td><td>10</td><td>2</td><td>2</td></tr>
<tr><td>CH_4</td><td>100</td><td>50,000</td><td>10,000</td><td>100</td></tr>
<tr><td>Nitrogen (N_2)</td><td rowspan="3">19,000</td><td>400</td><td>300</td><td rowspan="2">non-H_2</td><td rowspan="2">non-H_2</td><td rowspan="2">non-H_2</td></tr>
<tr><td>Argon</td><td>N/A</td><td rowspan="2">1</td><td>300</td></tr>
<tr><td>Oxygen</td><td>100</td><td>5</td><td>200</td><td>200</td><td>50</td></tr>
<tr><td>Helium</td><td>N/A</td><td>N/A</td><td>39</td><td>300</td><td>non-H_2</td><td>non-H_2</td><td>non-H_2</td></tr>
<tr><td>CO_2</td><td>N/A</td><td>N/A</td><td rowspan="2">1</td><td>2</td><td>non-H_2</td><td>non-H_2</td><td>2</td></tr>
<tr><td>CO</td><td>1</td><td>N/A</td><td>0.2</td><td>10</td><td>10</td><td>0.2</td></tr>
<tr><td>Sulfurs</td><td>1</td><td>10</td><td>N/A</td><td>0.004</td><td>0.004</td><td>0.004</td><td>0.004</td></tr>
<tr><td>Formaldehyde</td><td>N/A</td><td>N/A</td><td>N/A</td><td>0.2</td><td>3</td><td>0.2</td><td>0.2</td></tr>
<tr><td>Formic acid</td><td>N/A</td><td>N/A</td><td>N/A</td><td>0.2</td><td>10</td><td>0.2</td><td>0.2</td></tr>
<tr><td>Ammonia (NH_3)</td><td>N/A</td><td>N/A</td><td>N/A</td><td>0.1</td><td>0.1</td><td>0.1</td><td>0.1</td></tr>
<tr><td>Halogenated</td><td>N/A</td><td>N/A</td><td>N/A</td><td>0.05</td><td>0.05</td><td>0.050</td><td>0.05</td></tr>
</table>

APPLICATION EXAMPLES

Distributing pure H_2. A Belgian H_2 transporter needed to ensure product purity in its liquid H_2 custody transfer process. The company implemented a GC and QCL-based continuous gas analyzer on the incoming H_2 stream prior to cryogenic liquefaction for transport, as shown in **TABLE 3.**[a,b]

The transporter relied on the GC analyzer to perform comprehensive impurity composition analysis, with multi-minute cycle time and relied on the QCL analyzer to provide real-time, continuous analysis of critical components for process control.

Electrolysis purity analysis. A California-based company using electrolyzers implemented the technology to monitor the purity of its two main products, oxygen and H_2 gases. To do this, it used a GC with two streams,[a] one to measure H_2 and the other to measure O_2 (**TABLE 4**). By implementing reliable purity measurements, the company significantly reduced the risk of producing off-spec H_2 fuel, which can cause severe damage to H_2 fuel cells.

Refining green diesel. Green diesel is most frequently produced by reacting recycled animal fats, used cooking oil and inedible corn oil under elevated temperatures and pressures in the presence of a catalyst (**FIG. 2**). The product can supplement or even replace conventional fuel in diesel engines without any modification to the engines, and it produces far less GHG emissions than conventional diesel fuel when burned. Green diesel is sold in California, Canada and Europe, where it meets the low-carbon fuel classification.

A green diesel refinery in Western Canada installed a GC[a] to measure H_2 purity concentration in the recycle stream (**TABLE 5**).

The refinery also installed a non-dispersive infrared photometry-based continuous gas analyzer[c] to measure carbon H_2 impu-

TABLE 3. A Belgian H_2 transporter implemented continuous gas analyzers to measure H_2 purity prior to liquefaction and delivery, ensuring a high-quality product

Component	Range	Analyzer
Helium	10 ppm–100 ppm	GC
N_2	10 ppm–200 ppm	GC
THC (as C_1 and C_2+)	0.2 ppm–10 ppm	GC
CO_2	0.1 ppm–10 ppm	GC
CO	0.1 ppm–10 ppm	GC
CO	0.05 ppm–5 ppm	QCL
H_2O	0.2 ppm–25 ppm	QCL

TABLE 4. A California-based company used a gas chromatograph to measure the purity of its H_2 and O_2 product streams

Stream parameters		Stream 1			Stream 2	
Stream name		H_2 purity			O_2 purity	
Pressure at sample point		1 psig–10 psig			1 psig–10 psig	
Temperature at sample point		75°C–90°C			75°C–90°C	
Phase at sample point		Saturated vapor			Saturated vapor	
Tap distance to analyzer		5 ft			5 ft	
Stream components	**Normal**	**Measured range**		**Normal**	**Measured range**	
		Minimum	**Maximum**		**Minimum**	**Maximum**
H_2, mol%	99	–	–	0.5	0	1
O_2, mol%	1–5	0	5	99	–	–

rities at the H_2 pressure swing adsorption outlet (**TABLE 6**). The measurements empowered the company to ensure its green diesel met regulatory standards while providing a safe and reliable alternative to conventional diesel.

Preparing for decarbonization. Purity must be considered in H_2 applications to avoid equipment fouling, process failures or end-user issues. ISO 14687 lays a foundation for understanding purity requirements, and it details which components must be measured in each application; however, the list is not exhaustive.

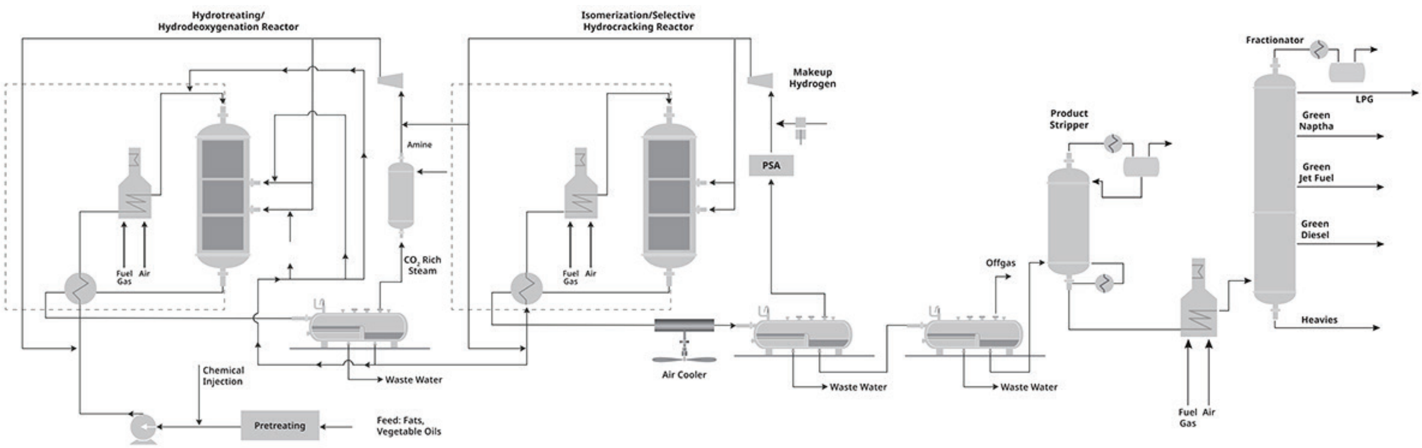

FIG. 2. A common process flow diagram for green diesel refining.

TABLE 5. A Western Canadian green diesel refinery uses a gas chromatograph to measure H_2 purity in the recycle stream

Stream parameters	**Stream 1**
Stream name	Recycle gas
Application type	H_2/H_2S analysis
Process control or monitor	Monitor
Pressure at sample point	859 psig
Temperature at sample point	104°F
Phase at sample point	Gas
Return sample to process/flare	No

Stream components	**Measured**	**Units**	**Normal**	**Concentration Variation**		**Alarm Value**
				Minimum	**Maximum**	
H_2O		Vol%	0.07			
H_2S	X	Vol%	0.02			180/220 ppm
CO		Vol%	0.44			
CO_2		Vol%	0.85			
H_2	X	Vol%		80.72	88.5	80.5% (low)
NH_3		ppm		1.40	2.3	
CH_4		Vol%	11	4.22	11.3	
Ethane		Vol%	1.82			
Propane		Vol%	4.7			
I-Butane		Vol%	0.021			
N-Butane		Vol%	0.12			
Naphtha		Vol%	0.12			
Diesel		ppm	60			

TABLE 6. The refinery uses a continuous gas analyzer to measure carbon impurities at the H_2 pressure swing adsorption outlet

Stream parameters	Stream 1
Stream name	PSA outlet
Application type	CO/CO_2 analysis
Process control or monitor	Monitor
Pressure at sample point	404 psig
Temperature at sample point	113°F
Phase at sample point	Gas
Return sample to process/flare	No

Stream components	Measured	Units	Normal	Concentration Variation		Alarm Value
				Minimum	Maximum	
CO	X	ppm	Trace	0	100	10 ppm
CO_2	X	ppm	Trace	0	100	10 ppm
H_2		Vol%	99.9			
N_2		Vol%		0.03	0.1	
CH_4		Vol%		0.05	0.07	

The ideal mix of gas analyzers for each application depends on the purity requirements and potential contaminants, the latter determined by the H_2 source. For example, green H_2 produced via electrolysis has no risk of hydrocarbon or sulfur contamination, so measuring for these impurities is not necessary.

As the world further reduces its dependency on fossil fuels, the need for uncontaminated H_2 gas for power generation and storage will continue to increase. While no single-analyzer solutions are on the market to universally measure all possible H_2 contaminants, the technologies are progressing quickly, helping processors ensure pure products for maximum reliability, uptime and profitability.

NOTES

[a] Rosemount™ 700XA Gas Chromatograph
[b] Rosemount™ CT5800 Continuous Gas Analyzer
[c] Rosemount™ X-STREAM Enhanced XEFD Continuous Gas Analyzer

LITERATURE CITED

[1] J.D. Power, "How long do electric car batteries last?" September 2022, online: https://www.jdpower.com/cars/shopping-guides/how-long-do-electric-car-batteries-last

DAN GUYMER is the application engineering lead for Rosemount Continuous Gas Analyzers at Emerson's Gas Analysis Solutions Center in Cumbernauld, Scotland. He has been with Emerson for 6 yr, initially working as a gas chromatograph application engineer before moving to continuous gas analyzers. Guymer has an MS in chemistry from the University of Aberdeen, with a research placement at the University of Bonn in Germany.