Application note

E-fuel production

e-Fuels: climate friendly energy that can put us in the driving seat to a sustainable future

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Introduction

November 2023 saw the "Conference of the Parties" to the UN Framework Convention on Climate Change (COP 28) begin in the gulf states of the United Arab Emirates, the backdrop to this event is a prediction that 2023 will be the hottest ever recorded for our planet, remarkably the prior 8 years (2015-2022) were the previous 8 hottest years for the climate recorded.[1]

Ahead of COP28 Secretary General of the United Nations António Guterres again warned of the risk of a global rise in temperature of 3°C above pre-industrial levels, citing this event as entering a dangerous and unstable world.[2] The UN is determined that the future is not fixed and a limit to temperature rises of 1.5°C is still obtainable, albeit with the need for "dramatic immediate climate action."

A transition from fossil fuels, a 45% reduction of greenhouse gas emissions by 2030 versus 2010 levels and net zero by 2050 remain the ambitions of the participants of the UN framework with near universal membership.

COP 28 was forced into overtime, extending beyond the scheduled close of 12th December as delegates debated the final text calling for a "transition away from fossil fuels". The UN Chief remarked "To those who opposed a clear reference to a phaseout of fossil fuels in the COP28 text, I want to say that a fossil fuel phase out is inevitable whether they like it or not. Let's hope it doesn't come too late."

e-Fuels

Given the emphasis on moving away from fossil-based fuel production and the requirement to sustain economies and lifestyles without contributing to further increases in atmospheric CO_2 levels it follows that the fuels that literally drive, sail and fly people and goods around the globe should receive great attention.

In this context, e-fuels can be described as derived from a combination of hydrogen generated by renewable energy (referred to as green hydrogen) and carbon dioxide removed from the atmosphere. A remarkably versatile feedstock called synthesis gas, syngas for short, can be generated from these ingredients from which many downstream products can be made (synthesized), some of these are fuels that would otherwise be generated from the refining of crude oil and from natural gas. Figure 1 shows the basic components of e-fuels production stages.

Green hydrogen

In the drive for cleaner energy, many different methods for producing hydrogen with less carbon emissions have been developed. Arguably the most carbon neutral method is by electrolysis, the separation of water into molecules of hydrogen and oxygen using electricity generated by entirely renewable means such as wind or solar.

A common form of electrolyzer is the Polymer Electrolyte Membrane (PEM), direct electrical current is applied to two electrodes (anode and cathode) separated by the membrane, the electrical current attached to the anode in contact with water "splits" the H_2O molecules into H_2 and O_2 with the excess protons passing through the membrane to form gaseous H_2 on the cathode. A diagram of a typical PEM is shown in Figure 2.

An alternative electrolyzer design is one that is membrane free, this type of cell produces a mixed gas stream, and while this requires careful handling it can be cryogenically separated into relatively pure hydrogen and oxygen.[3]

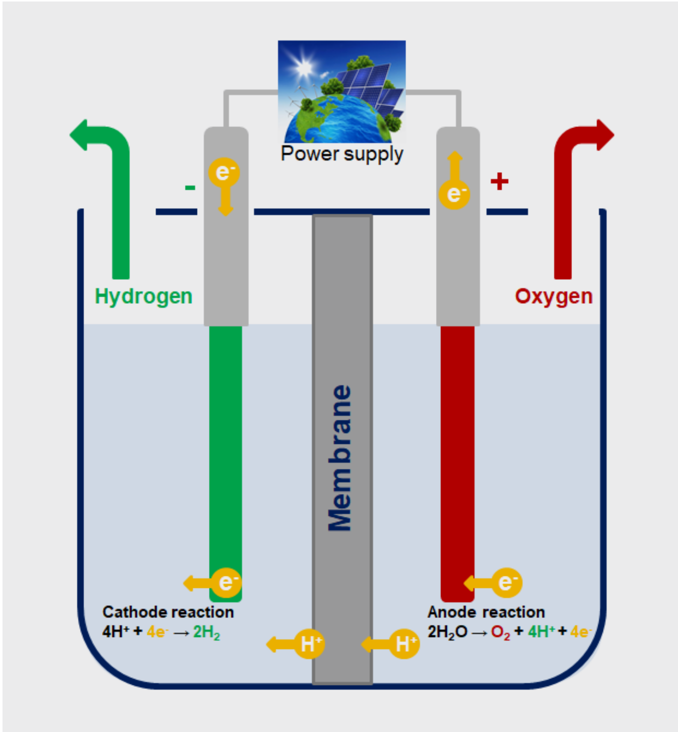

Figure 2: A schematic of a PEM cell.

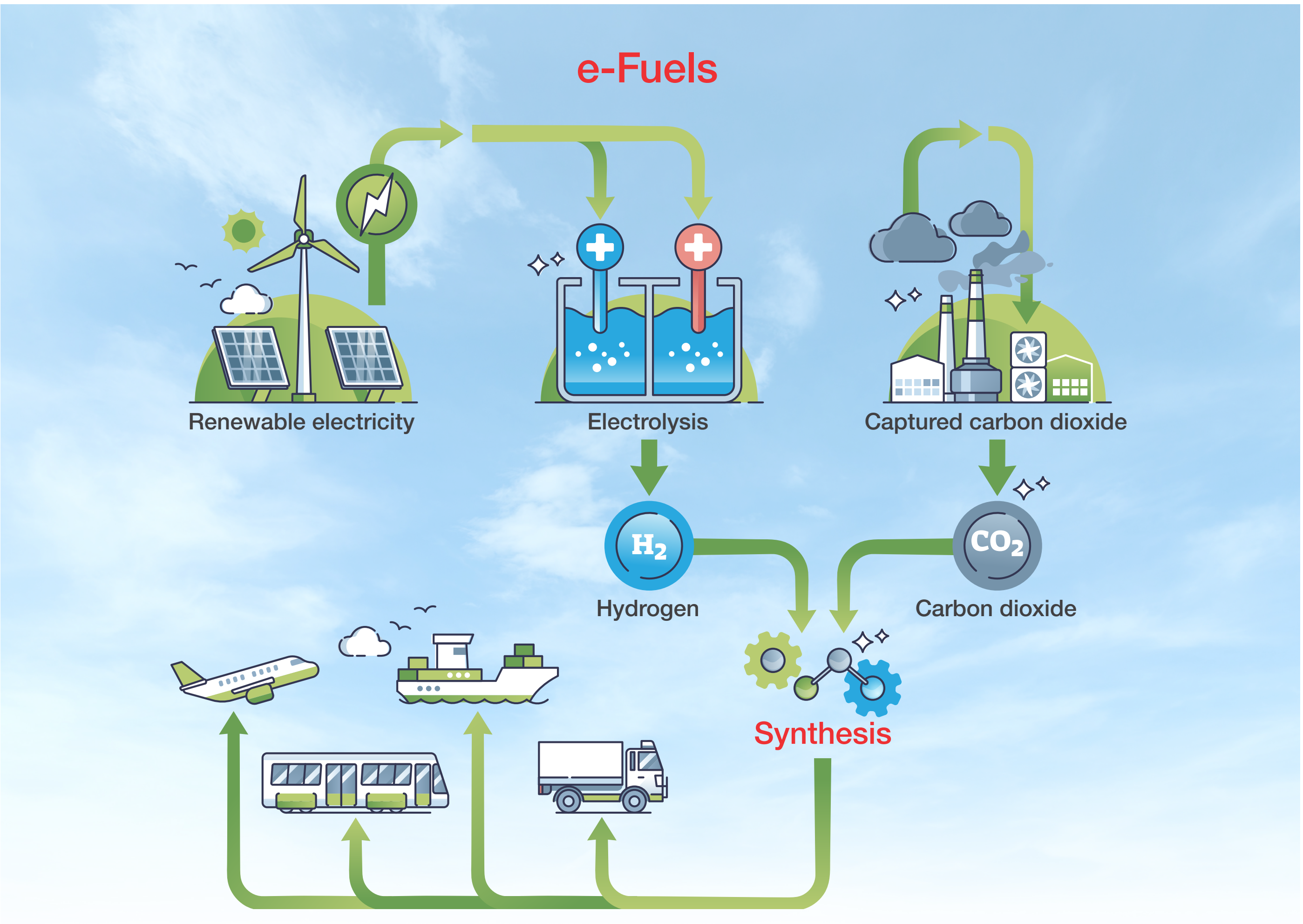

Figure 1: A simple schematic of e-fuels production.

Synthetic methane

Methane is the principal component of natural gas which is used ubiquitously for both industrial and domestic purposes, it is reported to contribute to global warming at a rate of 6 times that of CO_2 so it seems counter intuitive that methane can play a role in heading off climate change. As an e-fuel however it shares that characteristic of utilising CO_2 that has been removed from the atmosphere providing energy while not adding to atmospheric levels of CO_2. More than a century ago the French chemist Paul Sabatier devised a method for combining CO_2 with H_2 over a nickel catalyst to produce CH_4 and steam (4H2+CO2→CH4+2H2O).

Today scientists are working on variations of this discovery to deliver the most efficiently produced synthetic CH_4, an example is Tokyo Gas which supplies 8.6 million retail and wholesale users, and for power generation, requiring the importation of 12.6 million tonnes of liquified natural gas. Tokyo Gas teamed up with the Japan Aerospace Exploration Agency and Osaka University to find the most effective means of making synthetic methane. Two approaches are being studied, one is based on the Sabatier catalyst combined with water electrolysis within a single device, the benefits are that a modified catalyst allows reaction at lower temperatures (the process being highly exothermic), while the heat that is generated is absorbed during the endothermic water electrolysis, overall, these modifications are expected to boost efficiency of the original Sabatier process from 50–80%. The second approach is by use of a Polymer Electrolyte Membrane (PEM) to simultaneously combine electrolysis of water and the reduction of CO_2 to methane, this process does not require precious metals and is anticipated to have an efficiency of ~70%.[4]

Sustainable Aviation Fuel (SAF)

On 28th November 2023 an historic flight took place when a Virgin Atlantic Flight 100, a Boeing 787, departed London for New York JFK airport, this was the first transatlantic flight for an aircraft powered entirely by sustainable aviation fuel (SAF).[5]

The aviation industry accounts for ~3.5% of human contribution to climate change as a result of CO_2 and non-CO_2 emissions.[6] It is estimated that utilizing SAF could reduce this contribution by 70%.[5]

Flight 100 made its journey with SAF manufactured primarily from waste oils, the balance made up from Synthetic Aromatic Kerosene; but these are not the only pathways to SAF, once again we turn to syngas gas produced from captured CO_2 and green hydrogen, in this case the next stage is conversion of the syngas to synthetic oil and a slate of other hydrocarbons including jet fuel by a catalytic process known as Fischer-Tropsch.

Fischer-Tropsch is not new, this metal catalyst has been in use for many years for converting syngas to hydrocarbons, but when the source of syngas is captured CO_2 and green hydrogen, we now have a sustainable e-fuel to power aircraft.[7]

By 2050 the European Union (EU) requires that jet fuel consists of a minimum of 70% SAF.[8] This presents a challenge as there is a limit to that which can be produced from organic waste and used cooking oils, the aviation industry and indeed aircraft engine manufacturers expect e-fuels to play an increasing role in the supply chain.[9]

European refiners are already gearing up for this challenge, one such example is the collaboration between Repsol, Petronor and Saudi Aramco. They are embarking on the startup of a pilot plant which will produce 8,000 litres per day of SAF at the facility in the port of Bilbao.[10] This plant will utilize a combination of catalytic technologies from Johnson Matthey to convert green hydrogen and captured CO_2 into syngas then the Fischer Tropsch process will be employed to make synthetic crude oil which can be refined to aviation fuel.[11]

Process analytics for e-fuels

The e-fuels described above have varying methods of production, while they share the characteristics of the basic ingredients of green hydrogen and captured carbon dioxide their pathways to different fuel types vary widely. These processes are multi-stage and visibility to process conditions necessary for advanced process control depend on real-time gas analysis.

Syngas processes to produce chemicals including ammonia and methanol depend on real-time gas analysis which is often provided by process mass spectrometry (MS), the same MS has also been employed for the Fischer Tropsch process in both development laboratories and full-scale production units.

MS has been selected for gas analysis due to its inherent flexibility, high speed, and excellent precision. MS measures the individual concentrations of gas species in process gas streams by separating gases according to their mass.

The first stage of an MS analyzer is ionization where neutral gas molecules are ionized by electron impact, the resulting ions are accelerated into an electrical or magnetic field where mass separation occurs, then the resulting ion currents are measured at a Faraday type detector, MS are inherently very linear as ion currents at the detector are proportional to the number of molecules of each constituent gas component.

The highest performing process MS is the scanning magnetic sector type, it has the unique advantage that the signals (peaks) at each mass number are highly symmetrical and have a very flat top, unlike the peaks of the alternative quadrupole MS which are Gaussian in shape.

This flat top peak feature ensures that the magnetic sector MS is highly tolerant of mass position drift since the height of the peak is uniform across the flat top. Figure 3 shows the schematic of a Thermo Fisher Prima PRO scanning magnetic sector MS.

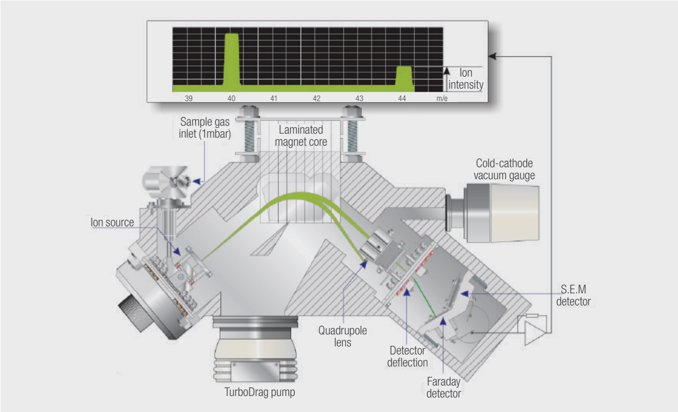

Figure 3: Schematic of Thermo Scientific™ Magnetic Sector MS analyzer.

Component	Concentration %mol
Nitrogen	9.00 ± 0.0150
Carbon dioxide	5.00 ± 0.0150
Methane	9.00 ± 0.0200
Ethane	5.00 ± 0.0130
Propane	10.00% 0.0250
Ethylene	5.00 ± 0.0015
Propene	5.00 ± 0.0130
Hydrogen	43.00 ± 0.0700
Carbon monoxide	9.00 ± 0.0150

Table 1: ISO 17025 accredited calibration gas used for relative sensitivities.

Independent tests on magnetic sector MS

Prima PRO was tested for fuel gas quality metering in accordance with ISO10723 in the ISO17025 accredited laboratory of Effectech UK. The MS was calibrated for relative sensitivity with a single calibration gas containing the nine components shown in Table 1. Then eight different fuel mixes were prepared, containing the same nine components but over a wide range of concentrations, to test the repeatability and linearity of the MS. Each gas was analyzed for 30 cycles over 5 minutes (10-second cycle time). The linearity plots are shown in Figure 4, and the Coefficients of Determination (R2) for the nine components are shown in Table 2.

Linearity Test: Coefficients of Determination (R^2)	
H_2, CH_4, C_2H_4, C_2H_6, C_3H_6	1.0000
C_3H_8	0.9999
CO_2	0.9995
CO, N_2	0.9994

Table 2: Coefficients of Determination for nine components shown in Figure 4.

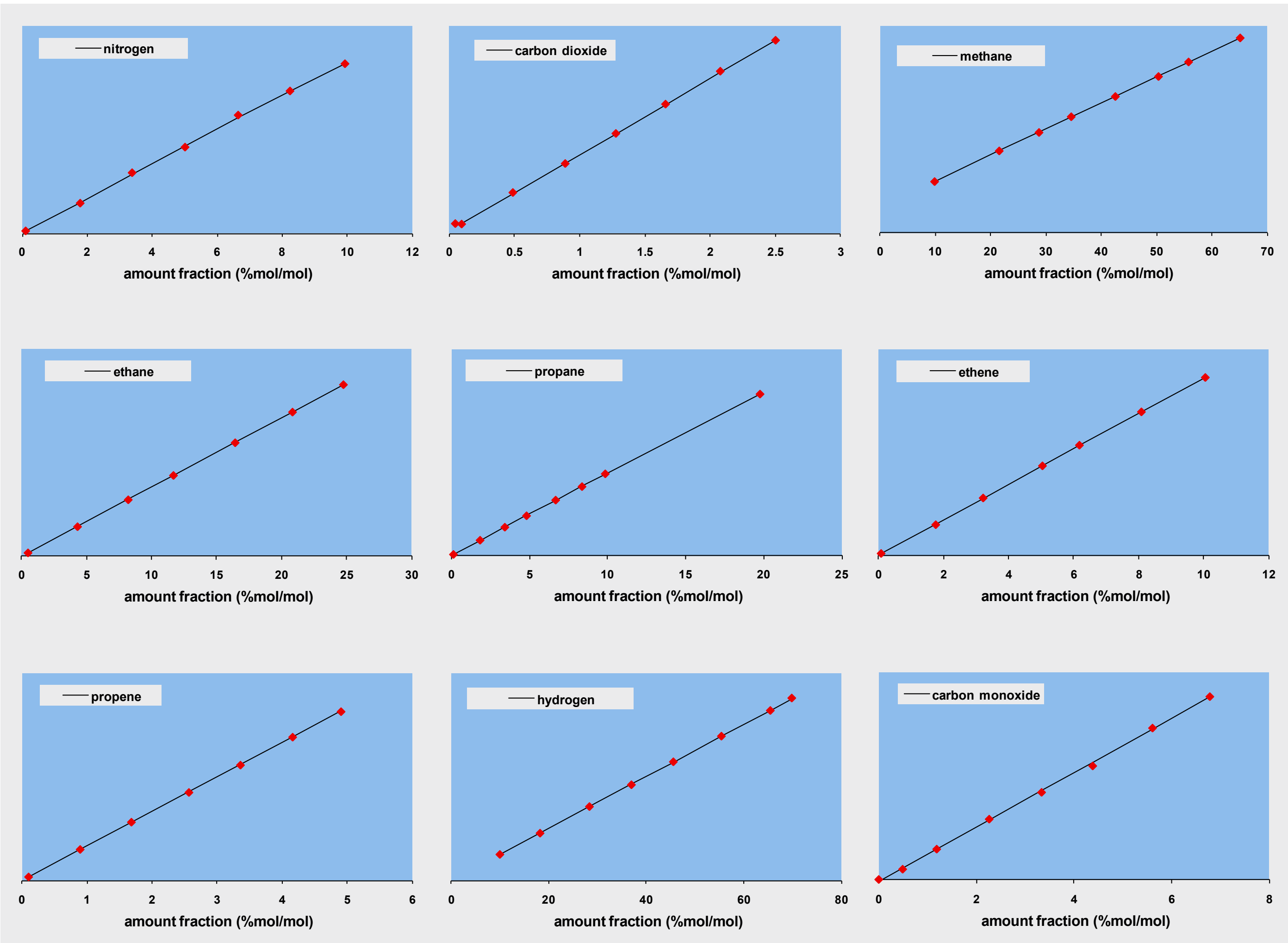

Figure 4: Linearity data for nine fuel gas components.

Analytical Performance of MS measuring synthesis gas

e-Fuels have in common the utilization of syngas and conversion to fuels by catalytic processes such as Fischer Tropsch, the analysis requirements at the various stages of production vary, and in some cases the process stream compositions may be complex. Table 3 shows the very high precision of the Thermo Scientific Prima PRO online mass spectrometer for gases commonly found in e-fuels processes, note the very high precision (expressed as single standard deviation) for gas components of differing concentrations.

Electrolyzer technology development

A Prima PRO MS was installed at the development and manufacturing site of UK electrolyzer supplier CPH2, at the experimental stage we can see how the ability of MS to measure multiple gas components in near real-time provides insight to electrolyzer performance. In Figure 5 we see a mixed gas stream where the separation of oxygen and hydrogen is incomplete, in this case the limiting condition was an excess of liquid oxygen, this early fault diagnosis speeds up product development and time to market.

At the full megawatt scale, the data shown in Figure 6 is of the pure oxygen stream, the ability of MS to measure water vapour enables continuous observation of the dryer efficiency, note how the oxygen purity improves as the water concentration reduces.

Component	Concentration vol.%	Precision absolute %
Hydrogen	Balance	0.05
Methane	5.5	0.01
Carbon Monoxide	15	0.05
Nitrogen	2	0.02
Ethene	0.3	0.002
Ethane	0.3	0.002
Argon	1	0.002
Propene	0.3	0.002
Carbon Dioxide	10	0.01
Propane	0.3	0.002
Butene	0.2	0.002
N-Butane	0.2	0.002
Pentene	0.15	0.002
N-Pentane	0.15	0.002
Hexene	0.15	0.002
Hexane	0.15	0.002

Table 3: Prima PRO analytical specification for Fischer Tropsch gas-to-liquids process.

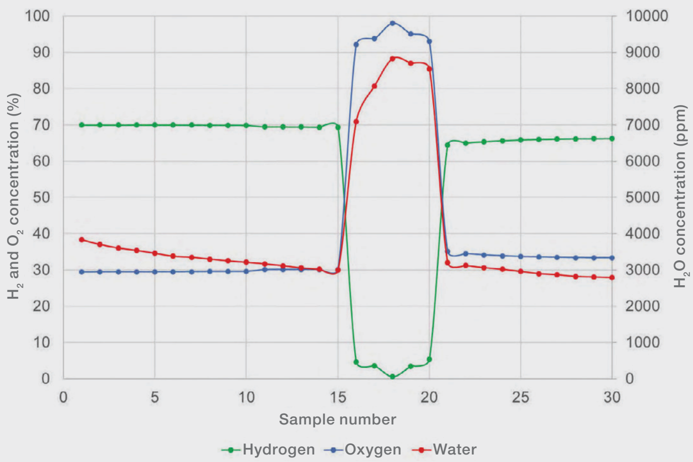

Figure 5: Analysis of a mixed gas stream from an experimental scale electrolyzer.

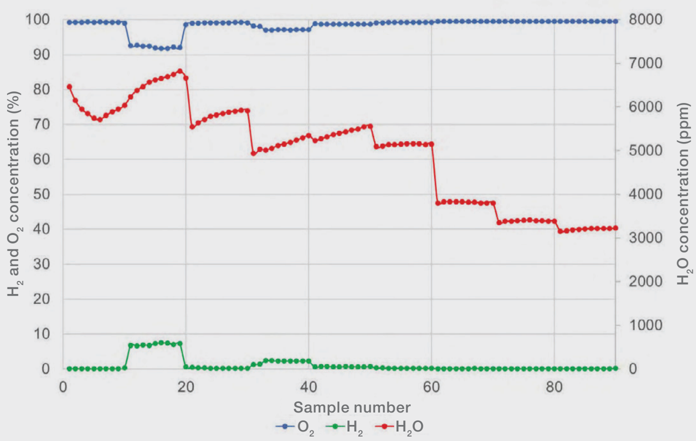

Figure 6: Measurements from the pure oxygen stream of a megawatt scale electrolyzer.

Long term stability of magnetic sector MS

Table 4 shows the magnetic sector analyzer's ability to run for long periods without calibration and still meet a demanding performance specification. A Prima PRO on a customer site had been running for eight months since calibration. It was then set to analyze a 16-component certified calibration cylinder for 11 consecutive analyses. The analyzer was still within specification, and the user is confident the MS could run for a year without the need for calibration.

Summary

Targets for the reduction in greenhouse gas emissions will require a seismic shift from fossil fuel consumption to the utilisation of renewable energy to produce e-fuels. The electrical and chemical processes to produce syngas and the downstream products by catalysis require continuous monitoring to ensure efficient production and maintain quality. Magnetic Sector MS has a proven track record in many chemical processes where syngas is used as well as in Gas to Liquids processes, recently the same technology is being applied to the development of electrolyzers for green hydrogen production.

Through independent testing at an accredited laboratory the scanning magnetic sector MS has been proven to have outstanding linearity performance when monitoring fuel gases at wide concentration ranges, these analyzers are able to measure the compositions of multiple process streams with very high precision in just a few seconds, they have also demonstrated the ability to remain accurate for very long periods between calibration.

The Prima PRO and Prima BT mass spectrometers from Thermo Fisher Scientific offer users the flexibility to place MS at the development laboratory and production sites with transferable analysis methods, the Prima PRO MS is available for Zone 1 and Class 1 Div 2 hazardous area installation.

Process MS continue to play their part in the mission of Thermo Fisher Scientific to make the world a healthier, cleaner and safer place.

Prima BT Bench Top Process Mass Spectrometer

Prima PRO 710 Process Mass Spectrometer

		Prima PRO data		
Component	Cylinder certified value	Mean	Absolute standard deviation	%RSD
Helium	0.2	0.196	0.001448	0.7384
Hydrogen	43.997	44.103	0.020100	0.0456
Methane	10	9.961	0.001592	0.016
Carbon Monoxide	25	25.039	0.016700	0.0667
Nitrogen	2.001	1.937	0.025400	1.3128
Ethylene	0.301	0.3	0.000689	0.2293
Ethane	0.4	0.399	0.001228	0.308
Argon	1.001	1.004	0.000702	0.0699
Propylene	0.299	0.292	0.001488	0.5093
Carbon Dioxide	15	14.972	0.006544	0.0437
Propane	0.5	0.498	0.000824	0.1654
Butene	0.3	0.296	0.001263	0.4271
N-Butane	0.4	0.401	0.000404	0.1008
Pentene	0.2	0.2	0.000444	0.2223
N-Pentane	0.2	0.201	0.000834	0.4155
Hexene	0.1	0.101	0.000452	0.4484
N-Hexane	0.1	0.1	0.000686	0.6841
H_2/CO Ratio	1.76	1.761	0.000991	0.0563

Table 4: Prima PRO validation check after 8 months without calibration.

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