Improving production of Syngas with fast, precise gas analysis MS

Thermo Scientific Prima BT & Prima PRO Process Mass Spectrometers

Authors

Daniel Merriman
Thermo Fisher Scientific
Winsford Cheshire UK

Keywords

Synthetic natural gas, reforming, direct reduction iron, biomass gasification, Fischer-Tropsch, gas to liquid

Introduction

Syngas, or synthesis gas, is a fuel gas containing a mixture of hydrogen, carbon monoxide, and sometimes carbon dioxide. Its name comes from its use in synthesizing important chemicals such as ammonia and methanol and producing synthetic natural gas (SNG). It is also a key intermediate in the Direct Reduction Iron (DRI) process, which uses natural gas to reduce iron oxide to iron.

Syngas has 50% of the energy density of natural gas and cannot be burnt directly,[1] but it can be converted into various energy products; examples include the production of synthetic petroleum by the Fischer-Tropsch process and the production of bioethanol from biomass gasification. It can be produced from a wide range of carbon-containing sources, including natural gas, coal, wood, and organic waste. The carbon source is reacted with steam (steam reforming), carbon dioxide (dry reforming), or oxygen (partial oxidation). Figure 1 shows examples of sources and uses of syngas.

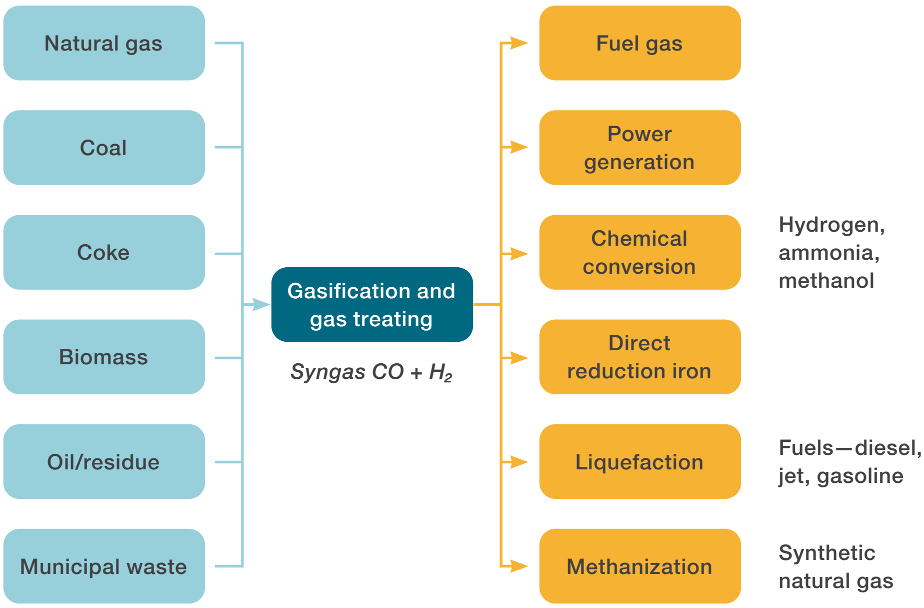

Figure 1: Examples of sources and uses of syngas.

thermo scientific

Syngas' chemical composition varies significantly depending on the carbon source and the type of process used to produce the desired intermediate. The chemical processes that utilize syngas are typically multi-stage, have many varying gas analysis requirements, and are usually dynamic—they depend on process gas analysis for optimization. Fast, multi-component, multi-stream gas analysis is a vital element in the efficient control of such processes.

Process analytical requirements

Hydrogen and carbon monoxide are always present in syngas, albeit in widely different concentrations depending on the process involved. A wide range of other chemicals can also be present and need to be analyzed if the process is to be controlled efficiently and the desired products generated. These include carbon dioxide, methane, and other hydrocarbons—ethanol, nitrogen, argon, and helium. Examples of process analytical requirements for some of the key syngas processes are detailed below, and Thermo Scientific™ Process Mass Spectrometers have a proven track record in all of these applications.

Ammonia synthesis

Natural gas and steam pass through various processes to convert the hydrocarbon stream into a hydrogen-rich stream. This hydrogen is then reacted with nitrogen from the air in a 3:1 ratio to produce ammonia. Eleven or more process streams need to be analyzed, and gas analysis mass spectrometry's combination of speed, multi-component analysis, and dynamic range enables one MS to analyze all the process streams. For example, it is important to provide the complete natural gas feed stream composition to determine the amount of steam required to react with the methane and other hydrocarbons present; this parameter is the steam to carbon ratio. By monitoring the complete natural gas composition, steam generation costs can be minimized by controlling the amount of steam to match the composition of the natural gas.

Table 1 shows an example of Prima PRO's specification for one of the key ammonia process streams, syngas feed to the ammonia converter. Analysis time, including stream switching, is approximately 20 seconds, and precision is measured over eight hours.

By this stage in the process, carbon monoxide has been removed from the syngas as it poisons the ammonia catalyst. Thermo Scientific™ Prima PRO Analyzes all five components, including argon and helium. The ammonia converter stream is recycled to increase ammonia yield, which also increases the concentration of these two inerts. If their concentrations are too high, then the energy used for compression is wasted, and the ammonia yield is reduced.

Raw material prices are heavily affected by the demand for power generation and heating fuels, and downstream fertilizer prices are affected by political, economic, and environmental factors. This puts great pressure on the ammonia production unit to maximize efficiency, and process analytical data plays a vital role in maximizing unit efficiency. The process analyzer needs a wide dynamic range to monitor methane slippage (the reduction in methane concentration from over 90% in natural gas to a few % in the secondary reformer effluent) and fast, precise measurement not only of the steam to carbon ratio, but also the H/N ratio. Syngas ideally should be made up of 75% hydrogen and 25% nitrogen; in practice, there will also be residual methane and inerts from the air. For optimum efficiency, it is vital to keep the ratio of hydrogen and nitrogen as close as possible to the stoichiometric ratio of 3 to 1. Prima PRO has a proven track record in meeting all these requirements.

Direct reduction iron

Traditionally iron was produced in blast furnaces, using coke to reduce iron ore. DRI does not require large stocks of coal to be converted to coke, instead, natural gas is converted to syngas, and iron oxide is reduced by carbon monoxide and hydrogen. These 'reducing' gases are generated by the reaction of natural gas (methane) with the by-products of the DRI process:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2$$

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

World DRI production grew from 78 million tonnes in 2016 to 111 million tonnes in 2019 and only fell back slightly to 104 million tonnes because of the COVID pandemic. Blast furnaces have continued to produce the majority of the world's iron, but production has remained relatively flat at around 1,300 million tonnes.[2]

As with the ammonia process, multiple process stages are required (typically eight to ten) and again process MS offers the ability to monitor all process streams quickly and completely. Table 1 shows an example of Prima PRO's specification for the DRI syngas stream, typically named 'Reformed Gas' in the industry.

Table 1: Prima PRO analytical specification for ammonia process syngas analysis.

Component	Concentration vol.%	Precision absolute %
Hydrogen	65.0 – 70.0	0.02
Methane	3.0 – 10.0	0.01
Helium	0.5 – 1.0	0.002
Nitrogen	20.0 – 26.0	0.01
Argon	0.1 – 5.0	0.002

Table 2: Prima PRO analytical specification for direct reduction iron syngas analysis.

Component	Concentration vol.%	Precision absolute %
Hydrogen	~ 58	0.05
Methane	~ 1	0.01
Carbon monoxide	~ 38	0.05
Nitrogen	~ 1	0.05
Carbon dioxide	~ 2	0.01

Analysis time, including stream switching, is approximately 20 seconds, and precision is measured over eight hours.

If the DRI process is to operate efficiently, it needs fast, accurate online monitoring of multiple gas streams containing various combinations of hydrogen, methane, carbon monoxide, carbon dioxide, and nitrogen over a wide range of concentrations. Prima PRO has a proven track record of providing the best combination of speed and accuracy compared with alternative methods of gas analysis, such as infrared analyzers or gas chromatographs. It optimizes the DRI process by optimizing the production of reducing gases, optimizing fuel gas mixing, and reducing energy consumption.

Biomass gasification

Here, biomass is typically reacted at high temperatures (>700° C) without combustion, with a controlled amount of oxygen and/or steam to produce syngas. This can be used directly as a fuel (which is more efficient than direct combustion of the original biomass) or to produce biofuels using micro-organisms to convert hydrogen and carbon monoxide to ethanol. Thermo Scientific™ Prima BT and Prima PRO Mass Spectrometers have been used on a wide range of biomass-based processes; Table 3 shows an example of a performance specification for a syngas-based bioethanol process.

Analysis time, including stream switching, is approximately 22 seconds, and precision is measured over eight hours.

A Prima PRO Ex was used to study the conversion of syngas and other gas mixtures into alcohols in continuously gassed batch cultivation experiments and identified CO as the preferred carbon and electron source for the growth and producing alcohols. However, the total yield of moles of carbon (mol-C) per electrons consumed was almost identical in all setups, which underlines electron availability as the main factor influencing product formation.[3]

Prima PRO provides a fast, linear, reproducible measurement of alcohols such as ethanol; alcohol measurement is very reproducible with its magnetic sector analyzer, and ethanol can be measured with a precision down to 10 ppm. It also provides valuable, reliable composition data on other species present in the process, such as hydrogen, carbon dioxide, nitrogen, oxygen, and argon.

Table 3: Prima PRO analytical specification for syngas-based bioethanol process.

Component	Concentration vol.%	Precision absolute %
Hydrogen	~ 60	0.05
Methane	~ 1	0.005
Carbon monoxide	~ 10	0.05
Nitrogen	~ 20	0.05
Carbon dioxide	~ 10	0.01
Argon	~ 1	0.002
Ethanol	~ 1 – 5	2% relative

Gas-to-liquid process using Fischer-Tropsch

Synthetic fuel breakthroughs such as the Fischer–Tropsch GTL process came from the desire to become ‘petroleum independent’ following a national threat of war, oil embargo, or crisis. Currently, synthetic fuel catalyst research has been extended to thermochemical approaches for the conversion of anthropogenic carbon dioxide as intermediates for chemicals and fuel production. This, coupled with the future advances in renewable energy and carbon dioxide capture from the environment, offers promising solutions to mitigate anthropogenic carbon dioxide increases.[4]

The two main parts of a GTL plant are:

1. A steam reformer to react natural gas with steam to generate syngas rich in hydrogen and carbon monoxide. Natural gas feed is monitored to determine the steam/carbon ratio. A complete composition analysis is required to determine the amount of steam required to react with the methane and other hydrocarbons present in natural gas.
2. A Fischer-Tropsch reactor to convert the hydrogen and carbon monoxide into liquid hydrocarbons. The reactor needs the H_2/CO ratio to be 2:1, but the steam reformer typically generates a ratio of around 5:1. This excess hydrogen needs to be removed, and gas analysis is used to control this removal. The excess hydrogen is used as fuel for the reformer or as a fuel or feedstock for another process on an adjoining plant. This gas also needs analyzing—if it is to be used as fuel for the reformer, then its calorific value and air requirement need to be monitored. The light gas outlet of the Fischer-Tropsch reactor also needs to be monitored since this is recycled via the reformer.

There are several different Fischer-Tropsch reactor types—fixed-bed, fluidized-bed, and slurry-phase reactors. Prima PRO provides a fast, precise, and complete analysis of all significant gaseous components in all the process streams.

Table 4: Example of Prima PRO analytical specification for Fischer-Tropsch GTL process.

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

Not all components are measured in every type of sample stream, but Table 4 shows a typical Prima PRO performance specification for a Fischer-Tropsch GTL process. Analysis time is 30 seconds, including stream switching time, and precision is measured over eight hours.

Multiple gas samples can be analyzed on one Prima PRO instrument; it provides a fast, precise, complete analysis of all significant gaseous components, from inorganics such as hydrogen and oxides of carbon to hydrocarbons from C_1 up to C_6. In some processes, H_2S is analyzed at ppm levels to monitor the desulfurization of natural gas.

Prima PRO's detailed natural gas composition data is used to minimize steam generation costs by controlling steam production to suit the composition of the natural gas. Reformer outlet stream composition is used to optimize the reformer, and the Fischer-Tropsch reactor's light gas outlet also needs to be monitored as it is recycled through the reformer. Prima PROs are also being used to improve & develop processes by evaluating the performance of different catalysts in both the reformer and the Fischer-Tropsch reactor.

Benefits of magnetic sector mass spectrometry

Two main types of mass spectrometers can be used for process gas analysis, with the magnetic sector MS providing greater stability and better precision than the quadrupole MS. Unlike the flat-topped peak generated by the magnetic sector, the quadrupole produces a Gaussian peak. So, it is 'fault sensitive'—any drift in the mass scale will produce an error in the peak height measurement by measuring intensity on the shoulder of the peak rather than the peak maxima. This must be corrected by more frequent calibration.

Figure 2 shows a schematic of our magnetic sector analyzer, together with the characteristic flat top peaks it produces.

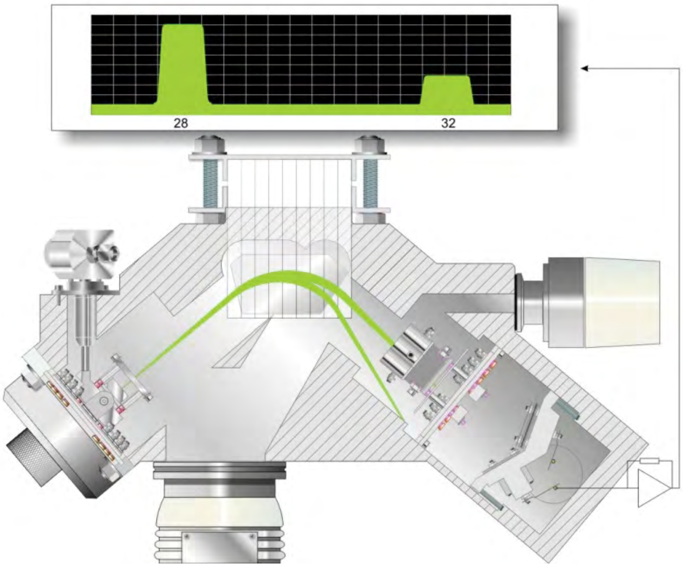

Figure 2: Schematic of Thermo Scientific™ Magnetic Sector Analyzer and flat-topped peaks for mass 28 (nitrogen) and mass 32 (oxygen).

Table 5 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 without being calibrated. It was then used 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.

Table 5: Example of Prima PRO calibration check after 8 months without calibration

		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

Independent tests on magnetic sector MS

Prima PRO was tested for fuel gas quality metering in accordance with ISO10723 in Effectech UK's ISO17025 accredited laboratory. The MS was calibrated for relative sensitivity with a single calibration gas containing the nine components shown in Table 6. 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 3, and the Coefficients of Determination (R^2) for the nine components are shown in Table 7.

Rapid multistream sampling

If the MS is to monitor all process streams, then a fast, reliable means of switching between streams is required. Solenoid valve manifolds have too much dead volume and rotary valves suffer from poor reliability, so we developed the unique RMS Rapid Multistream Sampler. It offers an unmatched combination of sampling speed and reliability and allows sample selection from 1 of 32 or 1 of 64 streams. Stream settling times are application-dependent and completely user configurable. The RMS includes digital sample flow recording for every selected stream. This can be used to trigger an alarm if the sample flow drops, for example, if a filter in the sample conditioning system becomes blocked.

The Prima PRO RMS can be heated to 120°C, and the position of the stream selector is optically encoded for reliable, software-controlled stream selection. Temperature and position control signals are communicated via Prima PRO's internal network.

The RMS is shown in schematic form in Figure 4. It has a three-year warranty as standard; no other multistream sampling device offers the same level of proven reliability.

Table 6: ISO 17025 accredited calibration gas used for relative sensitivities.

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 7: Coefficients of Determination for nine components shown in Figure 3.

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

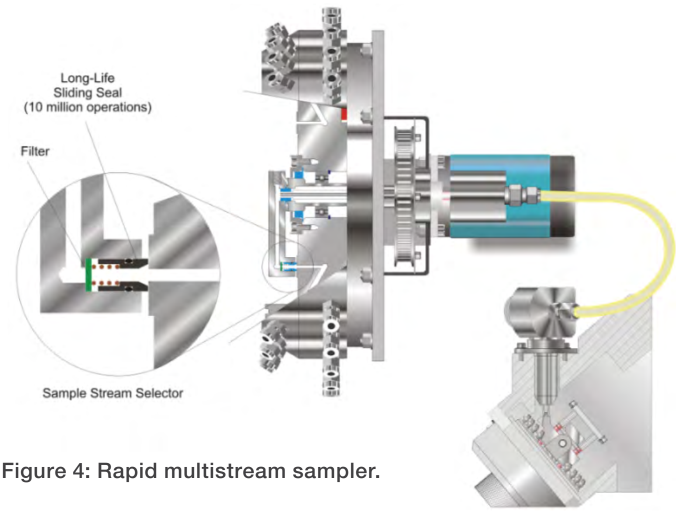

Figure 4: Rapid multistream sampler.

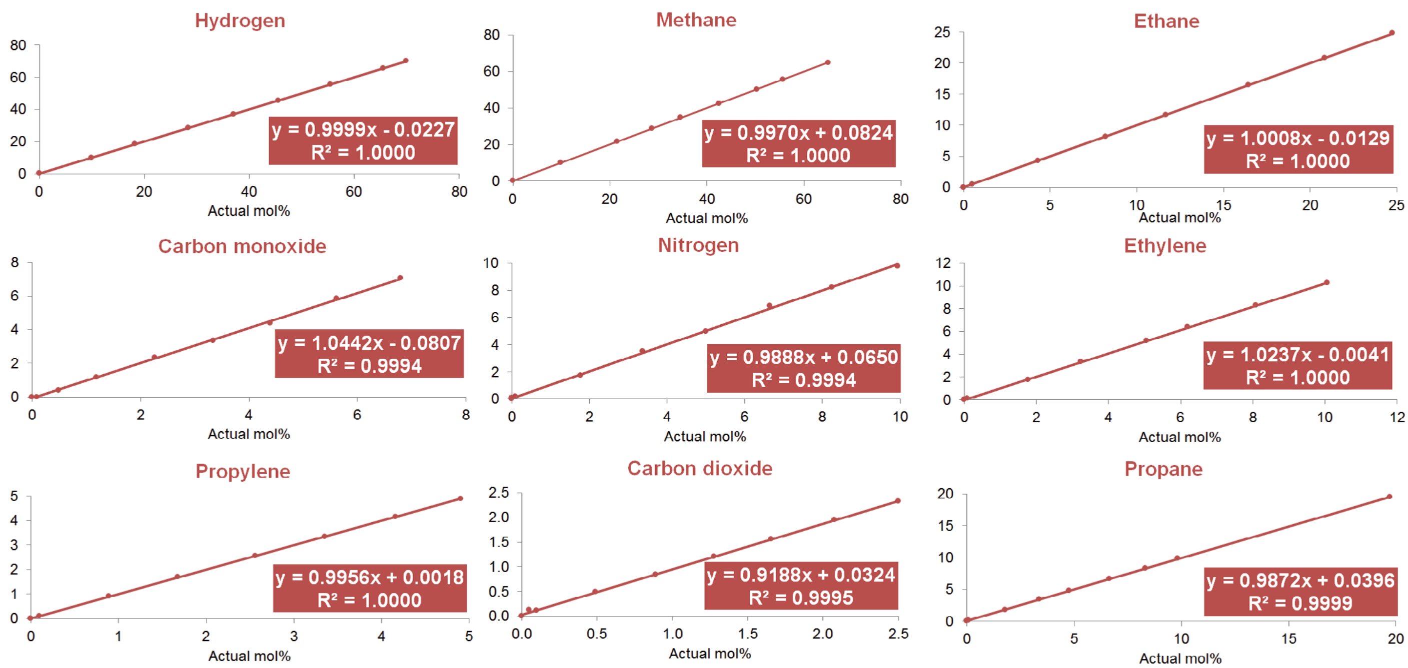

Figure 3: Linearity data for nine fuel gas components.

ThermoFisher SCIENTIFIC

Software

Thermo Scientific™ GasWorks™ Software supports the analysis of an unlimited number of components per stream and an unlimited number of user-defined calculations (called Derived Values), such as the Hydrogen/Carbon Monoxide ratio. An unlimited number of analytical methods can be set up, so different analyses can be defined for different process streams. Analog signals from temperature and pressure sensors, for example, can also be logged, displayed, and used in Derived Value calculations. A range of industry-standard protocols is available for communicating with plant process control systems.

Performance specification

As we have seen, there is no one single composition specification for syngas. However, Table 8 gives a 'typical' Prima PRO syngas performance specification. Analysis cycle time is approximately 20 seconds, including streams settling time, and performance is demonstrated during on-site commissioning by periodically analyzing a certified calibration gas over 16 hours. Additional components can, of course, be monitored if required—please consult us for advice.

Summary

Syngas manufacture requires fast, multi-component, multi-stream gas analysis, and Thermo Scientific gas analysis mass spectrometers are being used for fast, accurate analysis of a wide range of syngas-based processes:

- Ammonia & Methanol production
- Direct Reduction Iron
- Biofuels
- GTL process using Fischer-Tropsch

The magnetic sector analyzer provides high precision and excellent long-term stability, with long periods between calibration and superior resistance to contamination.

Thermo Scientific Prima BT and Prima PRO Magnetic Sector Mass Spectrometers are providing fast, precise off-gas analysis through laboratory research to pilot plant and full-scale production for this vitally important industry. Prima BT provides a bench-top solution for laboratory scale monitoring, being configured with 15 sample gas and six calibration inlets. Prima PRO is equipped to monitor 60+ sample streams and is available for Zone 1 and Class 1 Div 2 hazardous area installation. The highly precise and complete gas composition measurements provided by both models are easily incorporated into a process control system.

References

1. Biofuels UK, What is Syngas? (http://biofuel.org.uk/what-is-syngas.html)
2. 2021 World Steel in Figures, page 18, World Steel Association (https://worldsteel.org/wp-content/uploads/2021-World-Steel-in-Figures.pdf)
3. Electron availability in CO_2, CO and H_2 mixtures constrains flux distribution, energy management and product formation in *Clostridium ljungdahlii*, Hermann, Teleki, Weitz, Niess, Freund, Bengelsdorf, Takors, Institute of Biochemical Engineering, University of Stuttgart, Microbial Biotechnology, July 2021 (https://sfamjournals.onlinelibrary.wiley.com/doi/full/10.1111/1751-7915.13625)
4. Synthetic Fuel Development, Future Energy (Third Edition) 2020, Pages 561-580 (https://www.sciencedirect.com/science/article/pii/B9780081028865000268)

Table 8: Example of typical Prima PRO syngas performance specification.

Component	Range %mol	Prima PRO precision %mol	Prima PRO Lower Detection Limit %mol
Hydrogen	0 – 75	≤0.05	≤0.01
Carbon Monoxide	0 – 25	≤0.05	≤0.3
Carbon Dioxide	0 – 25	≤0.02	≤0.01
Methane	0 – 10	≤0.02	≤0.01
Nitrogen	0 – 50	≤0.05	≤0.3

Learn more at **thermofisher.com/primapro**

thermo scientific