Sustainable e-syngas: A decarbonisation win-win

Transforming syngas production with innovative methods for sustainable energy and carbon circularity in the quest for net-zero emissions

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A world without carbon would be one we could not live in. The foods we eat contain carbon in the form of carbohydrates and proteins. Our bodies rely on carbon to build flesh, blood, and bones. The most effective fuels are gaseous and liquid hydrocarbons. Eliminating carbon is not an option. Circular use of carbon is therefore a key pillar of sustainability on this planet.

The use of hydrocarbons generates carbon dioxide (CO_2). Therefore, circular carbon dictates circular use of CO_2. The carbon cycle is a natural cycle, as plants capture CO_2 via photosynthesis. Carbon circularity can be on an annual timescale, such as the growth of annual crops and their combustion, or on an evolutionary timescale, such as the generation of fossil fuels, their use, and then sequestration of the CO_2 emitted during their use.

Plastics and many of the petrochemical-derived materials we use daily rely on syngas for their production. If we are to continue to use these commodities and pursue a global journey to net-zero greenhouse gas emissions, a transition to sustainable syngas production is required.

Sustainable syngas can be produced from biomethane reforming or biomass gasification. E-syngas supports the ongoing electrification of industrial processes and utilises captured CO_2, avoiding its direct emission to the atmosphere. It is therefore a win-win solution to sustainable syngas production.

Syngas and CO_2 sequestration

Syngas is a mixture of predominantly carbon monoxide (CO) and hydrogen and may also contain some CO_2. It is one of the most common chemical intermediates. Syngas is the building

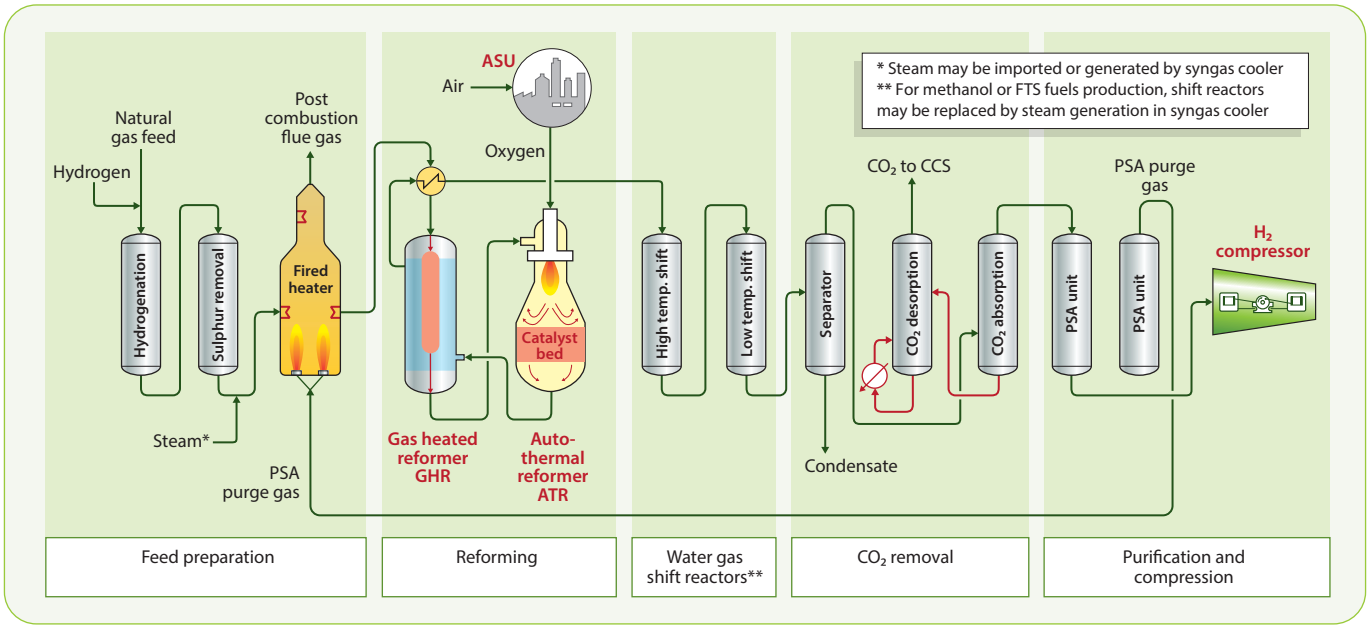


Figure 1 Blue hydrogen production process with gas heated reforming and autothermal reforming

block at the front of the value chains related to ammonia, methanol, and a host of petrochemicals.

In China, coal is gasified to make syngas, which is converted to ammonia, petrochemicals, and hydrocarbon fuels. In both steps, CO_2 is formed and released to the atmosphere. All around the world, coal is converted to coke for use in iron and steel making. During the coking process, syngas is created, which can be used as a fuel and a reducing agent in the blast furnace.

When forestry waste biomass is gasified, it also releases CO_2, which can be captured and sequestered or utilised. In this case, the CO_2 capture, utilisation, and release cycle is generally less than 50 years.

When natural gas is reformed to make syngas, and the syngas is shifted to hydrogen, CO_2 is formed in large quantities. As an alternative to atmospheric release, CO_2 generated from coal gasification and natural gas reforming can be captured and then sequestered in sub-surface geological formations.

Syngas produced this way may be considered 'blue' syngas. It is the precursor of 'blue' hydrogen. One of the most effective techniques for blue syngas production is gas heated reforming (GHR) combined with autothermal reforming (ATR). This configuration minimises low-pressure post-combustion CO_2 capture and thereby reduces the cost of achieving a high CO_2 capture rate (see **Figure 1**).

e-CO for green syngas

Electrification with renewable electricity is one of the most technically mature and scalable routes to clean molecules. The main hurdle holding this pathway back is the cost of electricity.

The economics of electrically driven chemical conversions, such as electrolysis of water to hydrogen, shift from unfavourable to favourable if low-cost power can be used. In mature electricity markets with a high degree of renewables penetration and fluctuations in daily demand, prices can swing from peak to trough in less than an hour. The number of hours of negatively priced electricity is rising each year.

Under these circumstances, the most economically advantageous operating mode shifts from a high-utilisation paradigm to an intentionally intermittent profile: operating when power prices are low.

To exploit intentionally intermittent operation, the equipment and process must be hyper-flexible and tolerant of extended idle periods. This favours lower-temperature operation to minimise the thermal mass, reactor configurations that perform well across a wide range of operating conditions, and a process with recycle loops that can help absorb the shock of rapid throughput changes.

Sisyphus Energy in Leoben, Austria, has implemented these concepts in an electrically heated, reverse water-gas shift (RWGS) reactor concept. The company's expertise is in the integration of cutting-edge materials development with scalable reaction configurations. Its e-RWGS reactor can be fed with green hydrogen from intentionally intermittent electrolyser operation and captured CO_2 to yield CO, one of the two main components of syngas.

The first innovation that makes the process unique is an improved RWGS catalyst with high selectivity to CO at low operating temperatures. This a significant advancement because traditional RWGS catalysts tend to produce methane at low temperatures. When syngas is the target, CO is helpful, but methane is not.

Downstream of the RWGS reactor, Sisyphus has engineered a functional material that is highly selective to CO. Other gases are recycled to maximise energy efficiency. Pulling the CO product out of the process stream, rather than removing individual impurities, is key to its integrated process.

The e-CO can be used for low-carbon chemical synthesis, notably reducing the CO_2 intensity of speciality chemicals and pharmaceuticals. Alternatively, when the resultant e-CO is blended with green hydrogen, e-syngas is the product and methanol or FTS fuels can be produced at scale.

The process flowsheet developed by Sisyphus Energy is optimised for flexibility, which improves its economic viability and accelerates the path to producing net-zero chemicals and fuels at cost parity with fossil-based equivalents.

Dry methane-reforming and turquoise hydrogen

Chemical reactions, such as reforming, rearrange molecules in the feedstock to syngas. A plasma arc can be used to activate these molecules by splitting them and letting them recombine into more favourable products. Essentially, it is an electrified process for molecule conversion.

When CO_2 is fed to a plasma under the right conditions, it is split into CO and oxygen atoms. When an additional carbon carrier is introduced along with the CO_2 (such as methane from biogas), oxygen is consumed to make even more CO, and hydrogen is also produced. In other words, dry reforming of methane (DRM) is performed (see **Figure 2**).

DRM can be used in combination with methane pyrolysis for e-syngas production. The German start-up Graforce GmbH has pioneered a process it calls 'Plasmalysis'. This can convert a typical biogas feed of 50% methane and 50% CO_2 to syngas with a 1:1 ratio of hydrogen to CO.

To enrich the syngas to a 2:1 ratio of hydrogen to CO, which is required for methanol production and FTS for liquid fuels, Graforce proposes to use methane pyrolysis to generate additional hydrogen and blend this with the 1:1 syngas from the plasma-induced DRM.

Methane pyrolysis can be executed in several ways, many of which can be electrically heated using renewable sources of power. In each case, solid carbon is generated by the process as the methane molecules are split into hydrogen and carbon. This avoids the formation of CO_2 and enables the production of a high-value carbon co-product (see **Figure 3**).

The nature of the solid carbon drives the economics of this pathway to e-syngas. Some methane pyrolysis processes produce low-value soot. Others can yield carbon black, graphite, or graphene, which may have a value between €1,000 and €5,000 per tonne. Some are able to produce ultra-high-value carbon nanotubes, which can be worth up to €20,000 per tonne.

Bi-reforming using plasma decomposition

The Belgian start-up D-CRBN uses a non-thermal plasma reactor for sustainable syngas production. Several years ago, its system was demonstrated with a biogas feedstock containing about 40% methane and 60% CO_2. The resultant syngas had approximately a 1:1 ratio of CO and hydrogen.

For hydrogen production, methanol synthesis or FTS fuels, the ideal ratio of hydrogen to CO in the syngas is 2:1. The addition of steam to the biogas introduces new reaction pathways into the plasma system. Methane reforms not only with the CO_2 but also with the water in the bi-reforming

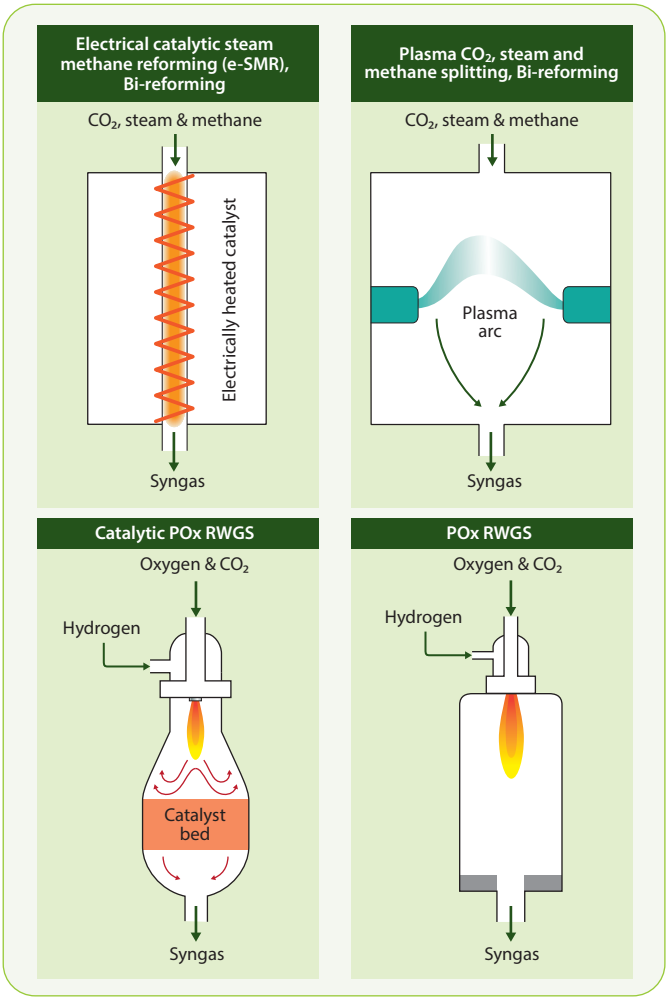


Figure 2 Green sygas production technologies

reaction. In this case, the atoms recombine to produce syngas at the 2:1 ratio.

Turquoise hydrogen is produced from methane pyrolysis using plasma to intentionally yield solid carbon. However, D-CRBN focuses on circular syngas production, and the steam injection assists in achieving this goal with the avoidance of soot, coke, or solid carbon production.

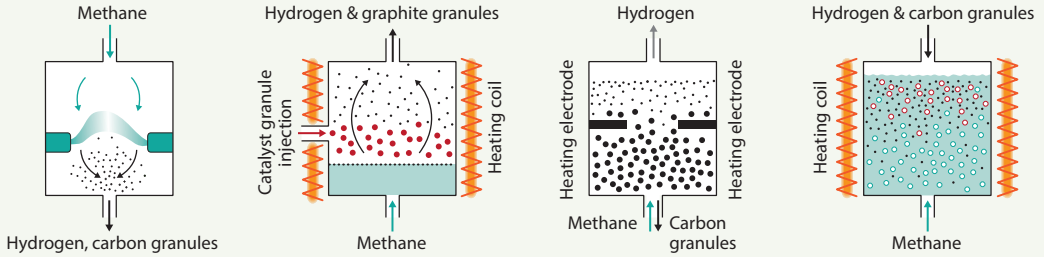
The long-term operability of plasma systems is a key factor for industrial users. During operation, the electrodes producing the plasma tend to be eroded by the intense heat and flow of electrical current. D-CRBN has an advantage over conventional plasma torches because its torch uses a high-frequency pulsed plasma system. This enables its electrodes to have an extended life, meaning lower maintenance costs and reduced downtime.

Electrochemical reduction of CO_2

The US-based start-up Twelve has developed an electrolyser that converts water and CO_2 to syngas. When the electrolyser is fed with

Notes:

- Unreacted methane can be separated from the hydrogen using PSA and recycled to the reactor.
- The size of the carbon granules is influenced by operating conditions and the residence time of the carbon in the reactor.
- Heat may be from renewable electricity.
- Methane can be from natural gas or biogas.



	Plasma pyrolysis	Fluidised bed	Moving carbon bed	Molten metal or molten salt
Process shown	Monolith materials	Hazer	BASF	TNO or C-Zero
Hydrogen content at reactor outlet	~95%	~92%	~92%	Up to 95%
Carbon production	Carbon black as powder or granules	80 to 95% graphite encapsulating catalyst dust particles	Carbon black as powder or granules	Carbon black as powder or granules
Catalyst required	No	Iron oxide granules	Carbon bed	Molten 27% Nickel-73% Bismuth, Molten manganese chloride
Heating mechanism	Direct heating with plasma	Indirect heat applied around the reactor	Electrodes to heat the carbon bed and indirect heat applied around the reactor	Indirect heat applied around the reactor or electrodes to heat the melt in a separate vessel
Reactor temperature	2,000˚C	900˚C	1,000 to 1,400˚C	Depends on melt, 650 to 1,100˚C
Reactor pressure	Close to atmospheric pressure	Close to atmospheric pressure	Close to atmospheric pressure	Up to 5 bar

Figure 3 Methane pyrolysis (cracking/splitting) for turquoise hydrogen production

renewable electricity, this is green syngas, ensuring CO_2 circularity.

The configuration and mechanical design of the electrolyser stack Twelve has developed looks like a proton exchange membrane (PEM) water electrolyser stack. It can therefore be manufactured at plants that have been set up for PEM electrolyser production to achieve manufacturing synergies and scalability.

Twelve has begun to commercialise high-value plastics for branded consumer products derived from circular CO_2. At this point on the road to net-zero, where small-scale electrolyser operations are easier to implement than GW-scale projects, focusing on high-value, low-volume plastics must be the right strategy.

When renewable power generation has significantly ramped up, there will be sufficient green electrons to produce clean energy vectors. However, until then, Twelve's focus on polymers and plastics is the better strategy.

Solid oxide electrolysis for e-syngas

Solid oxide electrolysis is an electrochemical process for the conversion of CO_2 to CO. In contrast to the Twelve process, which is a 'low temperature electrolysis' process and operates at less than 100°C, solid oxide is referred to as 'high temperature electrolysis' and operates between 600 and 800°C.

The higher end of this temperature range is ideal to promote the RWGS reaction, which combines hydrogen and CO_2 to yield CO. This reaction is exploited by Sunfire in its co-electrolysis technology. In this case, steam and CO_2 are simultaneously fed to a solid oxide electrolyser stack. The steam is converted to hydrogen, which then reacts with the CO_2 to form CO. When an excess of steam is fed to the electrolyser, some of the hydrogen remains, creating e-syngas as the product.

Solid oxide electrolysis is also used by Topsoe for electrolytic CO_2 reduction to CO. In its configuration, the solid oxide electrolyser is fed only with CO_2 and yields CO through electrochemical reduction. To generate syngas, another solid oxide electrolyser, or any other type of electrolyser, can be fed with steam or water to generate hydrogen. The separate hydrogen and CO streams are then blended at the appropriate ratio to generate e-syngas.

Increasing the syngas yield from natural gas

Partial oxidation (POx) of natural gas is an alternative to steam methane reforming,

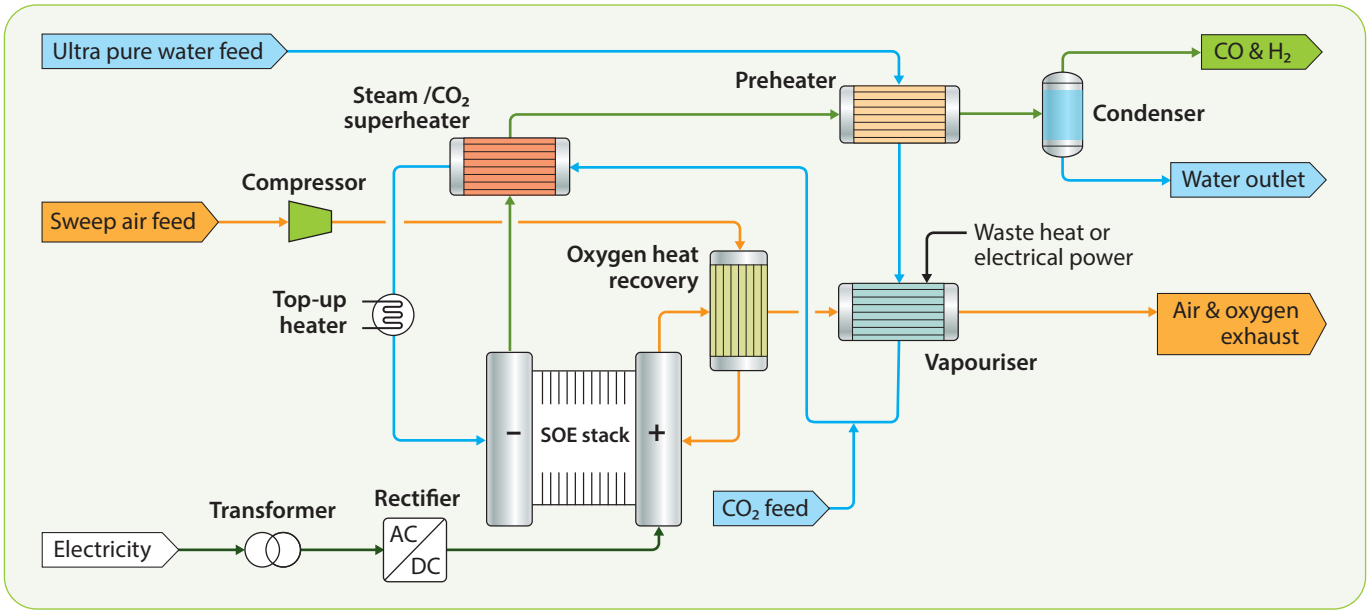


Figure 4 Solid oxide co-electrolysis process for syngas generation

autothermal reforming, and gas heated reforming for syngas or hydrogen production. It reacts oxygen and methane at high temperature without relying on a catalyst.

Air Liquide operates a POx unit at Stade in Germany to supply syngas to the nearby DOW Chemicals facility. During a recent upgrade, Air Liquide enabled CO_2 to be introduced with the oxygen and natural gas to the POx unit to increase the syngas yield. The implication is that captured and recycled CO_2 can be used to produce syngas, making a portion of that syngas circular.

This process at Stade still consumes natural gas and emits some CO_2. However, the upgrade resulted in a 15% increase in energy efficiency, with CO_2 emissions reduced by 15,000 tonnes per year. Every meaningful step towards net zero must be applauded.

POx and CPOx for e-syngas

POx of green hydrogen, oxygen, and captured, recycled CO_2 produces e-syngas. During this process, hydrogen combines with oxygen and CO_2 to produce water and CO during the RWGS reaction. POx can be enhanced with the use of a catalyst, in which case the term catalytic POx (CPOx) is used. The heat and high temperature required in POx and CPOx RWGS systems are derived from thermal oxidation of green hydrogen with oxygen.

Shell has patented a non-catalytic, POx-based RWGS system that operates in the temperature range of 1,000 to 1,500°C (*International Patent No. WO/2020/114899 A1, 2020*). The equipment is similar to classical natural gas-fed POx reactors currently used by industrial gas majors, such as Linde's POx reactor at La Porte and Singapore. As with the classical POx units, an air separation unit (ASU) or pipeline is used to supply the oxygen.

VTT, a Finnish research institute, patented a CPOx process for the RWGS reaction using a rhodium-based catalyst (*International Patent No. W0/2019/175476 A1, 2019*). This process operates at 800 to 950°C and 20 bar, lower than the range proposed by Shell in its non-catalytic RWGS POx reactor. Generally, the goal is for a catalyst to enable a process to operate at a reduced temperature.

USA Patent No. US 2023/0264955 A1, 2023 describes a CPOx process using a nickel-based catalyst. This technology would resemble an autothermal reformer. It proposes to use the oxygen and hydrogen from water electrolysis to feed the RWGS POx reactor. This process integration would reduce or eliminate the need for an air separation unit or pipeline oxygen supply.

The syngas processes described herein show we can build carbon circularity into commercially viable chemical processes. As these processes reach meaningful scale, they represent a win-win for more sustainable use of hydrocarbons.

VIEW REFERENCES IN ONLINE ISSUE

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