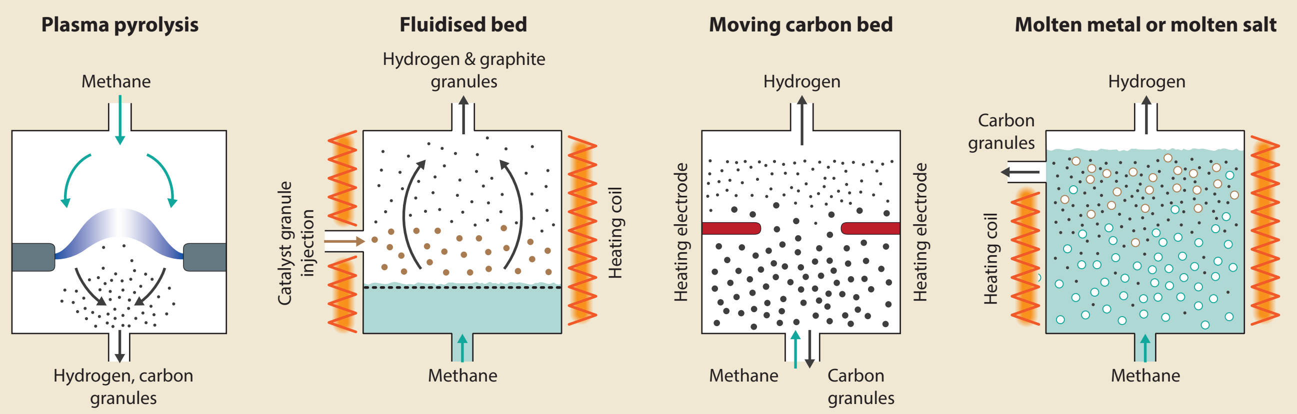
Turquoise hydrogen production by methane pyrolysis

Technologies for methane pyrolysis are at different levels of maturity up to early-stage commercial operations

STEPHEN B. HARRISON
sbh4 Consulting

Hydrogen is in general regarded as a clean energy vector. But whether or not hydrogen has a positive impact on mitigation of greenhouse gas (GHG) emissions depends heavily on its mode of generation. Nowadays, hydrogen is predominantly produced with a hefty fossil CO_2 footprint, while costs for fossil CO_2 are externalised. Within this article, hydrogen production by means of methane pyrolysis is examined. Different technical approaches to methane pyrolysis are presented, and their benefits and drawbacks are highlighted (see **Figure 1** and **Table 1**).

A major question in the whole value chain of hydrogen production through methane pyrolysis is the downstream utilisation of the produced solid carbon. If natural gas, shale gas or fracking gas is used in methane pyrolysis, fossil CO_2 emissions are unavoidable in downstream processes, which eventually result in downstream emissions similar to state-of-the-art, coke based processes. To overcome this intrinsic obstacle, the use of upgraded biogas and synthetic e-methane are presented. In both ways, the carbon is derived from the atmosphere, either via a biological pathway in terms of biogas, or via direct air capture (DAC) of CO_2. If atmospheric CO_2 is used as the feedstock in renewable methane production, then methane pyrolysis could provide a viable pathway to the supply of sustainable solid carbon or graphite for various industrial applications.

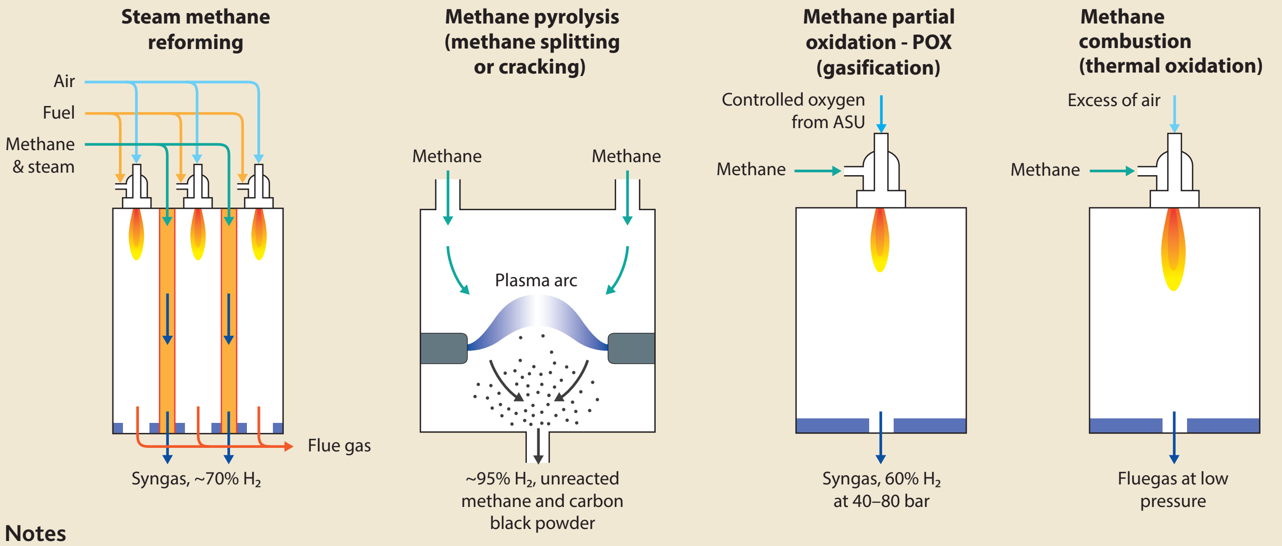


Notes
1. Unreacted methane can be separated from the hydrogen by PSA then recycled
2. Size of carbon granules depends on process conditions and residence time
3. Heat may be generated by renewable energy
4. Methane input may be natural gas or biogas

Figure 1 Methane pyrolysis (cracking/splitting) for turquoise hydrogen production

Methane pyrolysis processes				
Process	**Plasma pyrolysis**	**Fluidised bed**	**Moving carbon bed**	**Molten metal or molten salt**
Developer	Monolith materials	Hazer	BASF	C-Zero
Hydrogen at outlet	95%	92%	92%	95%
Carbon production	Carbon black powder/ Granules	80-95% graphite + catalyst dust	Carbon black powder/ granules	Carbon granules
Catalyst	None	Iron oxide	Carbon bed	Molten manganese chloride
Reactor temp, °C	1700	900	1000-1400	650
Reactor pressure	Close to atmospheric	Close to atmospheric	Close to atmospheric	Up to 5 bar

Table 1



Notes
1. Pyrolysis energy may be from fuel combustion or electric plasma arc
2. Thermal plasma pyrolysis shown
3. Non-catalytic partial oxidation shown

Figure 2 Methane reforming, pyrolysis, gasification and combustion

Methane based hydrogen production processes				
Process	**Steam methane reforming**	**Methane pyrolysis (splitting or cracking)**	**Methane partial oxidation (gasification)**	**Methane combustion (thermal oxidation)**
Oxygen feed	From steam	None	From ASU	Air
Catalyst	Usually nickel	None	None	None
Carbon product	as CO and CO_2	Carbon black powder	as CO and CO_2	CO_2
Hydrogen in product	70%	95%	60%	None
Product gas pressure, bar	15-40	15	40-80	15
Product gas temp, °C	850	1700	1400	1400

Table 2

At present, about 95% of the hydrogen that is produced worldwide is derived from fossil fuels using various thermochemical processes. Gasification consumes solids such as petcoke and coal. Other gas-phase processes are fed with methane, naphtha, or refinery gas.

Autothermal reforming (ATR), steam methane reforming (SMR) and partial oxidation (POX) are the main thermochemical hydrogen production processes in use today (see **Figure 2** and **Table 2**). In these processes, syngas is produced; this is a mixture of hydrogen and carbon monoxide. Sometimes, two out of the three processes may be combined in series to achieve the desired ratio of carbon monoxide to hydrogen in the resultant syngas. If hydrogen is the target gas, carbon monoxide may be converted to carbon dioxide and hydrogen in a subsequent water gas shift reactor.

As a rule of thumb, these thermochemical processes produce about 10 kg of CO_2 per kg of hydrogen. If CO_2 is not captured, the resulting hydrogen is referred to as grey or black hydrogen.

This grey hydrogen may be used in fuel cell powered cars with a consumption of about 1 kg of hydrogen per 100 km. This would result in emissions of 100g CO_2/km if upstream emissions are also considered. This exceeds current European fleet emissions of 95g CO_2/km. The direct use of natural gas as CNG in internal combustion engines would emit less CO_2 from a total system perspective.

Through this example, it is clear that hydrogen must be produced at scale as a clean energy vector to mitigate greenhouse gas (GHG) emissions and combat climate change. One option is to use carbon capture, utilisation and storage (CCUS) to reduce CO_2 emissions from grey or black hydrogen production in order to produce blue or purple hydrogen. Green hydrogen produced in electrolysers fed with renewable electrical power is another. Turquoise hydrogen produced by methane pyrolysis, also known as methane splitting or cracking, is a potential third pathway to low-carbon hydrogen production at scale.

Chemistry of methane pyrolysis

Methane pyrolysis is endothermic, meaning that it requires heat energy to drive the conversion of methane to hydrogen and solid carbon. The reaction is represented by:

$$CH_4 \rightarrow C_{(s)} + H_2$$

There are different options for the external heat supply. Indirect heating using burners fuelled by hydrogen or natural gas as a fuel is one option. It is also possible to use indirect electrical heating or direct heating with an electrical plasma. These heating modes could use renewable electricity, biomethane, or low carbon hydrogen to minimise CO_2 emissions from the process.

Research into methane pyrolysis has been undertaken since the 1960s but the technology was not implemented at scale for many decades. In the past 10 years methane pyrolysis has picked up momentum and several companies have piloted various technologies. Each project has sought to overcome some of the challenges inherent in this process. It is only in the past few years that we have seen commercial operations based on methane pyrolysis emerge.

Plasma pyrolysis from renewable power

Monolith Materials started the development of its methane pyrolysis process in 2012. In 2016 construction started on the Olive Creek 1 plant in Lincoln, Nebraska. It was commissioned in 2020 and has a production capacity of 14 000 t/y of carbon black and around 2500 t/y of hydrogen. A second, larger plant named Olive Creek 2 is planned to have a capacity of 194 000 t/y of carbon black and will produce close to 40 000 t/y of hydrogen which will be converted to ammonia for potential use in the local corn belt as a fertilizer.

In this process, which was initially developed by Kværner,[1] methane is heated to 1650°C using an argon plasma generated by electrodes powered by renewable energy sources. At this temperature, the methane molecule splits. This eventually leads to the formation of carbon black, while the protons split off from the methane molecule and recombine to form hydrogen molecules. The graphite electrodes may provide some catalytic effect and the initially formed carbon black granules catalyse the production of additional carbon black. In various papers related to methane pyrolysis, various additives to the methane have been identified that can either stimulate the reaction[2] or enhance the physical properties of the carbon black.[3] The reaction takes place without the need for an additional solid catalyst.

The prospect of producing turquoise hydrogen from renewable electricity means that this will be a carbon neutral hydrogen generation process, if the process can cope with the volatility of wind and solar electricity supply. If the electricity is sourced via a PPA then the operation would need to follow the electricity supply of the associated wind and solar farms, which seems to be challenging. Otherwise, green certificates can be purchased to cover for the electricity input, but then this process plant is just another constant load in the electricity grid, like an aluminium smelter.

Moving carbon bed thermal process

BASF has been conducting methane pyrolysis development since 2010. From 2013-2017, within a project funded by the Federal Ministry of Education and Research (BMBF), a lab-scale reactor was built and operated at Ludwigshafen, Germany to identify key process parameters.[4,5,6] A follow-up project, also funded by the BMBF, involves a larger pilot plant and construction began in 2019.

In the process under investigation, external electrical heating is used to create the 1000°C temperature required for the pyrolysis reaction. Since the heating is electrical, the process could use renewable energy. The reactor vessel is a vertical cylinder. Methane enters the reactor at the side and decomposes to carbon powder and hydrogen gas. Hydrogen rises to flow from the top of the reactor. Solid carbon falls to the lower part of the column onto a downward-moving bed of carbon granules.

The reactor is externally heated to drive the endothermic pyrolysis reaction and combat heat losses as the products are removed from the reactor. Heat recovery for energy efficiency is an essential aspect of all thermochemical hydrogen production processes. SMR and ATR configurations use large heat exchangers to recover waste heat from the process to generate steam and warm up the incoming gases. To make pyrolysis efficient, similar heat recover mechanisms must be implemented.

Fluidised bed catalytic process

The process that has been under development by Hazer in Australia since 2010 is based on an iron oxide catalyst. A fluidised bed reactor is externally heated to 900°C.[7,8] The carbon from the methane forms graphite on the catalyst surface and hydrogen is released. Subsequently the carbon covered catalyst exits the reactor together with the hydrogen gas. Hazer has operated a pilot plant in Kwinana, Western Australia since 2016 and has commenced work on a commercial scale demonstration plant.

Molten metal catalysed methane bubble reactor

In molten metal methane pyrolysis, methane gas is bubbled upwards through a column of molten metal which acts as a catalyst to convert methane to carbon and hydrogen. The process has been researched extensively as part of the EMBER project at TNO[9] in the Netherlands and is under consideration by Russian natural gas producers, including Gazprom, for hydrogen production.[9]

The technology was initially developed in combination with research into potential future Generation IV nuclear power plants. Numerous papers have been published in the past two decades and molten metals such as magnesium and tin have been used in experiments. Most recently, a nickel/bismuth mixture has been found to have high potential. Nickel is one of the predominant metals used in gas phase reforming catalysts. Despite recent progress, the commercialisation of this process is not anticipated during the current decade.

Molten salt catalysed methane bubble reactor

A main challenge of the molten metal bubbler reactor is to separate solid carbon from the molten metal. TNO has proposed a solution to this issue by floating a layer of molten salt on top of the molten metal. Other researchers have resolved the problem by replacing the molten metal with a molten salt in the entire bubble column. In California, C-Zero has experimented with this process and discovered that manganese chloride is particularly effective.[10,11]

Solid carbon utilisation

A fundamental question arises for methane pyrolysis: what happens to the solid carbon? Graphite, carbon black and activated carbon are functional materials, used in various applications. Carbon black powder is a structurally important filler material used in tyres and supports the vulcanisation process. Carbon black is also used in black consumer electronics goods such as cell phones and laptops. Activated carbon is a filter for gases and water to remove harmful pollutants. Graphite, a form of carbon, is used to produce electrodes for gold, silver, steel, and aluminium processing. It is also used as an electrode in modern lithium-ion batteries. Despite this range of applications for solid carbon, if turquoise hydrogen production becomes a mainstream pathway to hydrogen, the amount of solid carbon produced will greatly exceed demand from current applications.

Renewable methane as feedstock for methane pyrolysis

Organic methane, or biomethane, can be produced by upgrading biogas. Biogas is generated by anaerobic digestion of organic matter. The raw composition of biogas is typically 60% methane and 39% CO_2 and may also contain traces of other gases such as hydrogen sulphide. Corrosive hydrogen sulphide alone makes it inappropriate to inject raw biogas into natural gas pipelines. Hence, the raw biogas needs to be upgraded to biomethane and that organic methane can be injected into the natural gas grid. As the biogas was produced from organic matter, the carbon in the organic methane was extracted from the atmosphere by biological means.

Production of e-methane follows a synthetic route. Green hydrogen produced by electrolysis from water and renewable electricity from wind or solar farms is chemically synthesised with CO_2 into e-methane as described by the Sabatier reaction for methanation:

$$4\,H_2 + CO_2 \rightarrow CH_4 + 2H_2O$$

The process is also referred to as power-to-gas. CO_2 acts mainly as a hydrogen carrier, whereas 50% of the hydrogen can be recycled in the process. To be completely renewable, the CO_2 needs to be extracted from the atmosphere, either as organic CO_2 from biogas or bio-ethanol plants or via direct air capture of CO_2.

As both organic methane and synthetic e-gas have the same properties as natural gas they can utilise the established natural gas infrastructure. Hence, renewable methane can be easily transported from its place of origin to a location for methane pyrolysis.

Utilising renewable methane, both hydrogen and solid carbon are then renewable. If this solid carbon is employed in aluminium smelters or blast furnaces, the whole value chain is CO_2 neutral, as no additional fossil CO_2 is emitted to the atmosphere.

Carbon neutrality

A complete life cycle analysis, ranging from production through usage to subsequent product recycling or disposal is crucial to determine the net greenhouse gas emissions impact of any value chain and its potential long-term impact on climate change.

If methane pyrolysis is fed with renewable methane, either organic methane or e-methane, it can provide a viable supply of sustainable solid carbon for various industrial applications. On the other hand, if natural gas or shale gas is utilised as the feedstock, the final use of the solid carbon and its GHG potential needs to be carefully determined.

Conclusion

Turquoise hydrogen and solid carbon can be produced by means of methane pyrolysis. Various technologies are currently at different levels of maturity from laboratory scale to pilot plants to early-stage commercial operations.

Graphite and carbon black have a broad range of applications. To determine fossil CO_2 emissions, a detailed life cycle analysis from feedstock to final usage is required, as this will determine the GHG mitigation potential.

References

1 Kværner, System for the Production of Carbon Black, *International Patent WO 93/21053*.

2 Vander Wal R, Makiesse Nkiawete M, Carbons as catalysts in thermo-catalytic, hydrocarbon decomposition: a review, *Journal of Carbon Research*, 2020.

3 Florida Solar Energy Center. *Thermocatalytic CO_2-Free Production of Hydrogen from Hydrocarbon Fuels*, Final Report, Prepared for: United States Department of Energy Under Cooperative Agreement: No. DE-FC36-99GO10456.

4 BASF, Interview Methane Pyrolysis, www.basf.com/au/en/who-we-are/sustainability/we-produce-safely-and-efficiently/energy-and-climate-protection/carbon-management/interview-methane-pyrolysis.html (2021-04-19, date last accessed).

5 Marquardt T, Bode A, Kabelac S, Hydrogen production by methane decomposition: Analysis of thermodynamic carbon properties and process evaluation, *Energy Conversion and Management*, 221, 113125, 10.1016/j.enconman.2020.113125.

6 Bode A, Agar D W, *et al.*, Methane pyrolysis and CO_2 activation – technologies with application options for hydrogen, carbon and synthesis gas production, *Chemie Ingenieur Technik*, 88, 1342-1342. 10.1002/cite.201650483.

7 Raston C, Tong Chua H, *et al.*, *Process for Producing Hydrogen from Hydrocarbons*, US Patent US20120258374A1.

8 Andrew Cornejo, System for the production of hydrogen and graphitic carbon. International Patent WO2018170543A1, 2017.

9 Leal Perez B, Jiménez J, Bhardwaj R, Goetheer E, *et al.*, Methane pyrolysis in a molten gallium bubble column reactor for sustainable hydrogen production: Proof of concept & techno-economic assessment, *International Journal of Hydrogen Energy*, 46, 10.1016/j.ijhydene.2020.11.079.

10 D Kang, N Rahimi, *et al.*, Catalytic methane pyrolysis in molten MnCl2-KCl, Applied Catalysis B: Environmental, Vol. 254, 2019, pp. 659-666, ISSN 0926-3373, 10.1016/j.apcatb.2019.05.026.

11 E W McFarland, C Upham, *et al.*, Natural gas conversion to chemicals and power with molten salts. US Patent US20210061654A1, 2019.

Stephen B. Harrison is Founder and Managing Director of sbh4 GmbH, Germany. His work focuses on decarbonisation and greenhouse gas emissions control. Hydrogen, CCUS and the electrification of industrial processes are fundamental to his consulting practice.