Methane pyrolysis – hope or hype?

Cansu Doganay of Lux Research takes a look at the current technology landscape for methane pyrolysis for producing low-carbon hydrogen from natural gas.

The solid carbon byproduct of methane pyrolysis can be sold as carbon black.

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Methane pyrolysis – also known as methane cracking or turquoise hydrogen – is the high-temperature breakdown of methane into hydrogen gas and carbon. It competes directly with blue hydrogen – hydrogen from steam methane reforming and carbon capture and sequestration (CCS) – for producing low-carbon hydrogen from natural gas. In methane pyrolysis, all the carbon content in the methane is captured in solid form rather than emitted as CO_2. Methane pyrolysis also requires approximately half the amount of energy required by steam reforming to produce the same amount of hydrogen. Finally, the solid carbon byproduct can be sold as carbon black, offsetting the cost of hydrogen produced. Together, these factors make methane pyrolysis a

Table 1: **Methane pyrolysis technology landscape**

	Plasma	**Thermal**	**Catalytic**
Corporates	• Gazprom	• BASF • Sumitomo Chemical	-
SMEs	• Monolith Materials, • HiiROC, • Plenesys, • SEID AS, • Graforce GmbH, • Levidian, • H-Quest Vanguard	• Ekona Power, • Aurora Hydrogen, • Modern Electron, • Standing Wave Reformers	• Hazer group, • C Zero, • Eden Innovations, • Hycamite
Research institutes	• Centre National de la Recherche Scientifique (CNRS), • Dalian University of Technology, • Russian Academy of Sciences, • Tsinghua University, • Beijing Jiaotong University, • Chinese Academy of Sciences, • National Research Centre Kurchatov Institute, • Shahid Beheshti University, • University of Warsaw, • Zhejiang University.	• Karlsruhe Institute of Technology (KIT), • Netherlands Organisation for Applied Scientific Research (TNO), • Academia Sinica Taiwan, • Aligarh Muslim University, • Beijing Institute of Technology, • Chiba Institute of Technology, • Fritz Haber Institute of the Max Planck Society, • Pacific Northwest National Laboratory, • University of Alberta • United States Department of Energy (DOE)	• Netherlands Organisation for Applied Scientific Research (TNO), • Russian Academy of Sciences, • Chinese Academy of Sciences, • University of California Santa Barbara, • United States Department of Energy (DOE), • University of Seoul, • Ajou University, • Indian Institute of Technology System (IIT), • University of Calgary, • University of Milan.

Source: Lux Research

promising technology option to produce low-carbon hydrogen.

Methane pyrolysis takes different forms, and they can be categorised as thermal, plasma, and catalytic pyrolysis. Despite the variations, they all share common technical challenges: high process temperatures required for high conversion rates, hydrogen gas purity, and separation of solid carbon from the gas phase to avoid catalyst poisoning (if any) and reactor system blockings.

Plasma: The most mature form of methane pyrolysis utilises a plasma torch to pyrolyze methane gas at temperatures between 1,000°C (cold plasma) and 2,000°C (hot plasma). Cold plasma typically leads to methane conversion of less than 50% with no catalysts, while hot plasma typically results in conversion above 90%. Given the highest technology readiness level among all routes of methane pyrolysis, plasma pyrolysis is the strongest technology route today. The Norwegian company Kværner (now Aker Solutions) deployed the first and only commercial-scale methane pyrolysis facility utilising hot plasma technology in 1997, where the hydrogen produced was recirculated in the plasma torch. The facility was decommissioned in 2003 for underproducing carbon black. Nowadays, Monolith Materials is the leading startup closest to commercialisation. It utilises thermal plasma technology based on Kværner's process and launched its first demonstration facility in the US in 2020, outputting carbon black as the primary product. Other plasma pyrolysis companies include HiiROC (hot plasma) and SEID AS (cold plasma). Gazprom is the only corporation now active in plasma technology for methane pyrolysis – its cold plasma technology is supported by a nickel catalyst to reach methane conversion efficiencies of 80%, but the technology is still at the laboratory scale with no disclosed timelines for commercialisation.

"The misalignment of carbon black and hydrogen market size is still impeding commercialisation.

Thermal: In thermal, or hot, pyrolysis, methane dissociates into hydrogen and carbon at temperatures above 1,200°C with no catalysts. The main downside of this noncatalytic process is the long cracking times below 1,000°C. This technique favours low pressures and high temperatures to achieve the highest conversion rates. At low pressures, however, there is a tendency to produce intermediates, such as olefins and aromatics, which decompose to carbon and hydrogen with increasing residence time. Differentiation revolves around the type of reactor used in the process. BASF utilises an electrically heated moving bed reactor where carbon granules flow counter to the gas phases and methane pyrolyses directly on the granules at 1,400°C. KIT passes methane through a liquid tin bubble column reactor at 1,200°C, where the solid carbon formed floats on the liquid and can be separated through undisclosed means. TNO also uses a molten metal reactor operating above 1,000°C and separates out the carbon black from the liquid metal using a molten salt. Microwave-assisted methane pyrolysis, has recently emerged, bringing a new approach to conventional thermal pyrolysis. Sumitomo Chemical is the only corporate developing a methane pyrolysis technology using microwave energy – currently at lab scale, with commercialisation plans by the early 2030s. Alberta, Canada–based startup Aurora Hydrogen also develops microwave-assisted pyrolysis and raised $10 million to take its technology to pilot scale, targeting 200 kg of hydrogen production per day. Right now, all thermal pyrolysis platforms are at lab scale and aren't likely to reach commercial scale before 2030.

Catalytic: In catalytic pyrolysis, methane breaks down into hydrogen and carbon over a metal catalyst at temperatures between 600°C and 900°C. Packed bed and fluidised bed reactors are typically considered for catalytic pyrolysis, and iron, nickel, and cobalt, which are relatively abundant and cheaper than noble metal catalysts, are the most intensively studied catalysts for this process. While nickel shows the best catalytic activity, it deactivates above 600°C. Cobalt-based catalysts also show decent catalytic performance, but cobalt is more expensive and toxic than a nickel-based catalyst and requires an extra step to purify the carbon black. Iron-based catalysts are cheap, nontoxic metals with a more stable catalytic activity. Even though catalysts lower the activation energy to initiate the process, regeneration and quick deactivation of catalysts at operating temperature are the biggest obstacles to commercialisation of catalytic methane pyrolysis. While the necessity to regenerate could be avoided by using carbonaceous catalysts, their activity significantly drops over time. Catalytic pyrolysis is still at an early stage of development without a clear leader. Hazer Group uses a fluidised bed reactor with an iron ore catalyst, operating at 850°C. It's at pilot scale, with no clear targets for commercialisation. C-Zero is the newest entrant to the methane pyrolysis sector; the company uses a bubble column reactor, operating over 1,000°C, filled with undisclosed molten liquid that acts as both a catalyst and a heat transfer medium to crack methane. The company has recently raised funds to build its first pilot plant with a daily capacity of 400 kg of hydrogen.

Since Kværner's first commercial facility in 1997, the methane pyrolysis landscape has evolved to include novel approaches by startups with differentiated technologies. These new directions differ by the energy source, heat transfer medium, and/or catalysts. Most recently, Aurora Hydrogen and Sumitomo Chemical have been developing microwave-assisted methane pyrolysis as another means of energy supply and taking this technology to pilot scale. Similarly, C-Zero uses an undisclosed molten liquid as a combination of heat transfer medium and catalyst. It's likely that new startups developing unconventional approaches to methane pyrolysis will emerge as academic projects spin out into companies.

Despite all the companies endeavouring to commercialise their technologies, however, the misalignment of carbon black and hydrogen market size is still impeding commercialisation. The global carbon black market today is estimated at 15 million tonnes/annum – if all of this carbon black were to be supplied by methane pyrolysis, it would correspond to a hydrogen production of 6 million t/a, which is just 8% of the global hydrogen market. Therefore, deploying methane pyrolysis at the global scale will crash the carbon black market and essentially make it worthless. With the new entrants and increasing competition in the methane pyrolysis space, a handful of companies now claim they can compete on cost with blue hydrogen without selling the carbon black. These claims, though, have yet to be proven. ■