LCRI LOW-CARBON RESOURCES INITIATIVE

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EXECUTIVE SUMMARY

Methane Pyrolysis Process Model Development

Low-carbon hydrogen (H_2) has the potential to be deployed as an effective decarbonization tool across the energy economy. The majority of hydrogen produced today is through carbon intensive processes such as steam methane reforming (SMR), autothermal reforming (ATR) or coal gasification. These technologies could be equipped with carbon capture technologies, but this would require access to suitable geologic formations to permanently store the captured CO_2.[1] Emerging clean hydrogen production technologies include electrolyzers paired with low-carbon electricity sources and methane pyrolysis. The electrolyzer technology utilizes electricity to breakdown water molecules to generate gaseous hydrogen and oxygen, whereas methane pyrolysis utilizes heat to breakdown natural gas molecules to gaseous hydrogen and solid carbon. There are many commercial and emerging methane pyrolysis technologies which are at various stages of commercialization.[2] This report provides insight into the production of low-carbon hydrogen from catalytic methane pyrolysis, as catalytic pyrolysis requires a lower heat input compared to plasma or thermal pyrolysis. For catalytic pyrolysis, in-house Aspen plus models were developed for various process scenarios to develop mass and energy balances. These models were utilized to evaluate and produce data on Well-to-Gate (WTG) emissions and preliminary cost information.

KEY INSIGHTS

The objective of this report is to provide an in-depth analysis on the catalytic methane pyrolysis process including heat and material balances, life cycle analysis, product carbon markets and cost analysis. Key insights for this report include:

- From the literature reviewed, catalytic methane pyrolysis process requires lower heat input compared to thermal or plasma pyrolysis processes as catalytic processes operate at lower temperatures (700–900°C) than thermal or plasma (≥ 1200°C). Challenges such as catalyst deactivation, separation and reproduction vary significantly based on the type of catalyst used.
- For the catalytic methane pyrolysis process, both metallic and non-metallic catalysts are being studied. The metallic catalysts options are metal, or molten metal/salt form and the non-metallic catalyst options are carbonaceous catalyst. Though carbonaceous catalysts have easier catalyst separation process, the commercial development of this process is

1 *Blue Hydrogen Production*. EPRI, Palo Alto, CA: 2023. 3002021307.

2 *State of Technology – Methane Pyrolysis*. EPRI, Palo Alto, CA: 2022. 3002021275.

seen as challenging. As a result, metallic catalysts could be commercialized sooner relative to other catalytic methane pyrolysis processes as metallic catalysts have been utilized for other commercial processes for decades.

- Catalytic methane pyrolysis processes for three separate heat sources, hydrogen combustion, natural gas combustion and electrical heating where modelled and their associated efficiencies evaluated:
  - For hydrogen as heat source, 25% (mass basis) product hydrogen is combusted to produce the required heat. With carbon as a by-product the process efficiency is 79.8%*. The natural gas and electricity inputs for this process are 2.5 GJ and 0.05 GJ per GJ of hydrogen respectively.
  - For natural gas as heat source, the process efficiency with carbon as by-product is 83.3%*. The natural gas and electricity inputs for this process are 1.9 GJ and 0.04 GJ per GJ of hydrogen respectively.
  - For electricity as heat source, the process efficiency with carbon as by-product is 84.1%*. The natural gas and electricity inputs for this process are 1.9 GJ and 0.24 GJ per GJ of hydrogen respectively.
- The associated WTG GHG emissions for catalytic methane pyrolysis process with hydrogen, natural gas, and electricity as heat source are 0.77, 1.55, and 1.5 kg CO_2 eq/kg H_2 respectively*. Based on mass allocation, U.S. grid mix, steam displacement credits and carbon as by-product. For this study, the methane leakage rate during natural gas recovery, processing and distribution is assumed to be ~0.9% of methane consumed by reformer similar to the assumptions in GREET 2023 model.
- The WTG GHG emissions for catalytic methane pyrolysis process with hydrogen as heat source case but with 100% renewable natural gas (RNG) as feedstock are:
  - From landfill sourced RNG: 1.28 kg CO_2 eq/kg H_2
  - From wastewater sludge sourced RNG: 2.42 kg CO_2 eq/kg H_2
  - From animal waste sourced RNG: -8.93 kg CO_2 eq/kg H_2 (Negative Emissions)
  - From food waste sourced RNG: -4.37 kg CO_2 eq/kg H_2 (Negative Emissions)
  - All based on mass allocation, U.S. grid mix, steam displacement credits and carbon as by-product
- For scenarios with renewable and natural gas feedstock blends: The WTG GHG emissions for a catalytic methane pyrolysis process with hydrogen as heat source but with a blend of 90% natural gas and 10% renewable natural gas (RNG) as a feedstock:
  - From animal waste sourced RNG: -0.2 kg CO_2 eq/kg H_2 (Negative Emissions)

  Based on mass allocation, U.S. grid mix, steam displacement credits and carbon as by-product.
- Comparison of the catalytic methane pyrolysis process using hydrogen as heat source and carbon as by-product, alongside SMR with capture (96.17%) and ATR with capture (95%) were also made:
  - The process efficiency of methane pyrolysis case (79.8%)* is higher than SMR with capture case (64.5%) but lower that ATR with capture case (83.3%).
  - The WTG GHG emissions are lower than both SMR with capture case (3.3 kg CO_2 eq/kg H_2) and ATR with capture case (4.23 kg CO_2 eq/kg H_2).
  - For natural gas blended with renewable natural gas case (with carbon as waste product), the WTG GHG emissions decrease to -1.05 kg CO_2 eq/kg H_2 (Negative Emissions).

* If carbon is considered as waste product, the process efficiency decreases and the WTG GHG emissions increase. This scenario has been further evaluated in the report.

- Due to the limited availability of reactor cost data in open literature, only the estimated costs for the balance of plant of the catalytic methane pyrolysis process are included. The basic cost analysis indicated that with electricity as heat source, the total annual costs may be lower compared to the hydrogen and natural gas a heat source. However, substantially more detailed work is required, with fully engaged individual technology suppliers and developers to estimate the component costs of these emerging pyrolysis options.
- Potential carbon byproduct market applications highlighted are graphite, carbon fiber, carbon nanotubes, needle coke or carbon black. However, the final price of carbon and market size will depend on the specific morphological structure of the carbon formed during the individual methane pyrolysis process. Requiring further investigation with technology developers test samples.

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THE LOW-CARBON RESOURCES INITIATIVE

This report was published under the Low-Carbon Resources Initiative (LCRI), a joint effort of EPRI and GTI Energy addressing the need to accelerate development and deployment of low- and zero-carbon energy technologies. The LCRI is targeting advances in the production, distribution, and application of low-carbon energy carriers and the cross-cutting technologies that enable their integration at scale. These energy carriers, which include hydrogen, ammonia, synthetic fuels, and biofuels, are needed to enable affordable pathways to economy-wide decarbonization by mid-century. For more information, visit www.LowCarbonLCRI.com.

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