

A semi-continuous process for co-production of CO₂-free hydrogen and carbon nanotubes via methane pyrolysis

Hydrogen that is free of greenhouse gas (GHG) emissions is a key vector to fuel a net-zero emissions economy, but today's H₂ is sourced from fossil fuels mostly by the highly emissions-intensive processes of steam methane reforming (SMR) or coal gasification. Water electrolysis, the only viable technology that can produce CO₂-free H₂ today, produces H₂ at costs 3–4 times higher (~\$4/kg) than SMR and will have difficulty achieving the target \$1/kg H₂ production cost target of the US Dept. of Energy H₂ Earthshot.

Methane pyrolysis is a technology that could reach the \$1/kg-H₂ production target given that the energy intensity of H₂ production of methane pyrolysis is much lower than water electrolysis and given that the produced carbon byproduct can be sold to offset the H₂ production cost. However, methane pyrolysis technologies have historically been stymied by catalyst deactivation via coking.

With this technology, we developed a semi-continuous heterogeneous catalytic CH₄ pyrolysis process to produce CO₂-free H₂ and high-value carbon consisting of the following cyclic steps:

1. CNT growth by concentrated CH₄ pyrolysis in a fluidized-bed reactor
2. In situ CNT dislodging (i.e., inside the reactor) and CNT recovery and collection by vigorous fluidization with humidified argon

The term "semi-continuous" is defined as a process that can run continuously without requiring cooldown of the reactor or removal of the catalyst from the reactor for catalyst regeneration. In a commercial process, this semi-continuous process would be operated in a continuous manner by flow switching between multiple

reactors operating in parallel (pyrolysis, purge, regeneration, reduction, etc.).

Stage of Development

Proof-of-concept

Applications

- Hydrogen: ammonia/fertilizers, methanol, refining, steelmaking, fuel-cell vehicles
- Carbon nanotubes: composites materials like carbon fiber, concrete, cement; structural materials, electronics, automotive, aerospace, sporting equipment, tires, rubber

Advantages

- H₂ production at high H₂ yields and high CH₄ conversion with negligible process CO₂ production
- Highly crystalline CNT co-production at high yields
- In-situ CNT dislodging for repeated catalyst use
- Simple, scalable heterogeneous catalyst made from abundant materials
- Potential for \$1/kg H₂ production cost with further research and development

Publications

- Gigantino M, Moise H, Saad D, Fishman J, Nelson A, Voorhis H, et al. [Oxidant-assisted methane pyrolysis](#). *ChemRxiv*. 2024
- Sun, E., Zhai, S., Kim, D., Gigantino, M., Haribal, V., Dewey, O. S., ... & Majumdar, A. (2023). ["A semi-continuous process for co-production of CO₂-free hydrogen and carbon nanotubes via methane pyrolysis."](#) *Cell Reports Physical Science* 4, 101338.

Patents

- Published Application: [WO2024156001](#)

Innovators

- Arunava Majumdar
- Dohyung Kim
- Shang Zhai
- Eddie Sun
- Matteo Cargnello
- Raghbir Gupta
- Vasudev Haribal
- Andrew Tong
- Marco Gigantino

Licensing Contact

Evan Elder

Associate Director, Licensing and Strategic Alliances, Physica

[Email](#)