Docket #: S22-337

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

- H_2 production at high H_2 yields and high CH_4 conversion with negligible process CO_2 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 H_2 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
- Raghubir Gupta
- Vasadev Haribal
- Andrew Tong
- Marco Gigantino

Licensing Contact

Evan Elder

Senior Licensing Associate

Email