

Biomethane Pyrolysis: A Green Route to Ultrapure Carbon and Sustainable Nanomaterials

Presented by

Sanjay G. Chaudhri, Ph.D.

Project Leader: Prof. Sachin M. Chavan

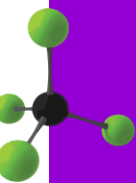
Postdoctoral Fellow,

University of Stavanger

3rd Sep. 2023



This project has received funding from the European Union's Horizon Europe Research and Innovation Programme under grant agreement No. 101069931 (ColdSpark). This output reflects only the author's view and the European Union cannot be held responsible for any use that may be made of the information contained therein.

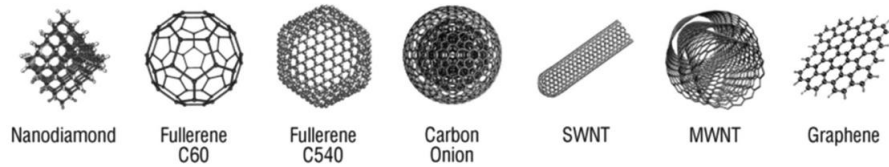
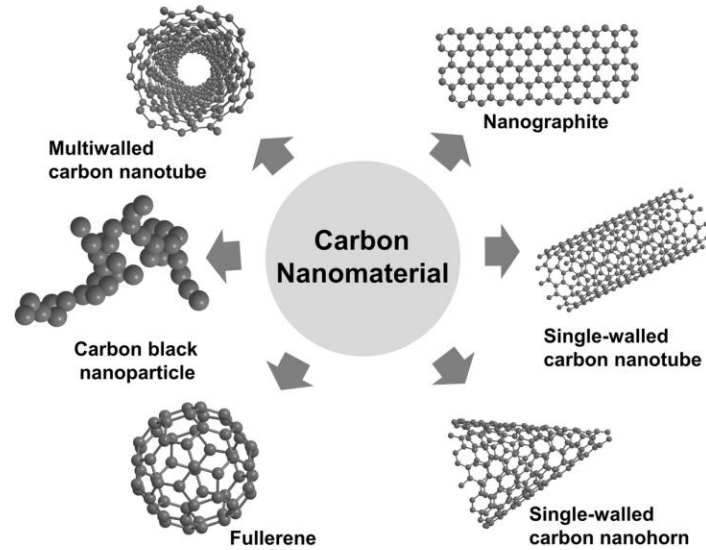


Outline

- 1. Carbon-based nanomaterials and its application***
- 2. Case study: Carbon black synthesis and CO₂ footprint***
- 3. Biomethane: CO₂-free fuel and source to prepare the carbon material***
- 4. What is biomethane pyrolysis: Process and Products?***
- 5. Technologies for Biomethane Pyrolysis: Carbon and Hydrogen Production***
- 6. Carbon Black Synthesis: Microwave Plasma Methane Pyrolysis***
- 7. CNT by Methane Pyrolysis in fluidized-bed reactor***
- 8. Economic and Industrial Viability of Biomethane Pyrolysis***
- 9. Challenges, Future Directions and Conclusion***

Carbon-based nanomaterials and its application

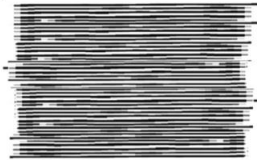
Types of Carbon



sp^3

$sp^2 + \pi$

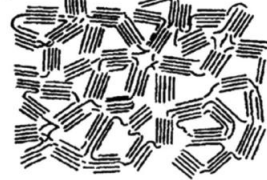
A



B



C



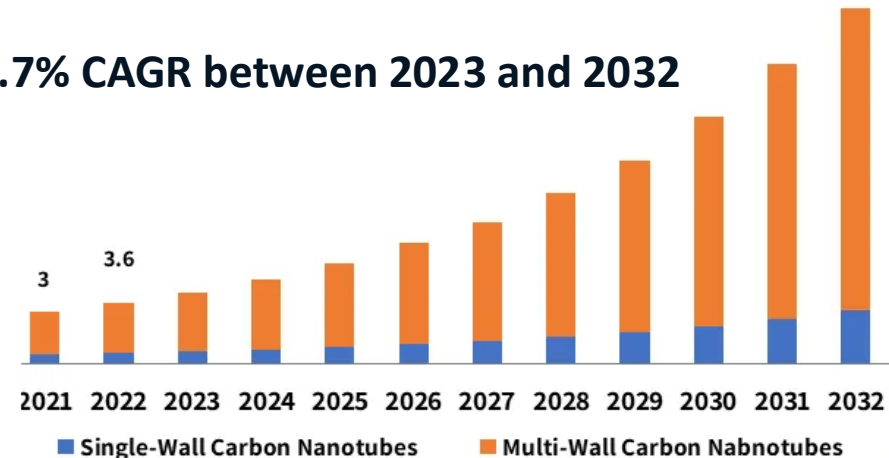
Market of carbon black



Market of CNTs

Global Carbon Nanotubes Market Size, By Product, 2021 - 2032 (USD Billion)

20.7% CAGR between 2023 and 2032

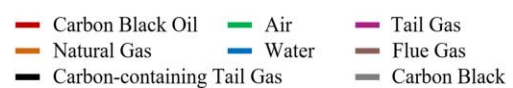
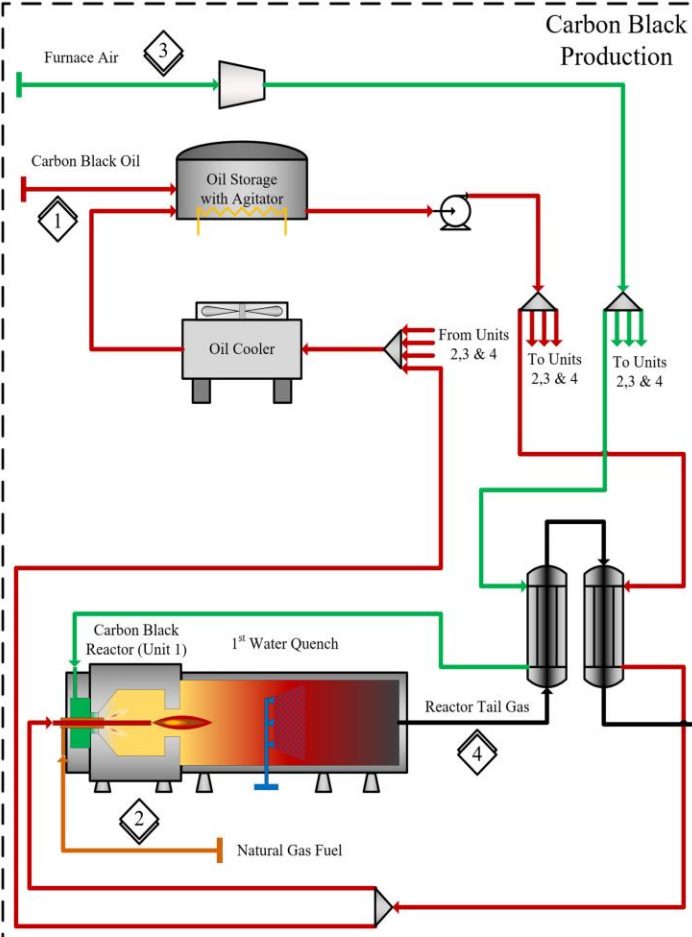


Source: www.gminsights.com

- (1) Fulcheri, Laurent, et al., *International Journal of Hydrogen Energy* 48.8 (2023): 2920-2928. (2) <https://www.gminsights.com>
 (3) Veeman, Dhinakaran, et al. *Journal of Nanomaterials* 2021.1 (2021): 5840645. (4) Yuan, Xia, et al., *Particle and fibre toxicology* 16 (2019): 1-27.

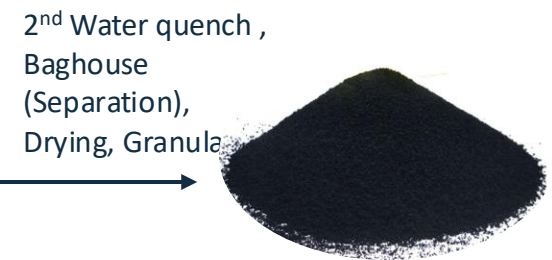
Case study: Carbon black synthesis and CO₂ footprint

Furnace black process

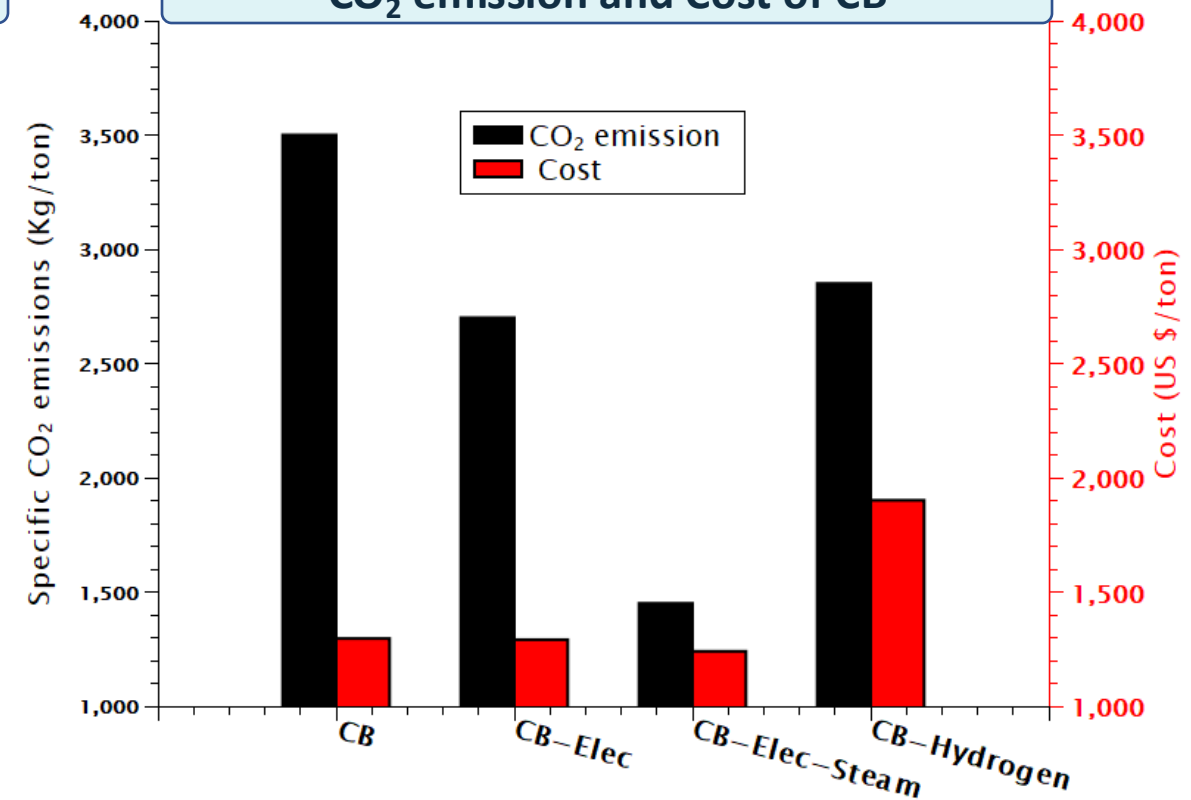


Feedstock composition

Compound	wt.-%
Naphthalene	10.0
Methylnaphthalene	20.0
Biphenyl	10.0
Fluorene	5.0
Anthracene	5.0
Pyrene	50.0
H ₂ S	40 ppm



CO₂ emission and Cost of CB

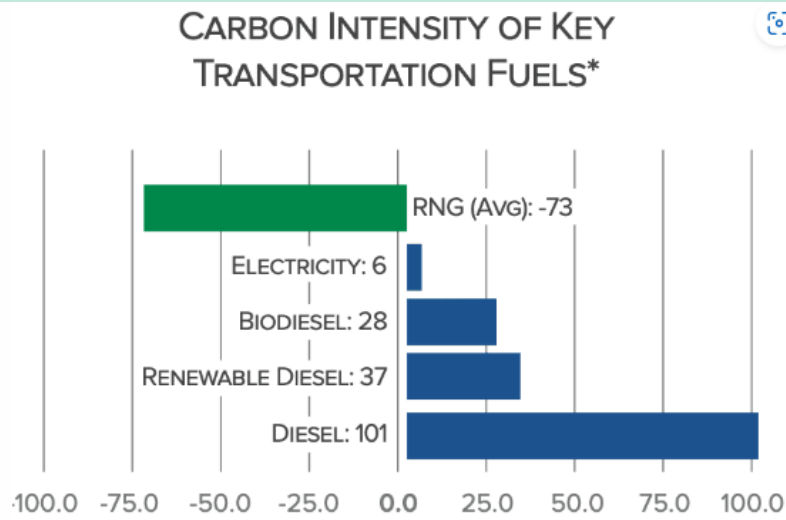
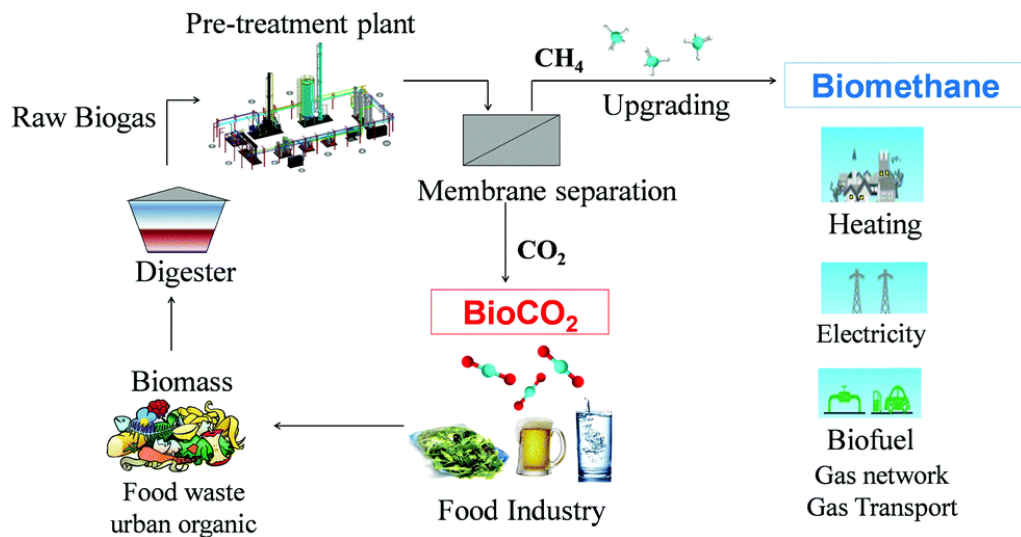


Process Scenarios : Furnace black process

- Conventional carbon black production emits approximately 3.50 kg CO₂ per kg of carbon black.
- Relies on fossil fuels, leading to high CO₂ emissions and other pollutants (CO, SO_x, NO_x, particulate matter).
- Current production processes are inefficient (39.6% energy efficiency) and environmentally harmful.

Ref: (1) [EFDB - Basic Search \(iges.or.jp\)](http://EFDB-Basic-Search(iges.or.jp))

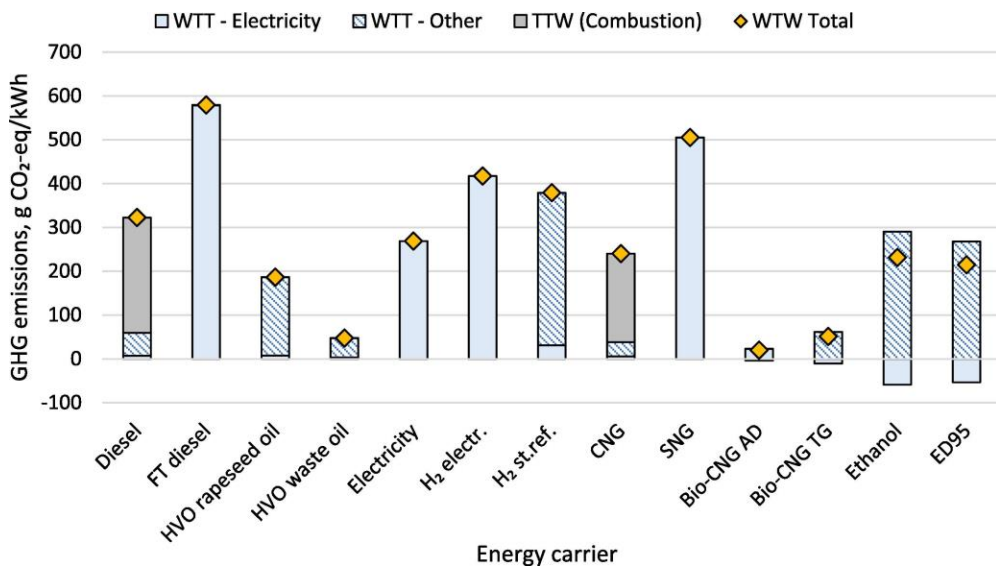
Biomethane: CO₂-free fuel and source to prepare the carbon material



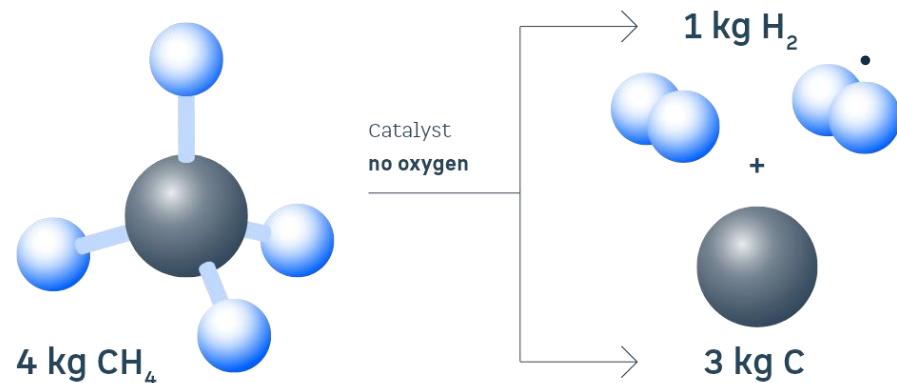
* CALIFORNIA AIR RESOURCES BOARD LCFS CERTIFIED PATHWAYS (2023); ADJUSTED FOR HEAVY-DUTY TRUCK APPLICATIONS

- The EU's REPowerEU Strategy has set a target of 35 billion cubic metres (bcm) of biomethane production by 2030.
- Anaerobic digestion biomethane can achieve negative (-30-70 % with Respect to Diesel) GHG emissions if the electricity used in the process is from a low-carbon source.

Total greenhouse gas emissions per kWh for the energy carriers (Well –to-wheel)



Carbon and Turquoise Hydrogen from methane



- If digestate from biogas production is considered to replace mineral fertilizer (ISO standards for LCA), the climate benefits of using LBM instead of diesel are even larger.

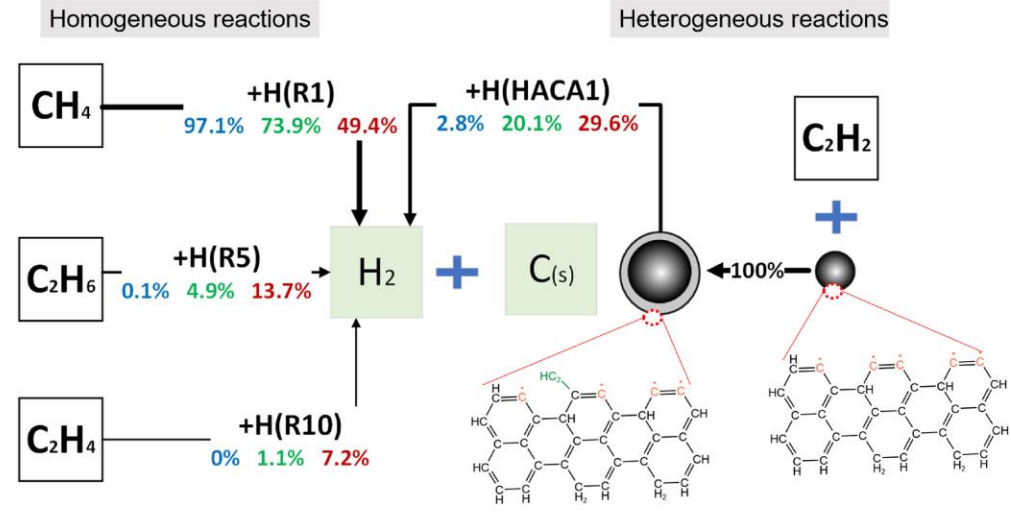
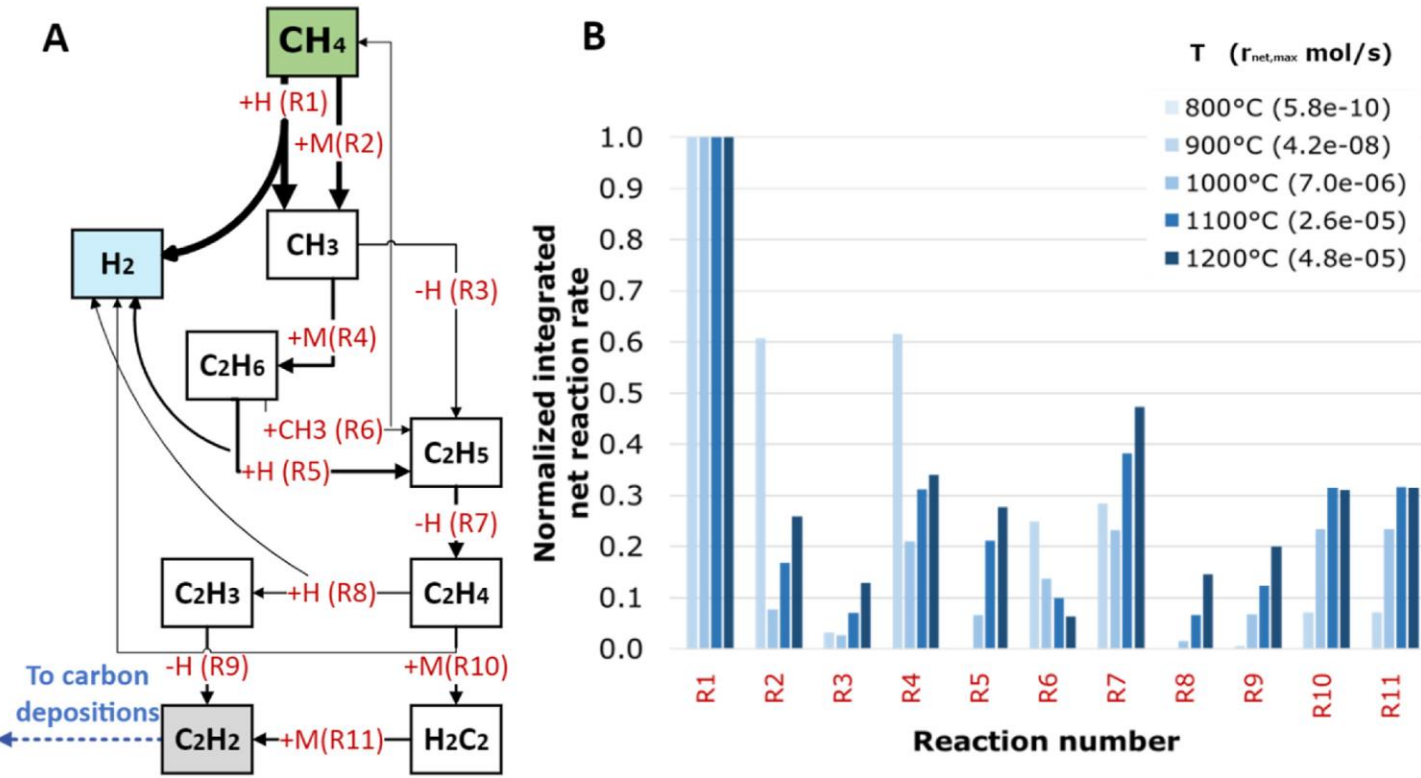
With LBM from manure, the climate change impact could be reduced by 100-125%, and with LBM from food waste by 80-105%

(1) Gustafsson, Marcus, and Niclas Svensson. "Cleaner heavy transports—Environmental and economic analysis of liquefied natural gas and biomethane." *Journal of Cleaner Production* 278 (2021): 123535. (2) Gustafsson, Marcus, and Niclas Svensson. *Journal of Cleaner Production* 278 (2021): 123535. (3) [Renewable Natural Gas – CNGVP](#) (4) [Green Fuel \(weltec-biopower.com\)](#)

What is biomethane pyrolysis: Process and Products?

Methane pyrolysis: It is a process that to split methane (CH_4) into hydrogen (H_2) and solid carbon in absence of oxygen.

Products Probability (%)
900°C (Blue), 1000°C (Green) and 1200°C (Red)



The formation of carbon (37 aromatic rings) is carried out by a combination of C₂ gases and hydrogen abstraction mechanisms, depending on the temperature and the use of a catalyst

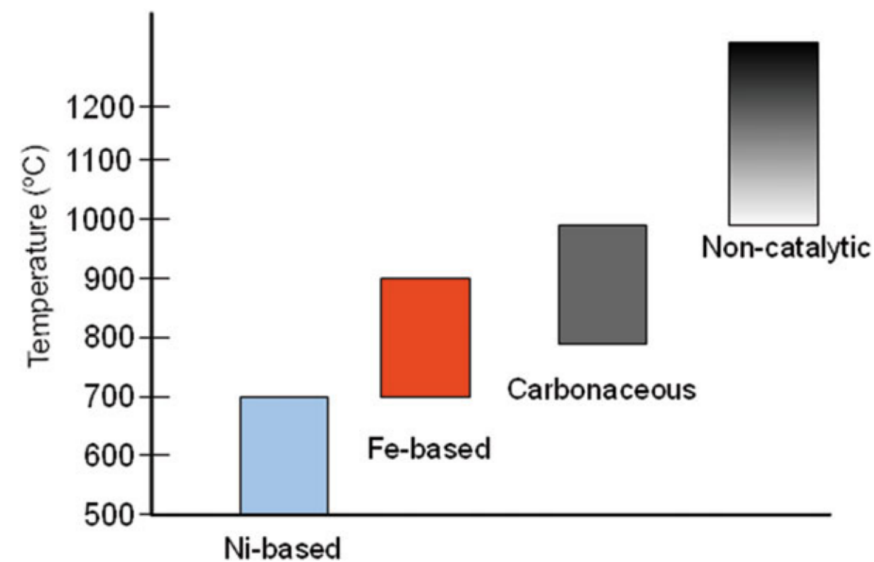
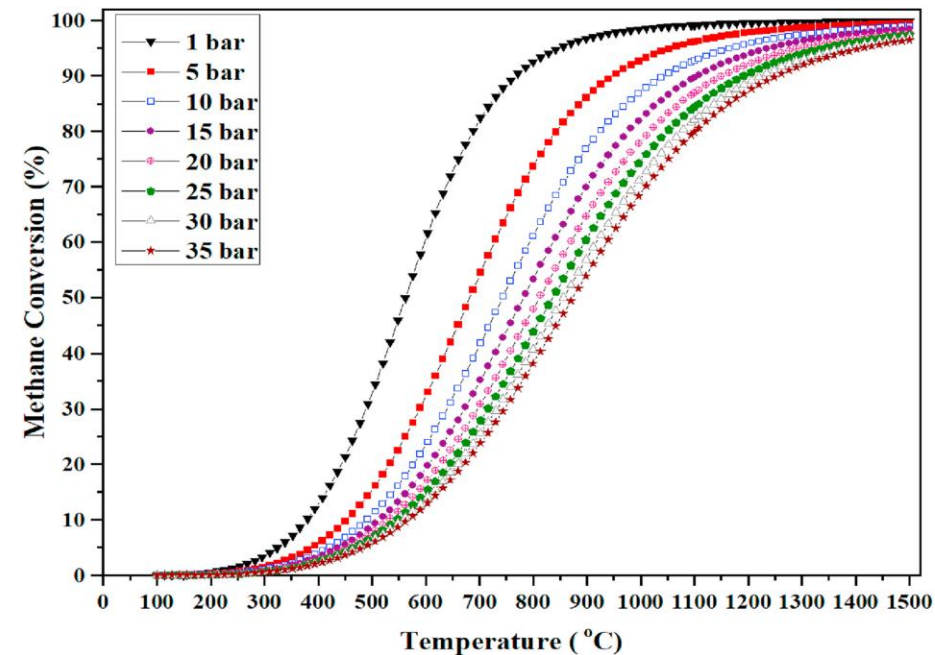
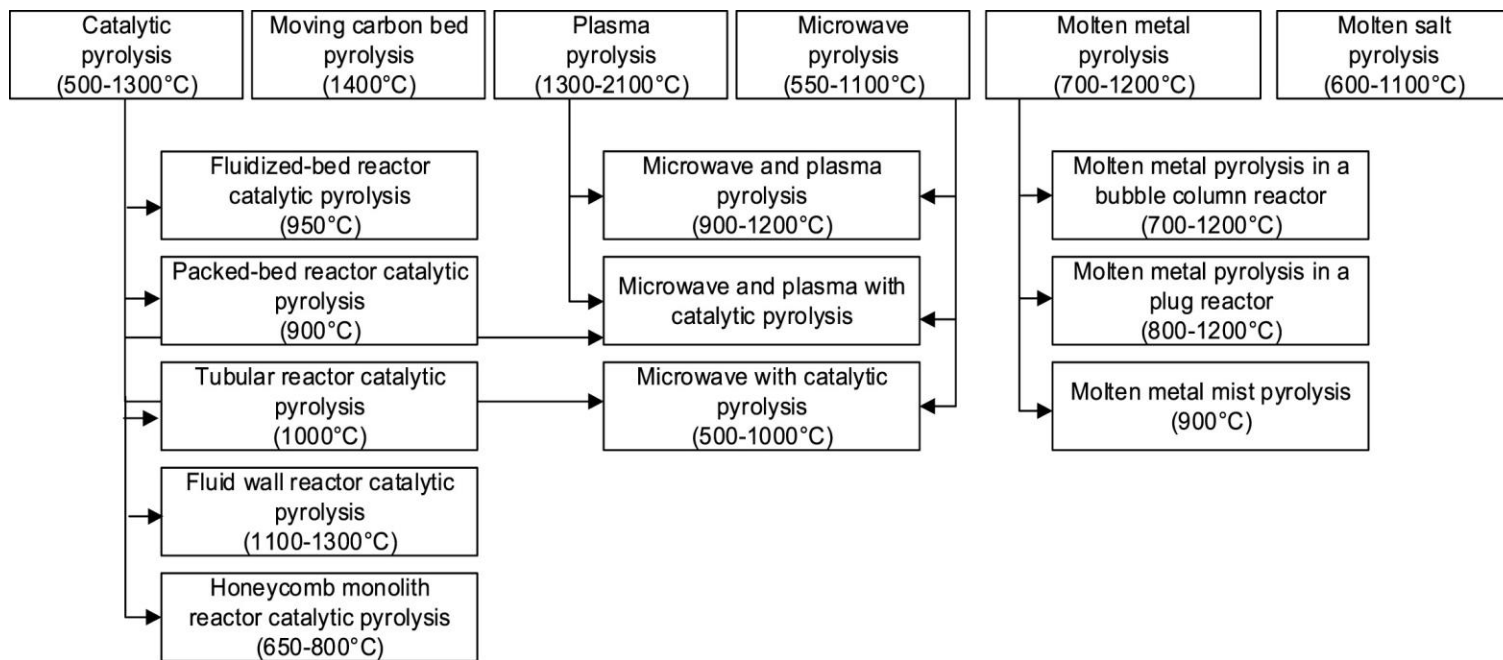
Probable gaseous products

H₂ (Hydrogen), C₂H₂ (Acetylene), C₂H₄ (Ethylene), C₂H₆ (Ethane), C₃H₆ (Propylene)

(1) Salakhi, Mehdi, Francisco Cepeda, and Murray J. Thomson. , International Journal of Hydrogen Energy 77 (2024): 997-1008.,

Technologies for Biomethane Pyrolysis: Carbon and Hydrogen Production

Breaking C-H bonds requires overcoming an energy barrier (75.6 kJ/mol, which makes overall process endothermic (Requirement of high energy input)).

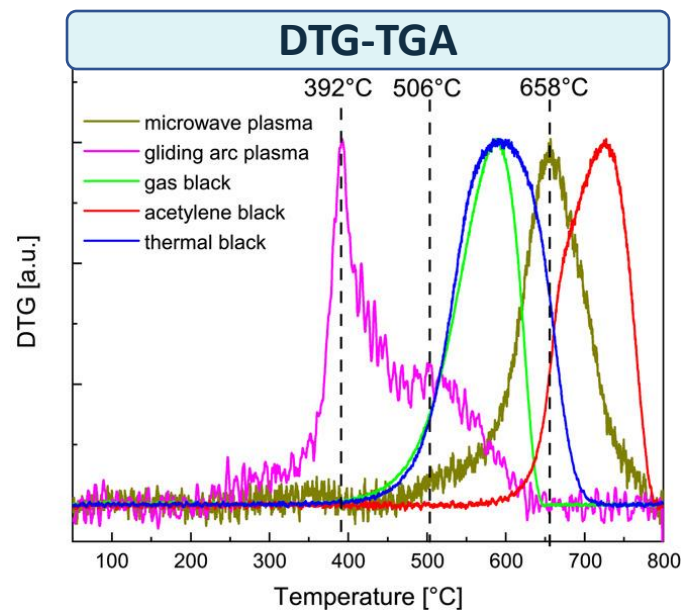
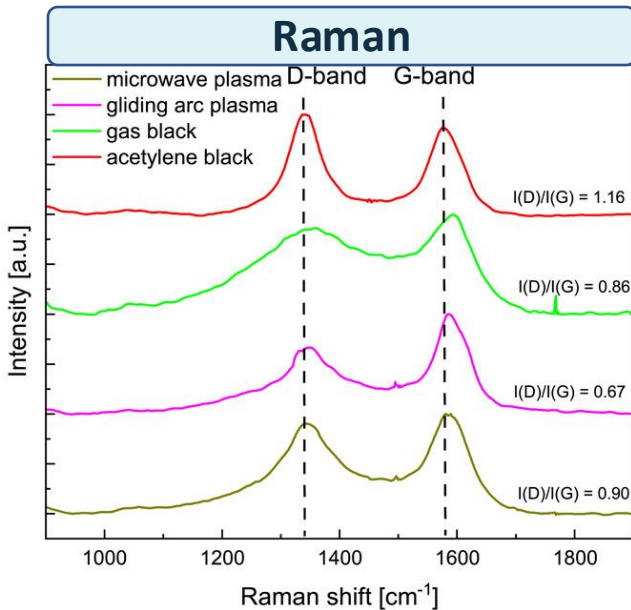
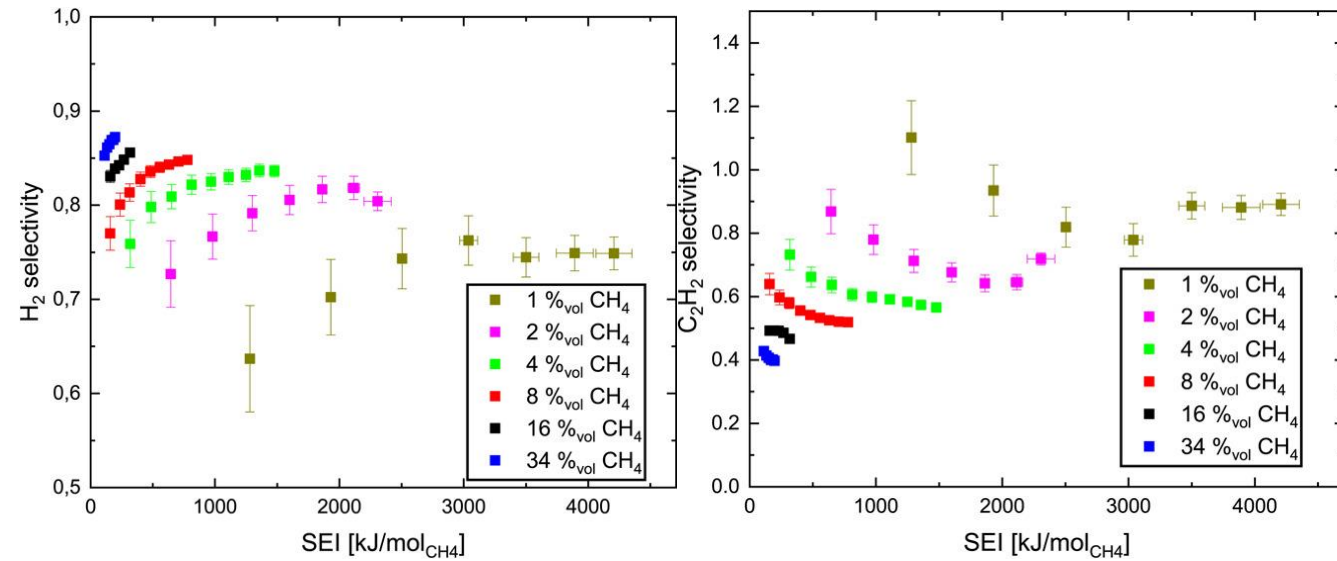
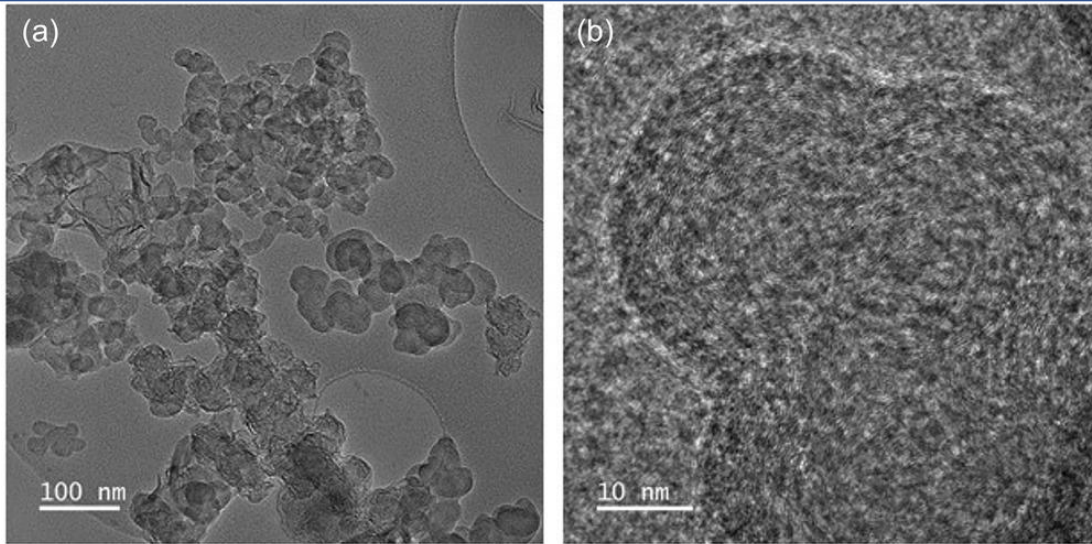


- Energy is provided by high-temperature heating with or without a catalyst.
- The use of a catalyst or plasma activation reduces the temperature requirement.

(1) Patlolla, Shashank Reddy, et al. ,Renewable and Sustainable Energy Reviews 181 (2023): 113323. (2) Abánades, Alberto. Production of hydrogen from renewable resources (2015): 149-177.

Carbon Black Synthesis by Microwave Plasma Methane Pyrolysis

Flow rate: 60 LPM (16 LPM CH₄, 24%), SEI = 235 kJ/mol



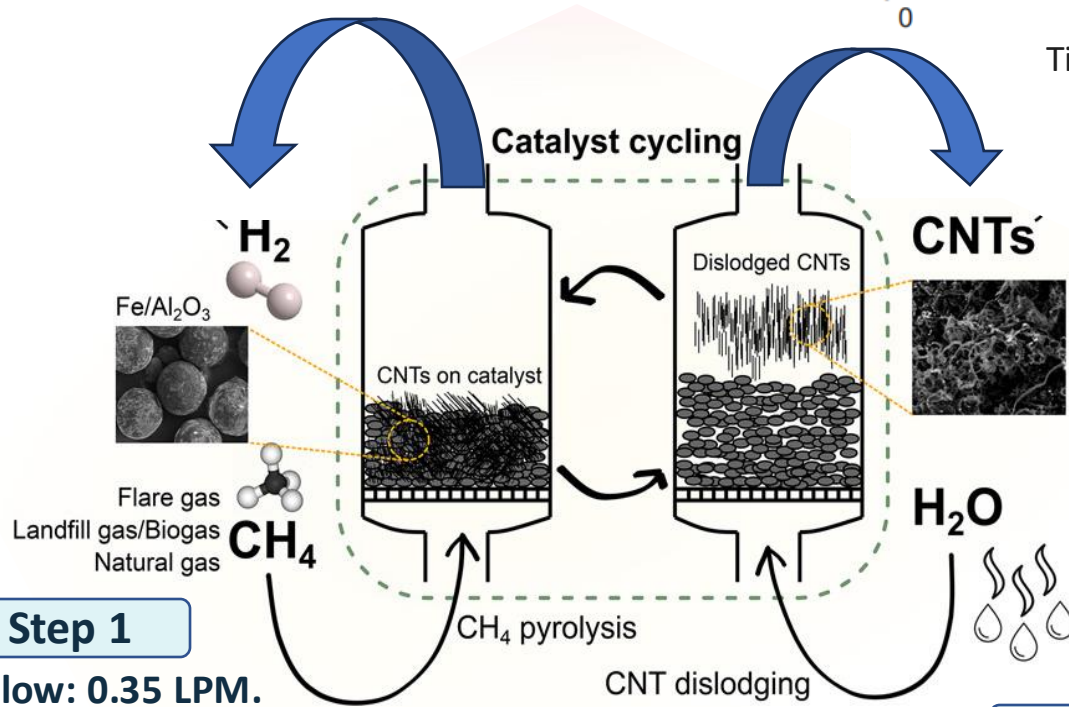
- A higher $I(D)_{1350}/I(G)_{1580}$ ratio indicates a greater amorphous nature of the carbon due to the presence of defects in the sp^2 lattice.
- Thermal analysis shows that carbon from MPT exhibits superior thermal oxidation stability, with the highest mass loss occurring at 658°C, which is comparable to acetylene black.

CNT by Methane Pyrolysis in fluidized-bed reactor

10 cycles of semi-continuous CNT growth was demonstrated by researcher (Stanford University)

Step 3

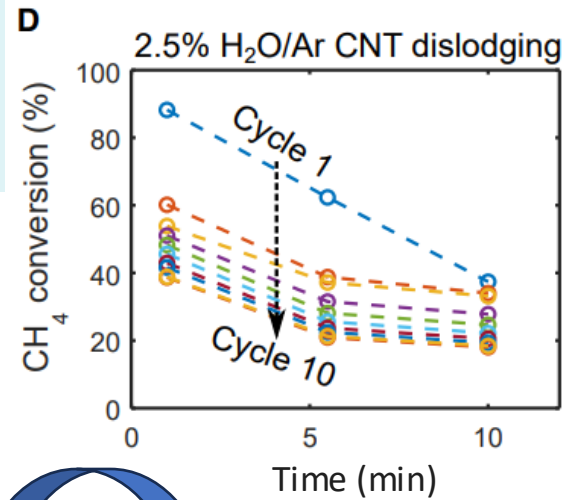
Catalyst generation (0.5 flow of pure H₂ for 10 min)



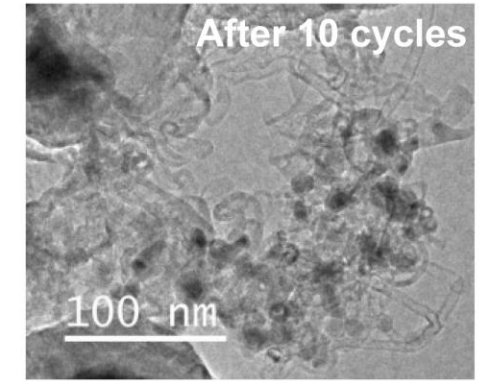
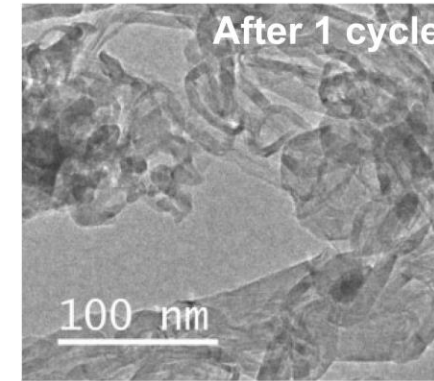
Step 1

CH₄ Flow: 0.35 LPM.
Temperature : 850° C
Catalyst: Fe/ γ -Al₂O₃

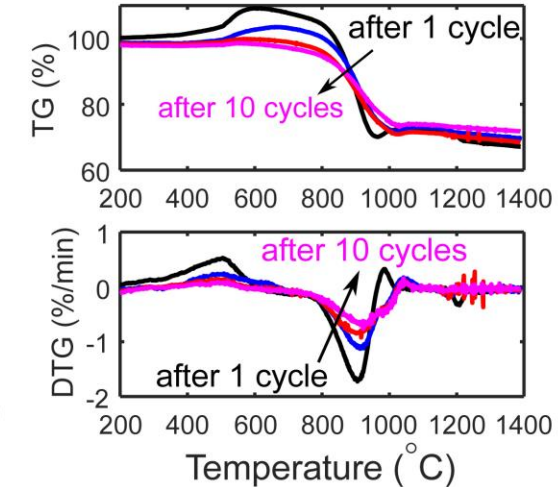
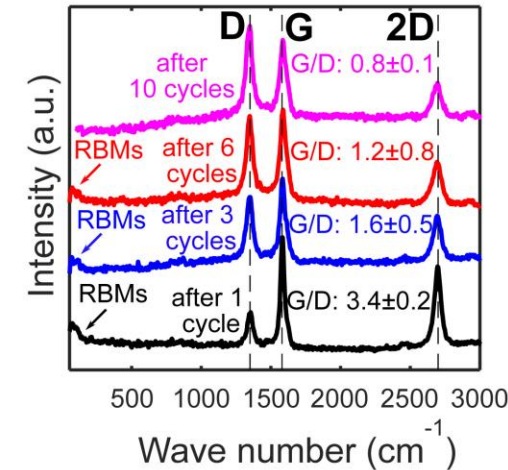
CNT was collected or dislodged by purging 2.5% H₂O/Ar at 3 LPM rate.



TEM



TGA-DTG analysis

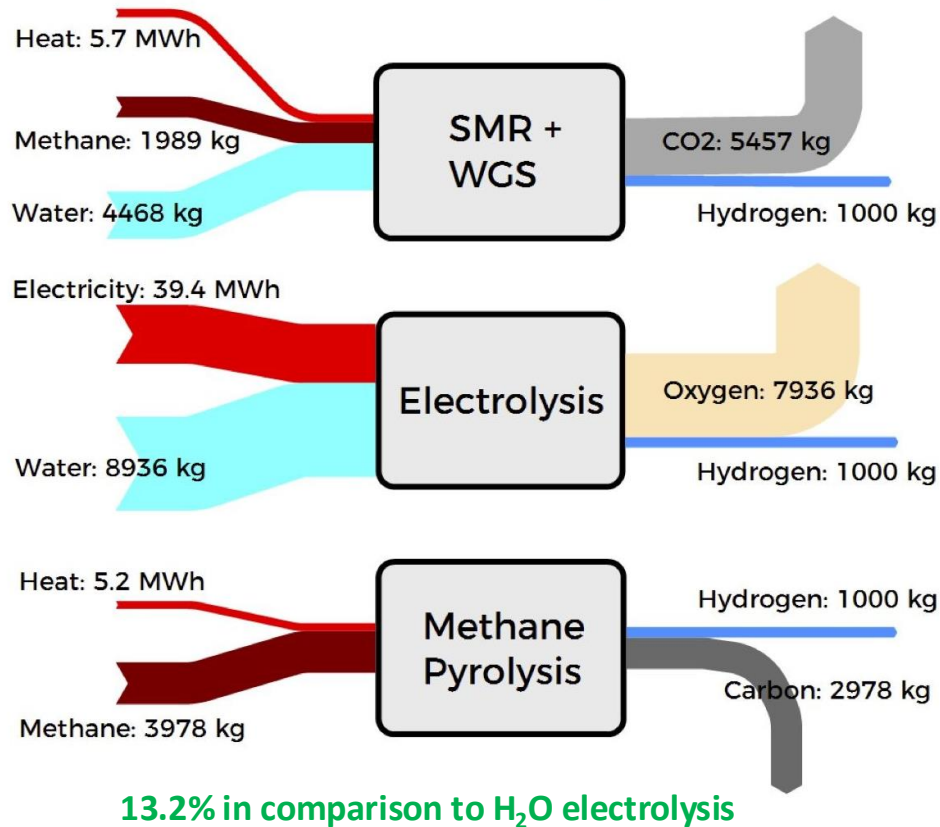


Economic and Industrial Viability of Biomethane Pyrolysis

Energy required for 1000 kg of H₂

HYDROGEN PRODUCTION PATHWAYS

(at 100% efficiency)



Hydrogen Production Technology Comparison

H ₂ production technology	reactor type	catalyst	cost of H ₂ (\$/kg)	GHG emissions (kg of CO ₂ equiv/kg of H ₂)	energy source	key cost factors
SMR without CCS	PFR	Ni-based	0.7–2.1	11.9	natural gas	natural gas price
SMR with CCS technology	PFR	Ni-based	1.40–3.60	1.54	natural gas	natural gas price, CCS cost
electrolysis (PEM)	polymer electrolyte membrane	no catalyst	3.56–7.7	3.49	electricity	electricity price, equipment cost
electrolysis (alkaline)	alkaline electrolyzer	no catalyst	3.2–5.8	3.40	electricity	electricity price, equipment cost
electrolysis (SOEC)	solid oxide electrolysis cell	no catalyst	9.6	6.91	electricity	electricity price, equipment cost
gasification (coal/biomass) without CCS	gasifier (FBR)	no catalyst	1.9–2.6	23 (coal); 4.0 (biomass)	coal/biomass	raw material price, equipment cost
MP (thermal)	PFR	no catalyst	0.50–2.14	0.50–1.10	natural gas	high energy input, carbon market
MP (molten salt)	LMBC	KCl–MnCl ₂	1.80	0.82–8.13	natural gas	salt cost, carbon market
MP (molten media)	LMBC	Ni–Bi metal and salt	1.70	0.76–2.58	natural gas	media cost, carbon market
MP (solid catalyst)	FBR	Fe-based	3.20–3.50	1.63–16.34	natural gas	catalyst cost, carbon market
MP (molten metal)	hot cyclone reactor	Zn-based	3.40	1.18–11.76	natural gas	Zn cost, carbon market
MP (molten Ga)	LMBC	gallium-based	2.20	0.70–2.20	natural gas	gallium cost, carbon market
MP (plasma)	plasma reactor	no catalyst	3.9	1.64	electricity	electricity price

- **Thermal Plasma:** Hydrogen cost is 27-68% lower than **SMR + CCS**.
- **Microwave Plasma:** Hydrogen cost is 6.1% higher than **SMR + CCS**.

- By offsetting the cost of produced carbon black, **the cost of hydrogen could reach as low as \$0.1–\$0.9 per kg**, potentially achieving negative CO₂ emissions if renewable energy is used.

U.S. Department of Energy has set a goal to produce GHG-free hydrogen at \$1/kg by 2030.

Challenges, Future Directions and conclusion

Challenges for methane pyrolysis

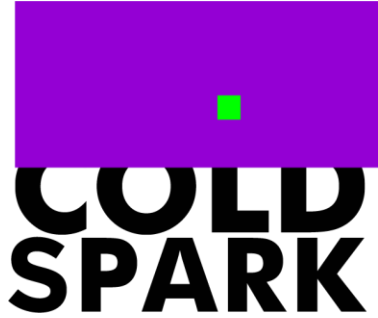
- **Carbon Quality:** Achieving consistent carbon quality while maintaining high hydrogen yield remains a significant challenge.
- **Catalyst Recycling:** Ensuring the long-term activity and stability of catalysts is a critical hurdle.
- **C2-C4 Hydrocarbon Purification:** Methane pyrolysis produces C2-C4 hydrocarbons as byproducts, which require thorough purification to obtain pure hydrogen
- **Biogas Impurities:** Complete removal of impurities from biogas is essential.

Future direction

- **Reactor Design** Designing reactor to ensure uniform temperature distribution and efficient energy delivery is crucial for enhancing carbon quality and hydrogen yield.
- **Catalyst Optimization:** Further research is required to make more effective and recyclable catalysts, such as iron (Fe), to improve long-term performance and cost-effectiveness.
- **Enhancing hydrogen selectivity:** By refining reactor design and optimizing pyrolysis conditions (tailored to the specific reactor configuration) can decrease the C2-C4 production and increase the hydrogen yield.

Conclusion

- Biomethane pyrolysis is one of the most promising routes to produce CO₂-free hydrogen at a cost lower than \$1/kg, with the technology already at TRL 8.
- Improving carbon quality is crucial for the commercialization of methane pyrolysis, which will further drive down hydrogen production costs below \$1/kg.



Thank you.....

Question?

“To know how to wonder and question is the first step of the mind toward discovery.”

-Louis Pasteur



This project has received funding from the European Union's Horizon Europe Research and Innovation Programme under grant agreement No. 101069931 (ColdSpark). This output reflects only the author's view and the European Union cannot be held responsible for any use that may be made of the information contained therein.

