Industrial Methane Pyrolysis

2024 07

Difference to Electrolysis in energy cost

Gas clean up

Solids handling and disposal/sale. Large SMR makes 500 T H2/day and so 1500 T carbon.

Liquids

Equilibria Hydrogen Carbon at temperature

Conversion

Residence time

Fouling

Competitiveness without carbon taxes/subsidies

Competitiveness to SMR+CCS

The Opportunity: Much Less Energy

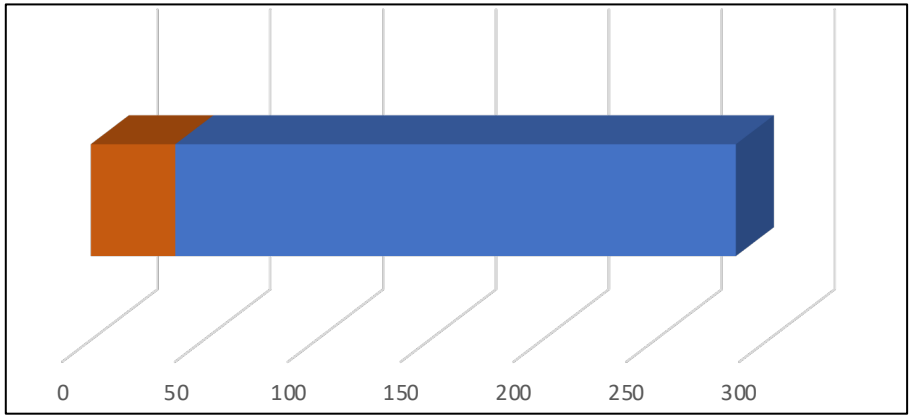
$CH_4 \rightarrow C_{(s)} + 2H_2$ $\Delta_f H°_{gas}$ -75 kJ/mol or -37 kJ/mol H_2

$2H_2O_{(l)} \rightarrow 2H_2 + O_2$ $\Delta_f H°_{gas}$ -286 kJ/mol H_2

Splitting water takes ~ 7.5 times the energy

This energy must come from electricity

- High Xergy
- High cost of green electricity
- Need hydrogen storage to just produce with excess renewable electricity



Pyrolysis Issues

Needs to take place at high temperatures

- ΔH to heat NG to 1300°C ~90 kJ/mol or 45 kJ/mol H_2

Solids handling and disposal/sale

- Large SMR's make 500 T H_2/day and so 1500 T carbon/day.
- Perhaps 75 trucks a day!

Fouling of reactor and catalyst by carbon

Slow reaction rates or even higher temperatures/pressures

Difficult to get the reactions to go to completion

Equilibria between carbon and hydrogen at temperature that makes CH_4 or C_2H_2 (>1500°C)*

Generates PAH's: Difficult to dispose of and handle.

- Gas at reactor temperature. Liquid at filtration temperatures. Solid/viscous liquid at room temperature.

Gas Clean Up: CH_4, C_2H_2, CO, PAH, Carbon vs SMR's CH_4, CO_2 & Moisture

Competitiveness without carbon taxes/subsidies

Competitiveness to SMR+CCS

*ntrs.nasa.gov/api/citations/19650010880/downloads/19650010880.pdf

Cost Competitiveness North America

SMR produces 4 mol H_2 / mol of NG. NG cost of ~$0.32 $/kg H_2 in NA.

- CCS for concentrated CO_2 streams ~$25/T[1] or $0.21/kg H_2
- More than half of the CO_2 is from combustion so more dilute, perhaps $100/T
- For comparison permits for the 8.5 kg CO_2 in Europe would cost ~1.10 $/kg

Pyrolysis produces 2 mol H_2 / mol of NG, or less. ~$0.65 $kg in gas cost in NA.

- Additional NG cost similar to CCS for SMR

SMR has about $1.50 / kg H_2 for process costs and profit.

Pyrolysis process will need to process twice the NG volume, handle the resulting carbon, and do that for ~20% less in processing cost

- Not counting losses of NG to the environment to get it to the reactor
- The new process also needs scaling up

NG cost in Europe and Asia much higher (~3x) so lower yield per kg NG costs more.

If burying carbon is free, how to compete in NA?

What if the carbon can be sold?

1. CCS concentrated streams $15-25/T. https://www.iea.org/commentaries/is-carbon-capture-too-expensive

Carbon Collection & Disposal/Sale

Will generate a lot of carbon

Given hydrogen demand there is not enough demand for carbon black, let alone nano-tubes or even graphite

- Demand for Hydrogen 120 MT/y
- Demand for Carbon Black 18 MT/y
- Demand for Graphite 3 MT/y
- Demand for Asphalt 1,400 MT/y (but ~$23/T)

Hydrogen demand is distributed with few regional hydrogen pipelines

- Generation at point of H_2 use complicates carbon handling
- Also complicates CCS

Carbon Deposits

Difficult to keep carbon off the reactor walls

Will also deposit on any solid catalyst

- Regenerating catalyst typically involves generation of CO_2 emissions, but may be the best option.

Liquids that contact the reactor wall will form coke

Carbon particles that stick to solids will form hard deposits in the presence of PAH's

Fluid wall reactors show a potential pathway for eliminating deposits

CFD can provide good guidance on completing reactions in free space

Liquid reactor systems would need a near ideal solid liquid separation

- And keep rising bubbles away from the walls

Size of Equipment

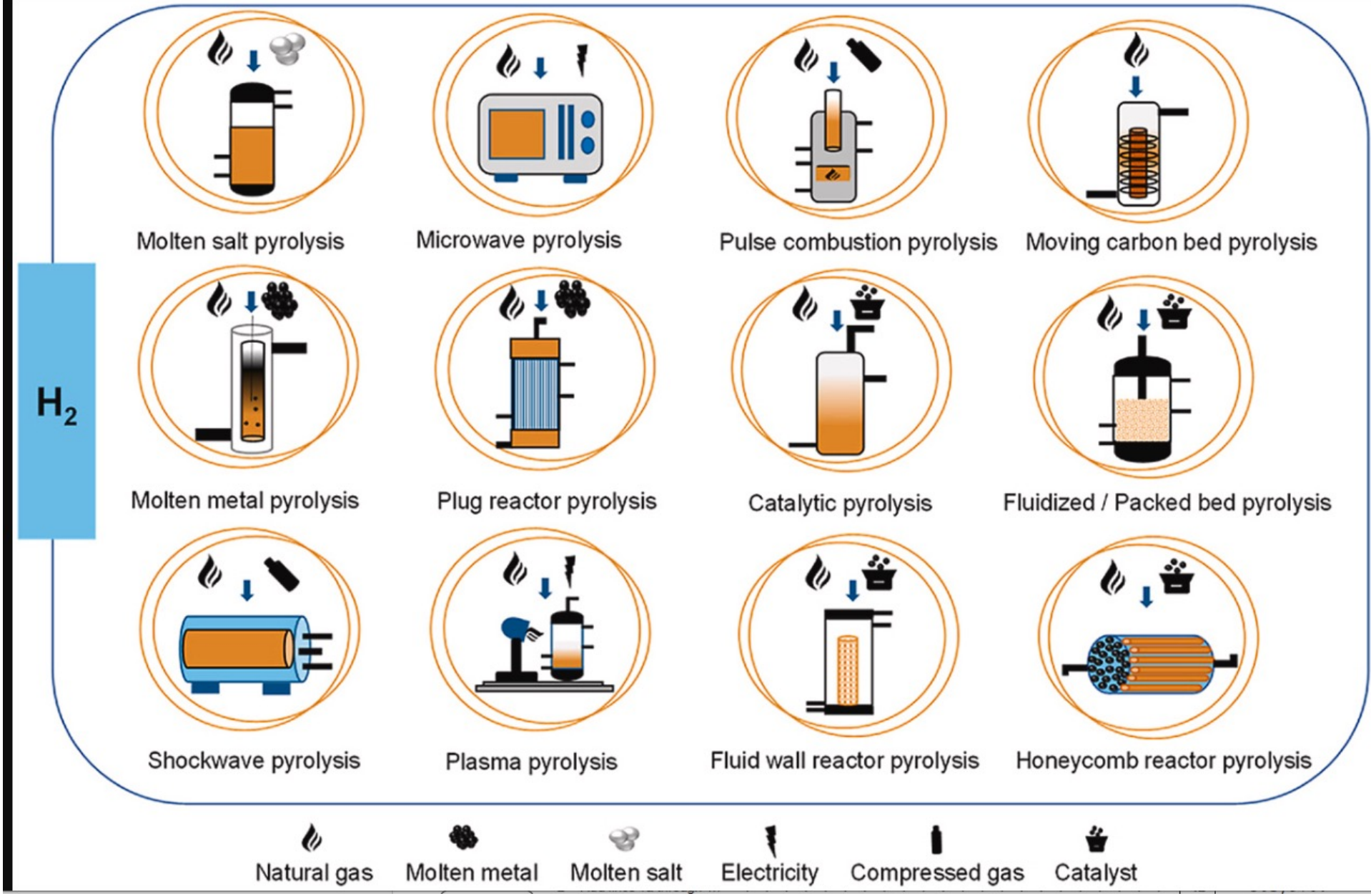
SMR reactors have residence times of well under 100 ms.

Carbon black reactors have a residence time of up to 2.0 s.

Methane pyrolysis literature reports several seconds.

Higher temperatures reduce the residence time required to 0.5 s.

I expect higher temperatures, 1500+°C will prevail in industry



A review of methane pyrolysis technologies for hydrogen production
https://doi.org/10.1016/j.rser.2023.113323