Plasma Assisted Catalysis for CO_2 Utilization

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U.S. Department of Energy

National Energy Technology Laboratory

Carbon Management and Natural Gas & Oil Research Project Review Meeting

Virtual Meetings August 2 through August 31, 2021

Project Overview (1/2)

- Funding and Performance Dates
  - Source: DOE
  - Phase I: $149,998 (02/2019 – 11/2019)
  - Phase II: $1,049,923 (04/2020 – 04/2022)
- Project Participants
  - Advanced Cooling Technologies, Inc (ACT):

    Yue Xiao (PI), Chien-Hua Chen, Jay Uddi, Patryk Radyjowski, Josh Kintzer
  - Lehigh University:

    Prof. Jonas Baltrusaitis

Project Overview (2/2)

– Overall Project Objectives

- Plasma-Assisted Dry Methane Reforming (PADMR)

  $$CO_2 + CH_4 = 2H_2 + 2CO$$

- Improve reactor performance
- Evaluate coking formation and decoking
- PADMR modeling
- Scaling analysis and scaled-up reactor design
- Industrial process flow analysis

Technology Background (1/2)

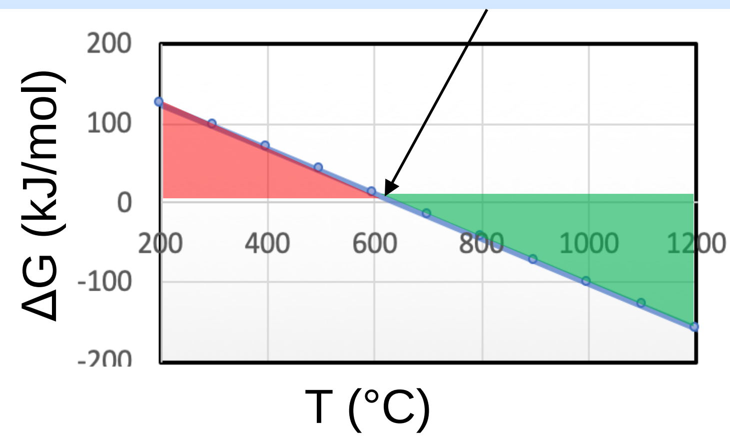
- Current: Steam Methane Reforming (SMR)

  $H_2O + CH_4 \rightarrow 3H_2 + CO$; $H_2/CO=3$, $\Delta H=206$ kJ/mol
- Dry Methane Reforming (DMR)

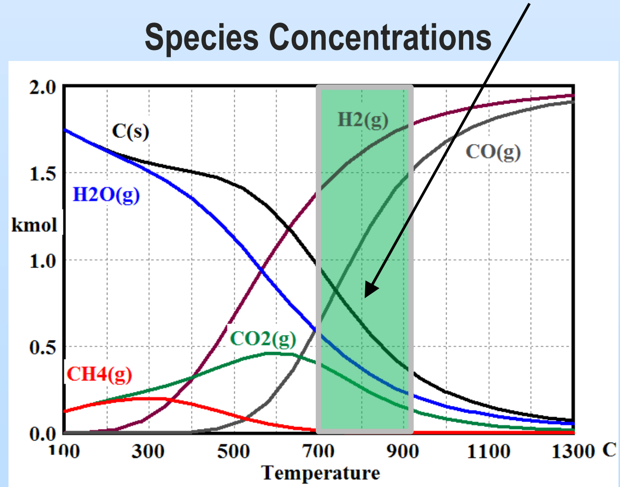
  $CO_2 + CH_4 \rightarrow 2H_2 + 2CO$; $H_2/CO=1$, $\Delta H=247$ kJ/mol

- DMR advantages:
  - Consumes two greenhouse gases
  - Better and tunable H_2/CO ratio
- DMR disadvantages:
  - High temperature
  - Coking

ΔG<0 @ 600 ° C

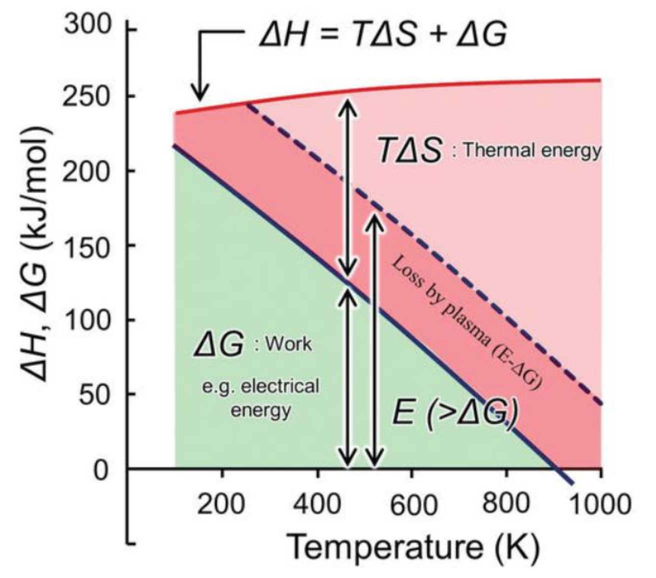


Always has carbon



Technology Background (2/2)

– Plasma-Assisted Dry Methane Reforming (PADMR)
  - Non-thermal plasma to sustain reactions
  - Electrons obtain energy from electric field
    → High energy electron (~10^4 K scale) but room temperature gas (300–400 K)



Sheng et al. *Plasma Chemistry and Gas Conversion* (IntechOpen, 2018).

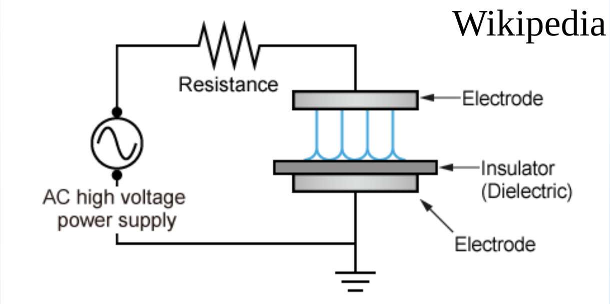
- Electrical energy consumed by non-thermal plasma (E) = Electron energy (ΔG) + Energy loss
- ΔG passed from electron to molecules

$$CH_4 + e \rightarrow CH_3 + H^-$$
$$CH_3 + H + CO_2 \rightarrow 2H_2 + 2CO$$

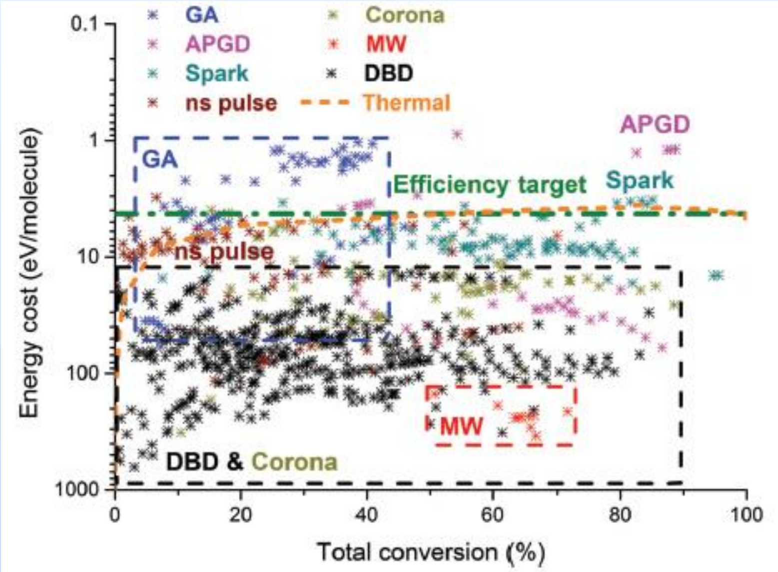
- Enables low temperature DMR reactions
- Catalysts for synergetic effects

Technical Approach/Project Scope (1/2)

– Dielectric barrier discharge (DBD) plasma reactor
  - Low temperature and atmospheric pressure
  - High conversion (>90%)
  - Suitable for industrial scale
  - Catalysts: Efficiency ↑



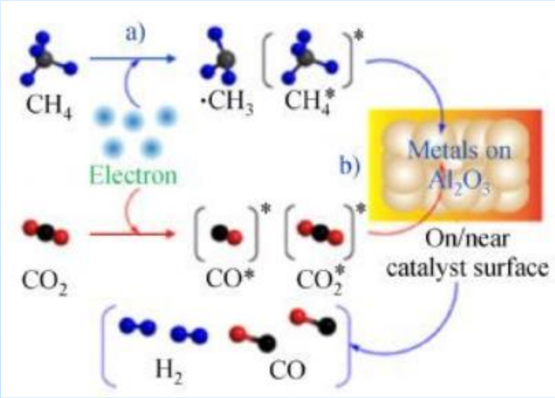
Source: Wikipedia



Snoeckx & Bogaerts, *Chem. Soc. Rev.*, **46**, 5805-5863 (2017).

DBD Ozone Generator

Source: SUEZ – Water Technologies & Solutions



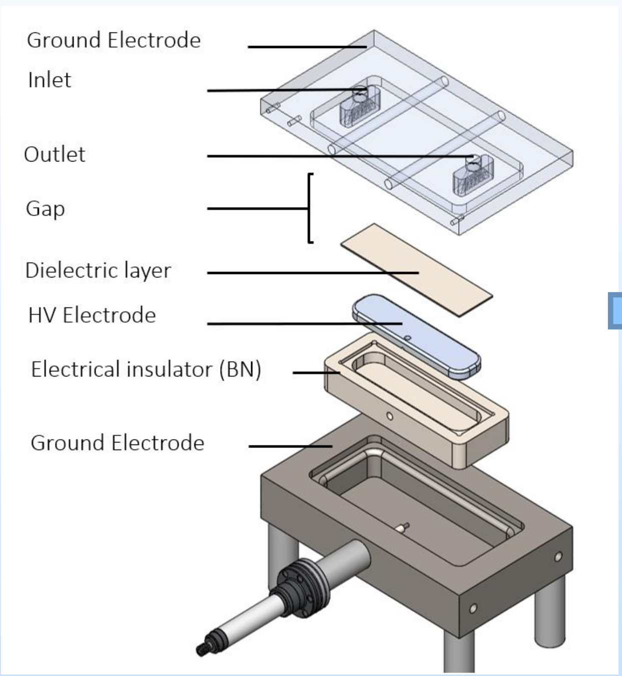
Zhao et al., *Front. Of Chem. Sci. and Eng.* **13**(3), 444-457 (2019).

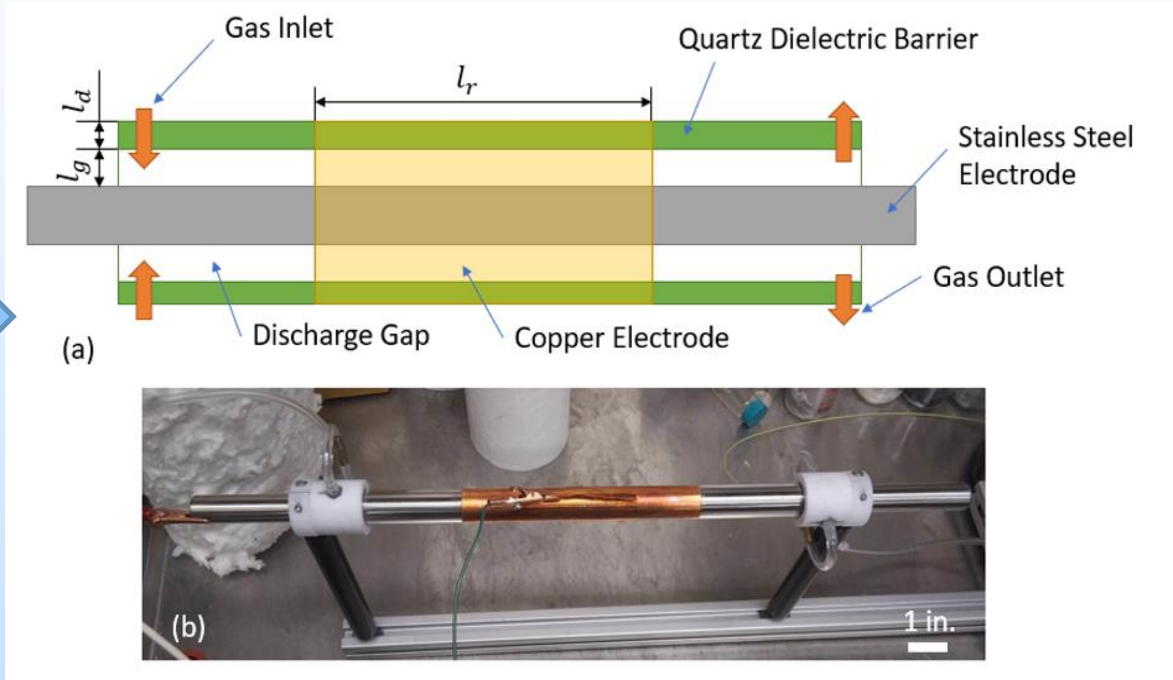
Technical Approach/Project Scope (2/2)

– Project Scope
  - Achieve high conversion and syngas production
  - Increase energy efficiency
  - Scaled-up reactor design
  - Plasma chemistry modeling → Reactor and process condition optimization
  - Industrial process modeling → Economic analysis
– Goal
  - Develop a economically viable PADMR-involved process
– Risks and Mitigation Strategies
  - Lower initial efficiency
    - Catalysts
    - Reactor and process optimization
    - Utilize waste heat and cheap electricity

Progress and Current Status of Project (1/8)

Upgraded DBD plasma reactor: Parallel plate → Cylindrical





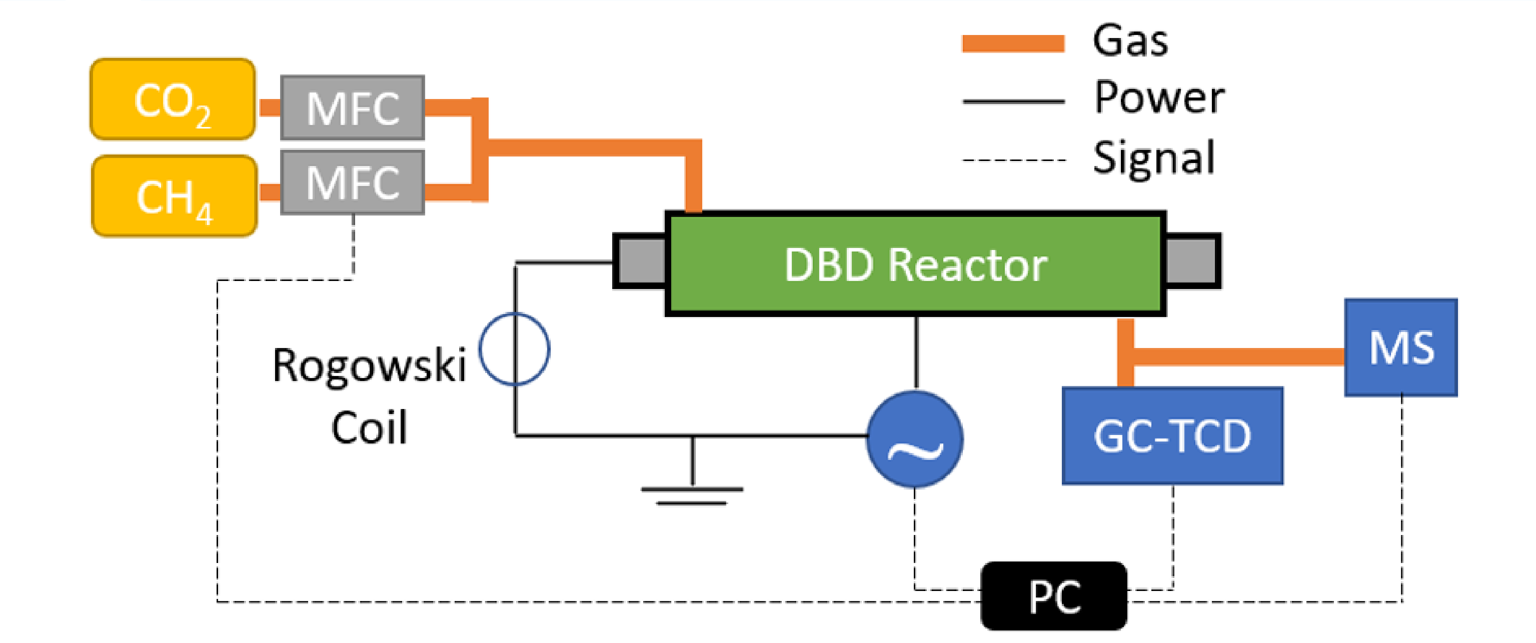
Phase I: Parallel plates reactor

Phase II: New cylindrical reactor

- Reduced bypass flow
- Uniform electric field
- Flexible reactor configuration

Progress and Current Status of Project (2/8)

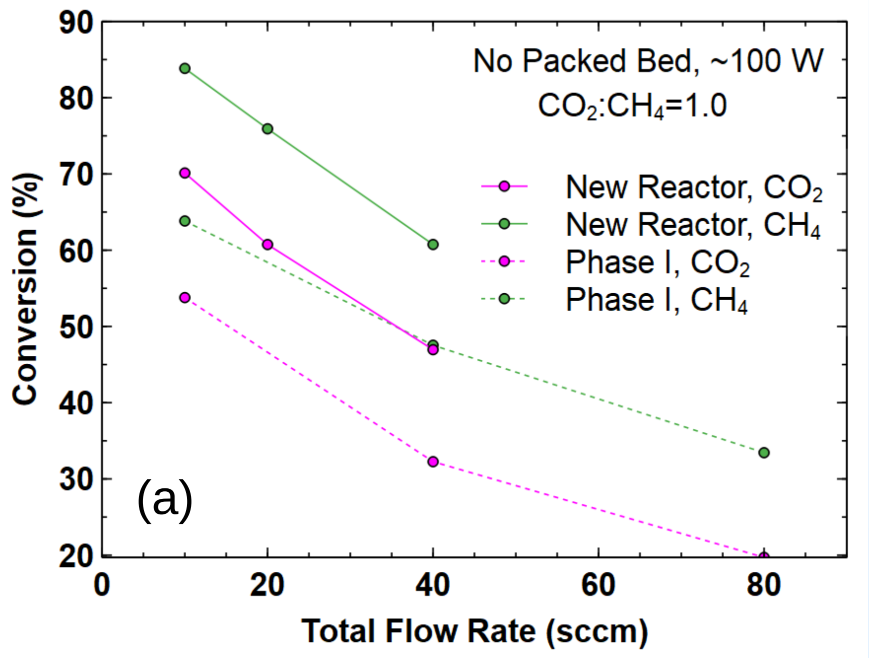
Testing Setup

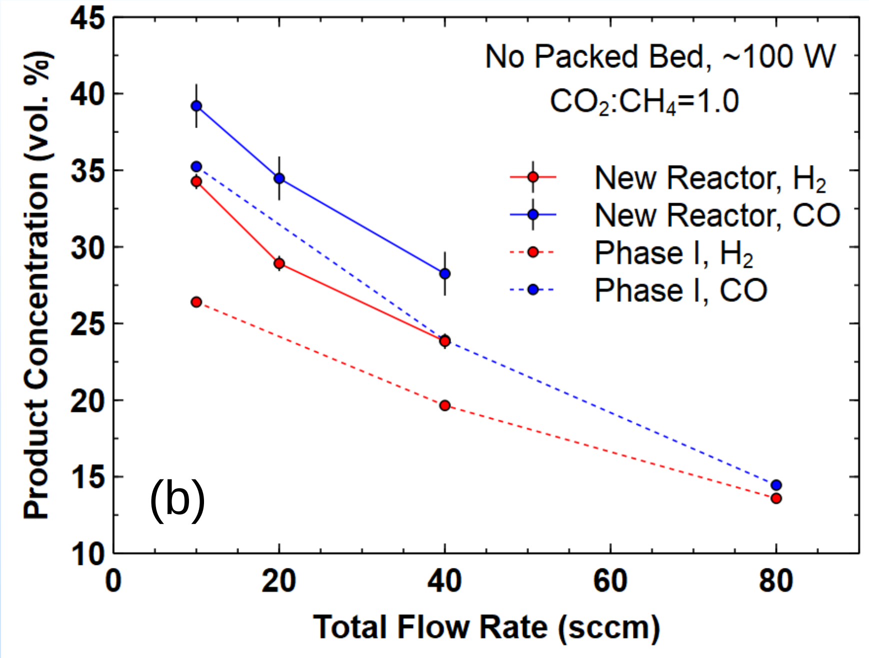


GC-TCD: Gas Chromatography – Thermal Conductivity Detector
MS: Mass Spectroscopy

Progress and Current Status of Project (3/8)

Further improved conversion and syngas production **DMR: $CO_2 + CH_4 \rightarrow 2H_2 + 2CO$**





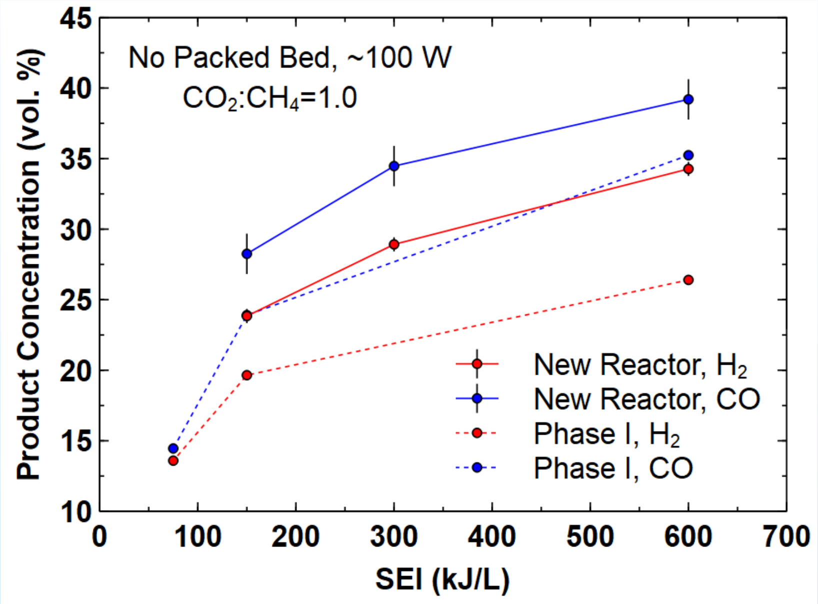
- Flow rate ↓, Conversion & production concentration ↑
- Compared with Phase I:

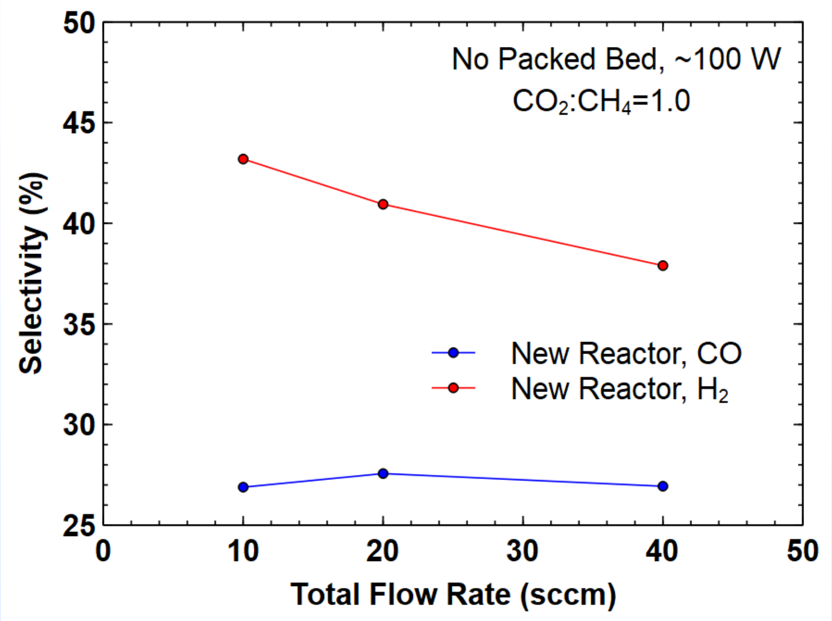
  CO_2: 54% → 70%, CH_4: 65% → 84%.

  H_2: 27% → 34%, CO: 35% → 39%.

Progress and Current Status of Project (4/8)

Further improved conversion and syngas production **DMR: $CO_2 + CH_4 \rightarrow 2H_2 + 2CO$**





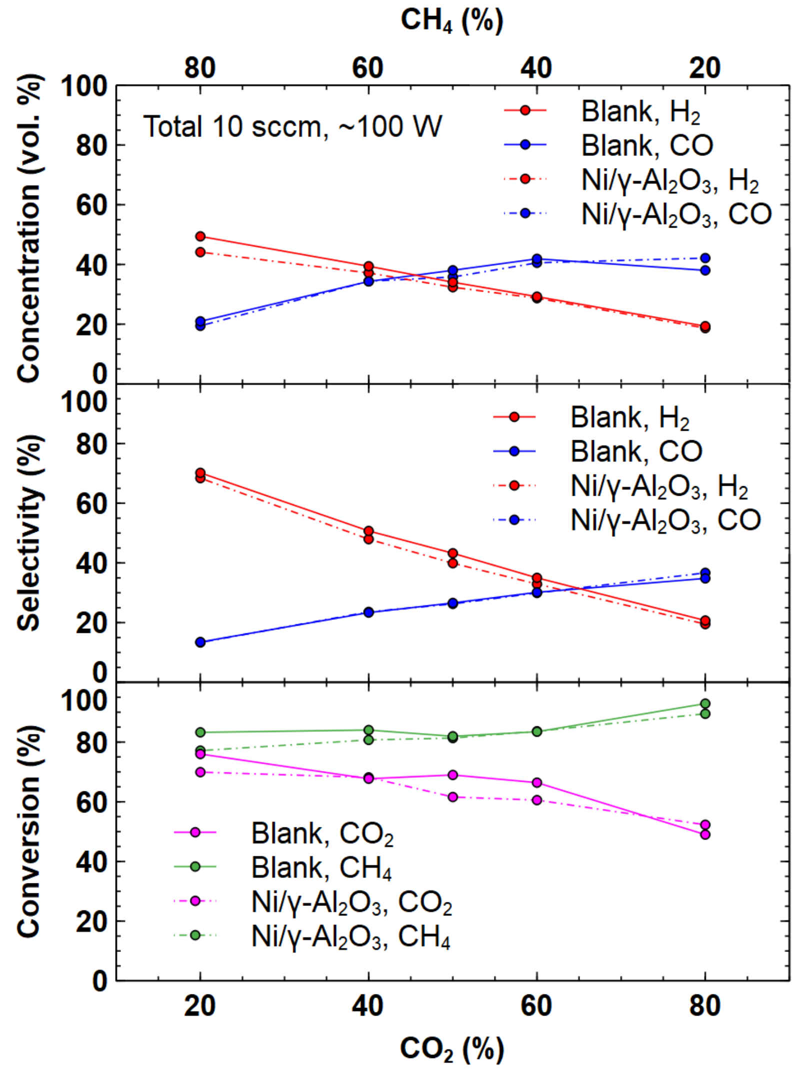
SEI: Specific energy input

$$\mathrm{SEI} = \frac{\mathrm{Power}}{\mathrm{Vol.\ Flow\ Rate}}\left(\frac{\mathrm{kJ}}{\mathrm{L}}\right)$$

- SEI ↑, conversion & production ↑

- CO selectivity insensitive to flow rate / SEI
- Flow rate ↑ (or SEI ↓), H2 selectivity ↓

Progress and Current Status of Project (5/8)



Parametric studies:

Alumina catalyst and varying CO_2:CH_4 ratio

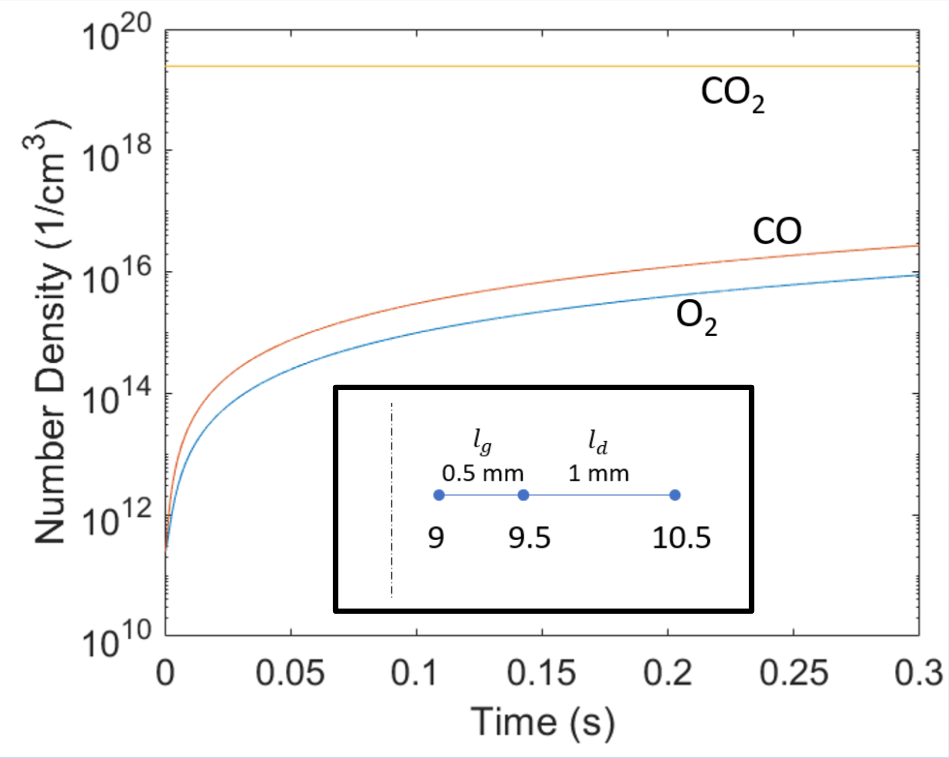
- 20% Ni/ γ-Al2O3 tested
- Concentration crosses at ~45%
- Selectivity crosses at ~65% CO_2.
- Low initial concentration
  → higher conversion
- CH_4 promotes CO_2 conversion
  → Tunable syngas ratio
- No significant performance improvements for catalysts
  - Reduced residence time
  - Low temperature

Progress and Current Status of Project (6/8)

Plasma chemistry modeling: 1D CO_2 conversion

Entry	Reaction	Rate coefficient
1	$e^- + CO_2 \rightarrow CO_2^+ + 2e^-$	5.4×10^{-11}
2	$e^- + CO_2 \rightarrow CO + O + e^-$	5.8×10^{-11}
3	$e^- + CO_2 \rightarrow CO + O^-$	7.0×10^{-12}
4	$e^- + O_3 \rightarrow O + O_2 + e^-$	2.0×10^{-9}
5	$e^- + O_2 \rightarrow O + O + e^-$	2.0×10^{-9}
6	$e^- + O_2 \rightarrow O + O^-$	4.0×10^{-11}
7	$e^- + O_2 + M \rightarrow O_2^- + M$	3.0×10^{-30}
8	$O^- + CO \rightarrow CO_2 + e^-$	5.5×10^{-10}
9	$O^- + O_2 \rightarrow O_3 + e^-$	1.0×10^{-12}
10	$O^- + O_3 \rightarrow O_2 + O_2 + e^-$	3.0×10^{-10}
11	$e^- + CO_2^+ \rightarrow CO + O$	6.5×10^{-7}
12	$O_2^- + CO_2^+ \rightarrow CO + O_2 + O$	6.0×10^{-7}
13	$O + O + M \rightarrow O_2 + M$	$5.2\times10^{-35}\ \exp(900/T[K])$
14	$O + O_2 + M \rightarrow O_3 + M$	$4.5\times10^{-34}\ (T[K]/298)^{-2.70}$
15	$O + O_3 \rightarrow O_2 + O_2$	$8.0\times10^{-12}\ \exp(-17.13/T[K])$
16	$O + CO + M \rightarrow CO_2 + M$	$1.7\times10^{-33}\ \exp(-1510/T[K])$
17	$O_3 + M \rightarrow O_2 + O + M$	$4.1\times10^{-10}\ \exp(-11\,430/T[K])$

Aerts et al., *Chem. Sus.. Chem.*, **8(4)**, 702-716 (2012).



After 0.3 s:

- CO 10^{16} /cm^3 scale → Match with previous study
- Longer residence time to be performed

Progress and Current Status of Project (7/8)

Reduced CO_2 modeling → Detailed DMR Modeling

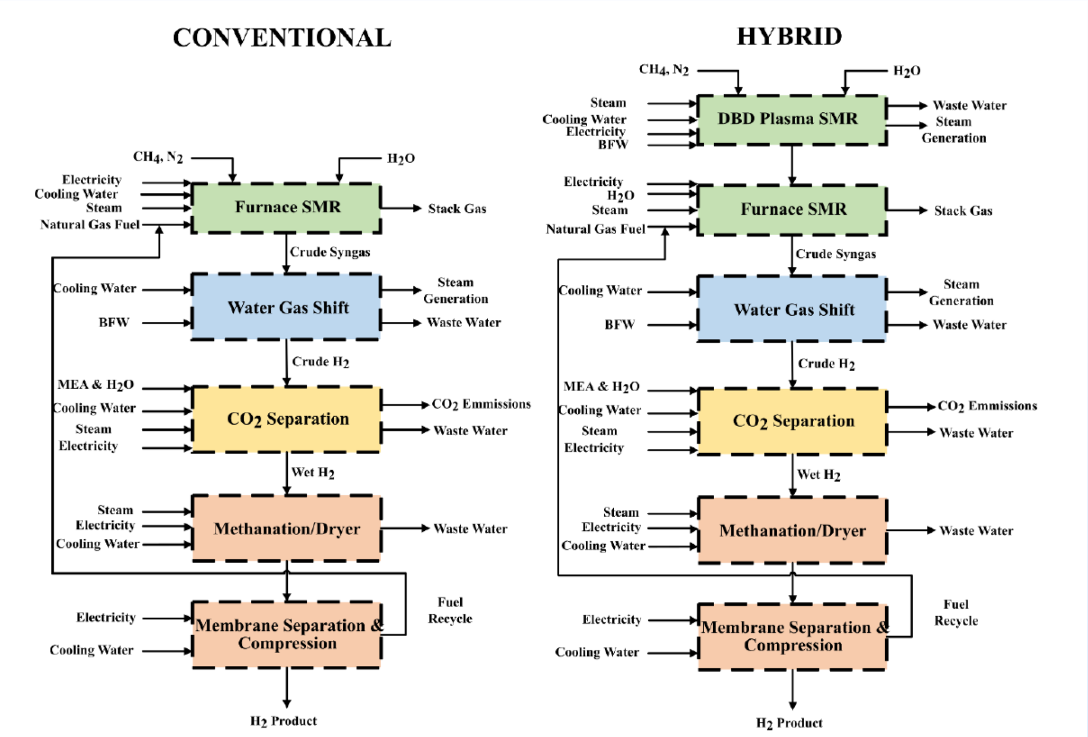
Molecules	Charged Species	Radicals	Excited Species
C_3H_8, C_3H_6, C_2H_6, C_2H_4, C_2H_2, CH_4	$C_2H_6^+$, $C_2H_5^+$, $C_2H_4^+$, $C_2H_3^+$, $C_2H_2^+$, C_2H^+, CH_5^+, CH_4^+, CH_3^+, CH_2^+, CH^+	C_4H_2, C_3H_7, C_3H_5, C_2H_5, C_2H_3, C_2H, CH_3, CH_2, CH	
CH_2CO, CH_3OH, CH_3CHO, CH_3OOH, C_2H_5OH, C_2H_5OOH, CH_2O		CHO, CH_2OH, CH_3O, CH_3O_2, C_2HO, CH_3CO, CH_2CHO, C_2H_5O, $C_2H_5O_2$	
	C_2^+, C^+	C, C_2	
O_3, O_2	O_3^-, O_4^-, O_4^+, O_2^-, O_2^+, O^+, O^-	O	O(1D), O(1S), O_2(a1), O_2(b1)
H_2	H_2^+, H^+, H^-, H_3^+	H	H(2P), H_2(V), H_2(E)
CO_2, CO	CO_2^+, CO^+, CO_3^-, CO_4^-, CO_4^+, $C_2O_4^+$, $C_2O_3^+$, $C_2O_2^+$	C_2O	CO_2(E1), CO_2(E2)
H_2O, H_2O_2	H_2O^+, H_3O^+, OH^+, OH^-	HO_2, OH	

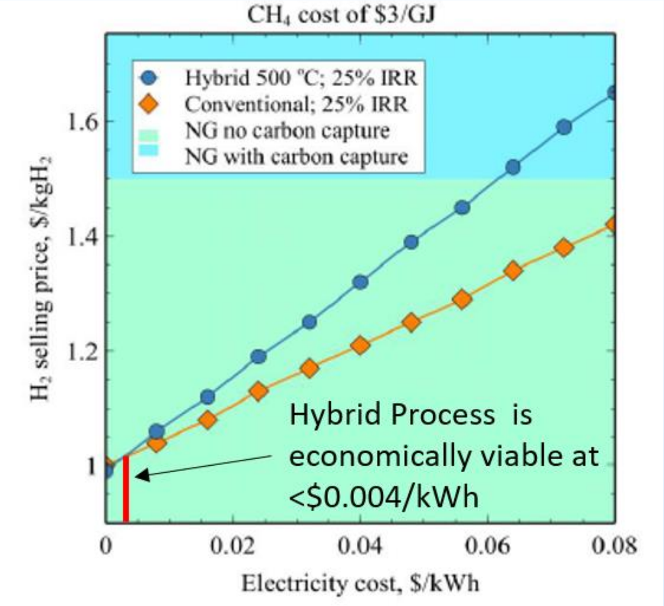
- Includes hydrocarbons and many excited species
- Total 75 species and >1000 reactions
- Data collected from multiple sources
- Currently tuning for convergence

Koelman *et al. Plasma Process. Polym.* **14**, 1600155 (2017).
Wang *et al., J. Phys. Chem. C* **122**, 8704–8723 (2018).
…

Progress and Current Status of Project (8/8)

Process Flow Analyses: SMR case as baseline

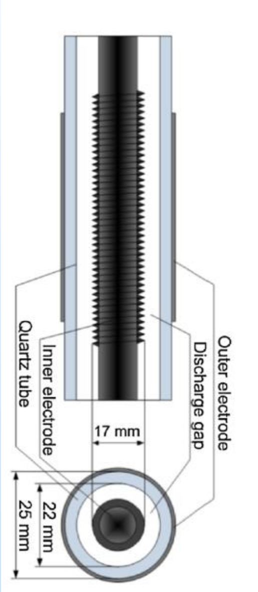




- Conventional and hybrid SMR modeled
- Low electricity cost need to be economically competitive
- Results published on King et al., *Fuel* **304**, 121328 (2021).
- Currently developing DMR analysis model.

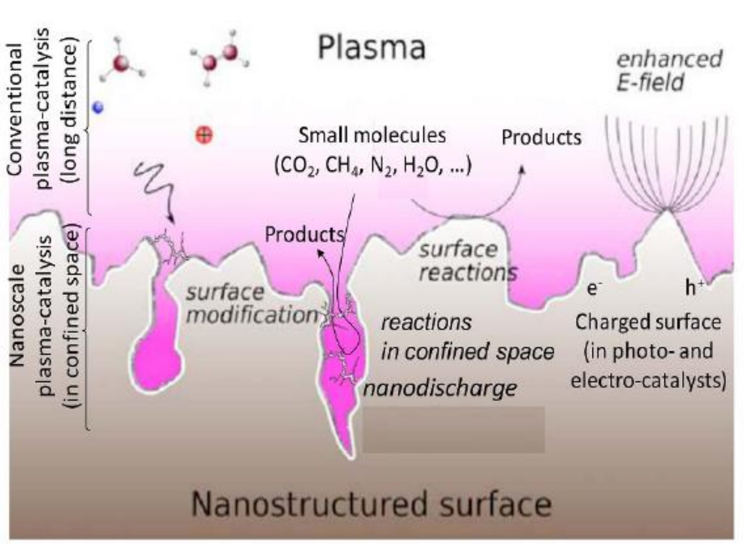
Plans for Future Testing/Development/Commercialization

– Further improvement of efficiency under high conversion
  - Achieved through reactor configuration, catalysts, and power source setup

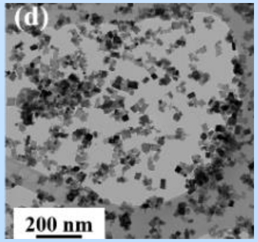


Mei & Tu, *J. of CO2 Utilization* **19**, 68–78 (2017)

Reactor Configuration



Neyts, & Bogaerts, *J. Phys. D. Appl. Phys.* **47**, 224010 (2014).



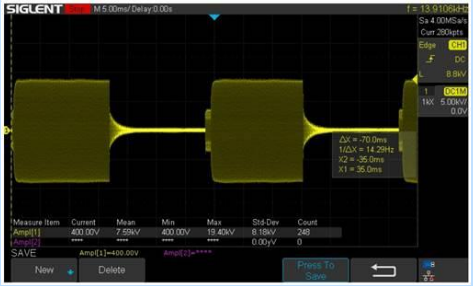
Ru/CeO_2 nanocubes

Ranganathan et al. *Int'l. J of Energy Eng*. **10**(3), 67-79 (2020).

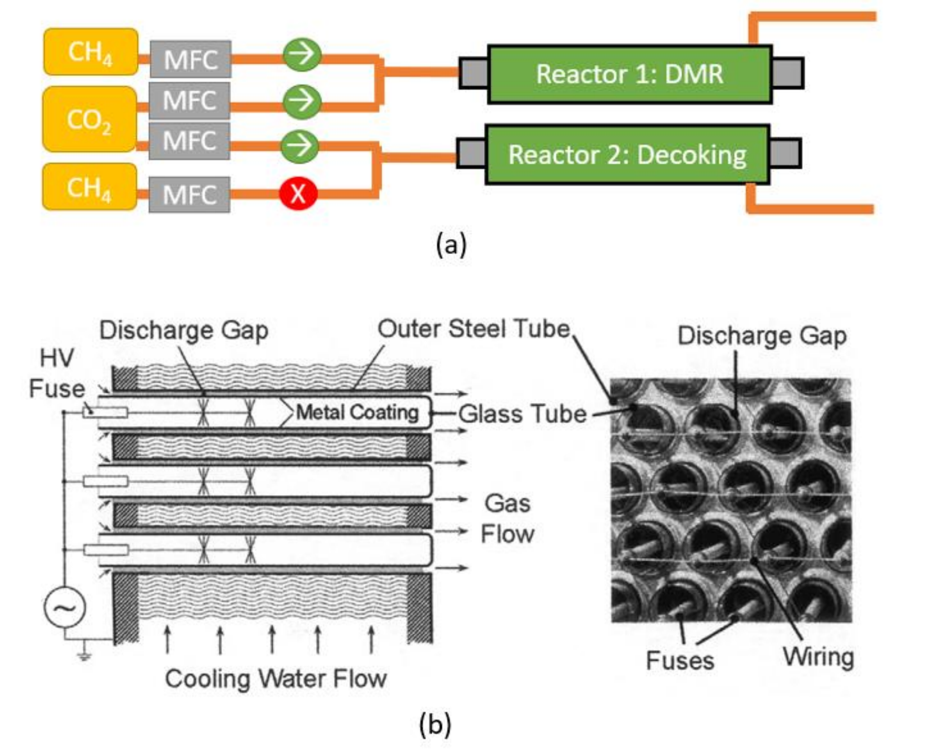
Conventional and Nanoscale Catalysts

Nanosecond Pulse Source

Burst Signal



Plans for Future Testing/Development/Commercialization



Scale-up design:

- Twin reactor for consecutive production and decoking
- Currently designing scaled-up reactors

Summary

PADMR:

- Consumes two greenhouse gases → Produces syngas
- Demonstrates high conversion and syngas production
- Efficiency can be further improved

1) The new reactor, compared with Phase I effort:

  - Total conversion 59% → 70%
  - Maximum CH_4 conversion: 78% → 92%
  - Efficiency improved by 35%

2) 1D and 2D Plasma chemistry modeling

  - Predict the experimental results
  - Investigate the effects of the dielectric constant

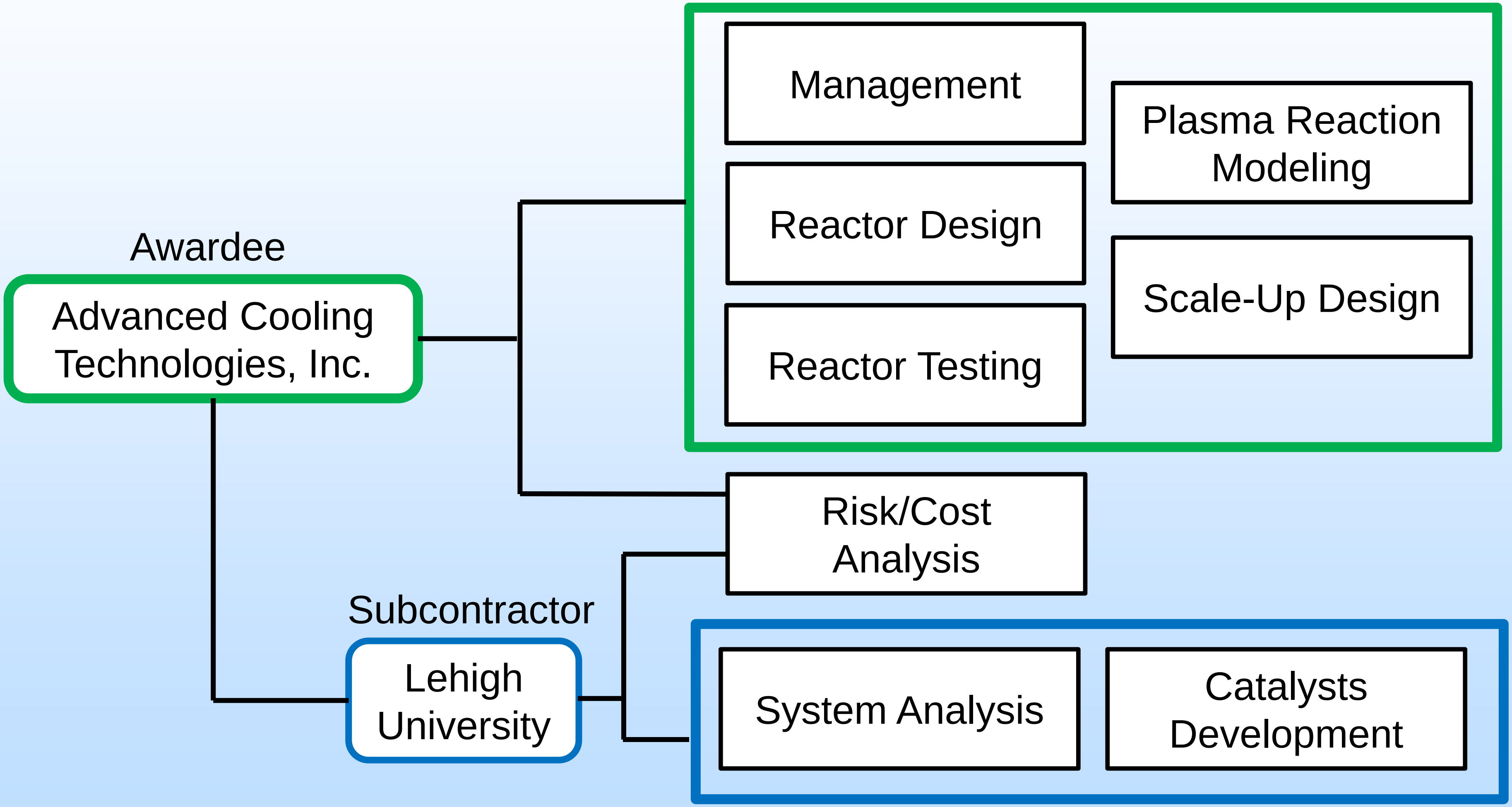
3) Industrial process modeling

  - Baseline case with SMR process

Thank you!

Appendix

Organization Chart



Gantt Chart

Task Description		Quarter							
		1	2	3	4	5	6	7	8
Task 1: Evaluate increase the energy efficiency using a packed bed, plasma with catalysts and nanosecond pulses		X	X	X	X	X			
Task 2: Evaluate extent of coke formation in extended duration tests using our plasma DMR reactor				X	X	X			
Task 3: Perform lab tests and evaluate conversion and selectivity using simulated feedstocks that may contain steam, nitrogen, and/or impurities						X	X		
Task 4: Develop a predictive tool for plasma DMR by combining our CH_4 and CO_2 plasma chemistry models in one code including coupling reactions		X	X	X	X				
Task 5: Improve scaling analysis and develop a scaled-up reactor design					X	X	X	X	
Task 6: Perform process flow analyses and optimization studies							X	X	X
Reporting	Briefings	X	X	X	X	X	X	X	X
	Midterm/ Continuation Report				X				
	Final Report								X