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Plasma-Assisted Methane Reforming and Catalyst Decoking

DE-SC0019664

Yue Xiao
Advanced Cooling Technologies, Inc.
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National Energy Technology Laboratory
2022 Carbon Management Project Review Meeting

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)
  - Phase IIA: $1,149,997 (04/2022 – 04/2024)

- Project Participants
  - Dr. Yue Xiao, Dr. Jay Uddi, Dr. Chien-Hua Chen (Advanced Cooling Technologies, Inc)

  - Prof. Jonas Baltrusaitis (Lehigh University)

Project Overview (2/2)

Overall Project Objectives

- Low-temperature syngas production through plasma-assisted methane reforming

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

$$CO_2 + CH_4 + H_2O \rightarrow xH_2 + CO, x=1–3$$

- Improve reactor performance
- Evaluate coking formation and decoking techniques
- Plasma physics modeling
- Scaling analysis and scaled-up reactor design
- Industrial process flow analysis and TEA

Background (1/2)

Syngas ($CO+H_2$): critical mid-product

Syngas H_2:CO Ratio	Products
≤1	Ethanol
~2	Methanol → Acetic Acid, Ethylene-Propylene, etc.
≥2	Fischer-Tropsch Process → Wax, Gasoline, etc.
≥50	Hydrogen

Hernández et al., *Green Chem.*, **19** (10) 2326–2346 (2017).

Current mainstream: Steam Methane Reforming (SMR)

$$CH_4 + H_2O \rightarrow 3H_2 + CO, \Delta H=206\ \mathrm{kJ/mol}$$

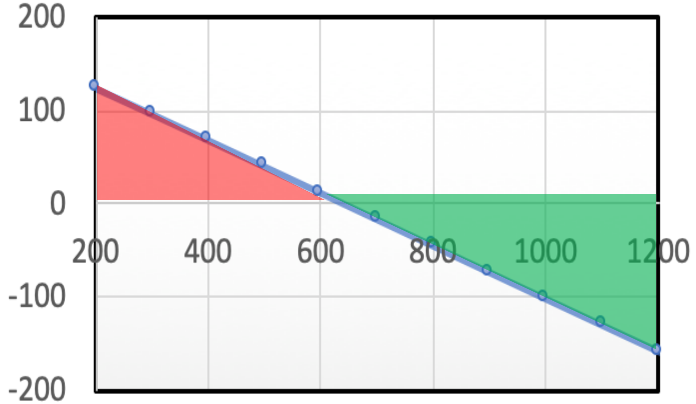
- High H_2/CO ratio: 3—5

Alternative: Dry Methane Reforming (DMR)

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO, \Delta H=247\ \mathrm{kJ/mol}$$

- Consumes CO_2
- Problems:
  - <u>High temperature</u>: 700—900 °C
  - <u>Coking</u>: deactivates catalyst, reformer clogging…

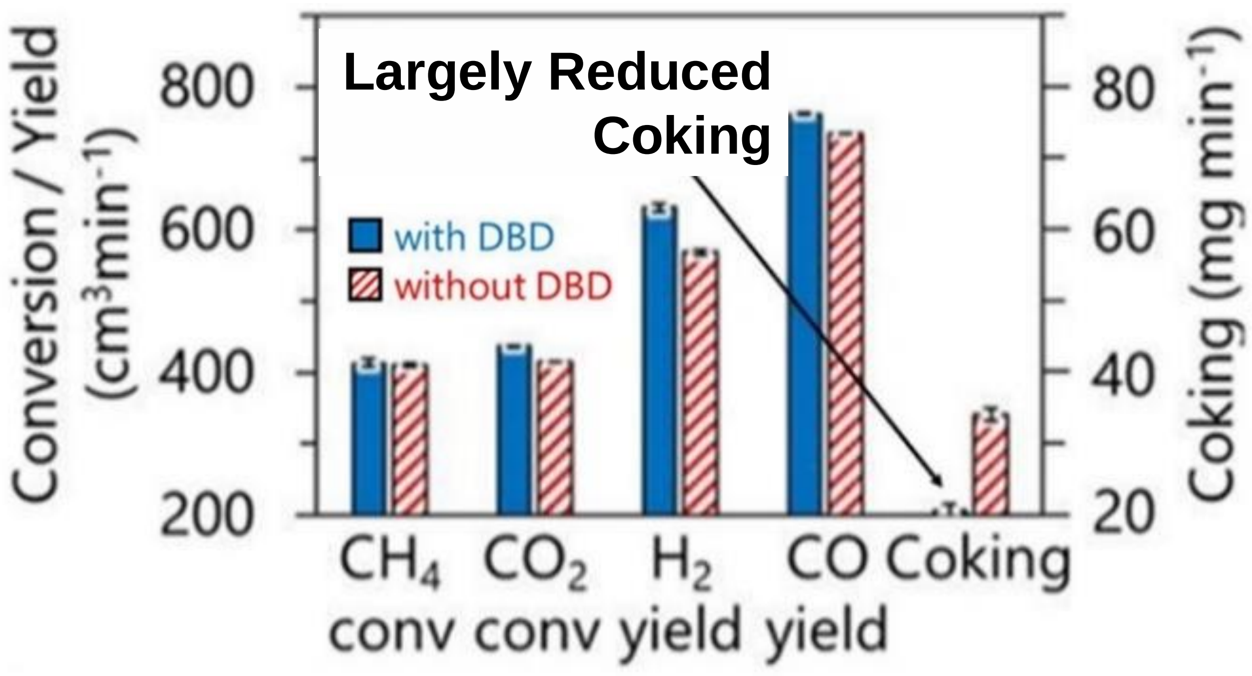
T (°C) vs.ΔG (kJ/mol)



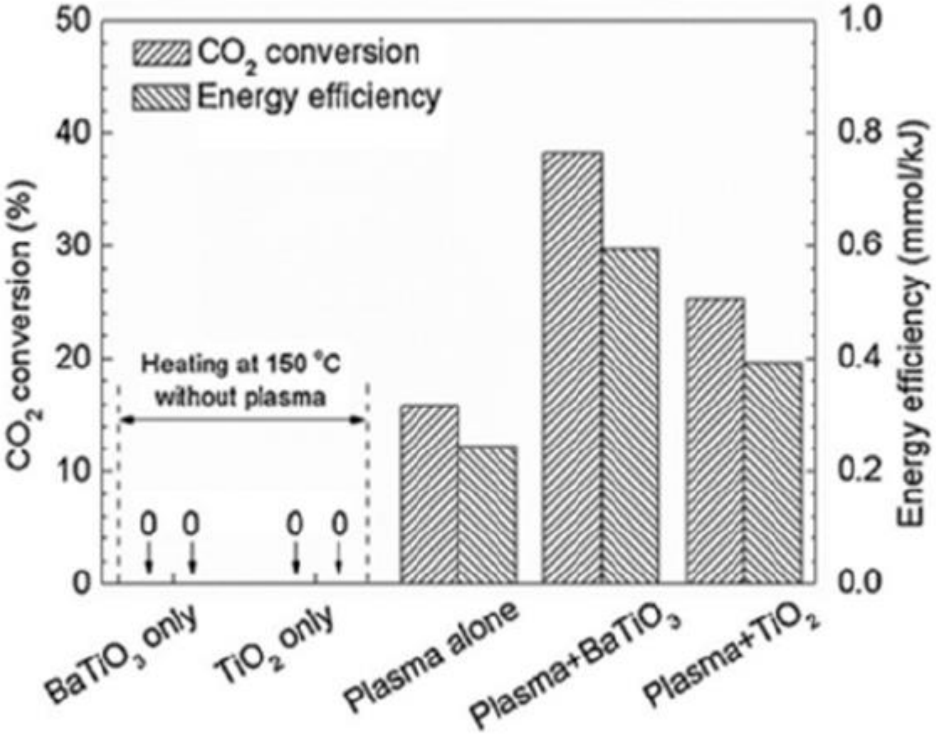
Background (2/2)

Plasma-Assisted Dry Methane Reforming (PADMR) and catalyst decoking

- Non-thermal plasma → Lower temperature reactions
- High energy electrons enables unique reaction pathways → Coke reduction
- Synergistic effects of plasma-catalysis reactions → Higher efficiency
- Dielectric barrier discharge (DBD) plasma adopted

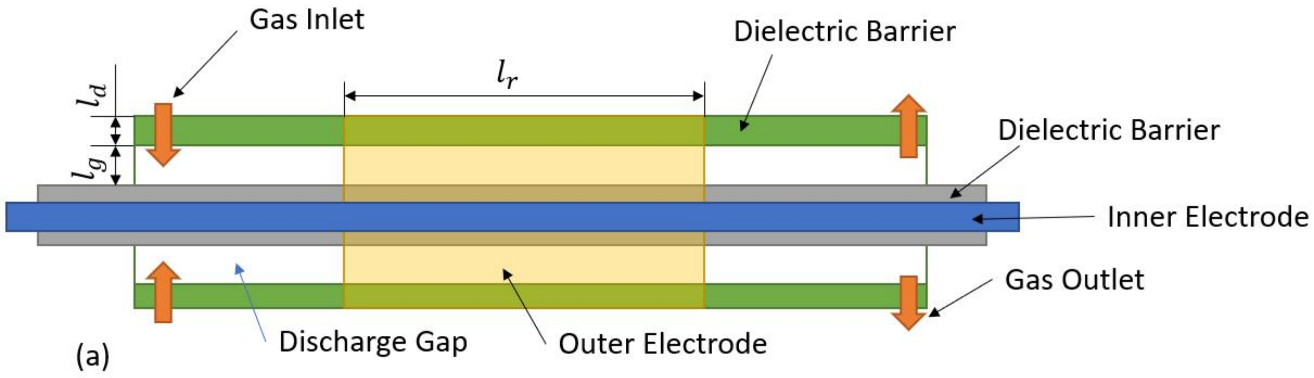


Kameshima et al., *Int'l J. of Plasma Enviro. Sci. & Tech.* **9**(1),201797785 (2015).

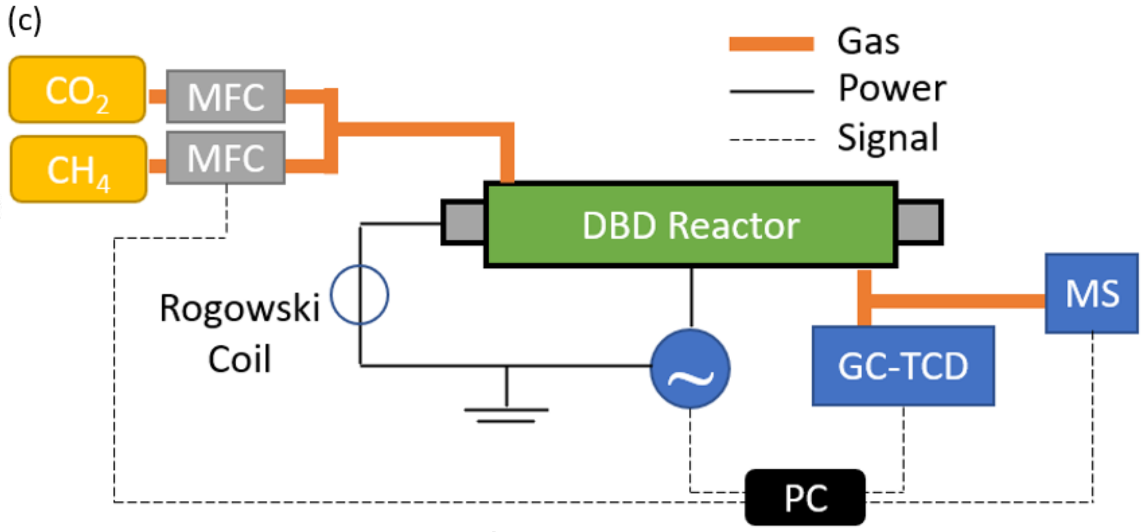


Li et al. *Nanomaterials* **9**, 1428 (2019).

Concept (1/1)



Cylindrical DBD reactor



Test Setup

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

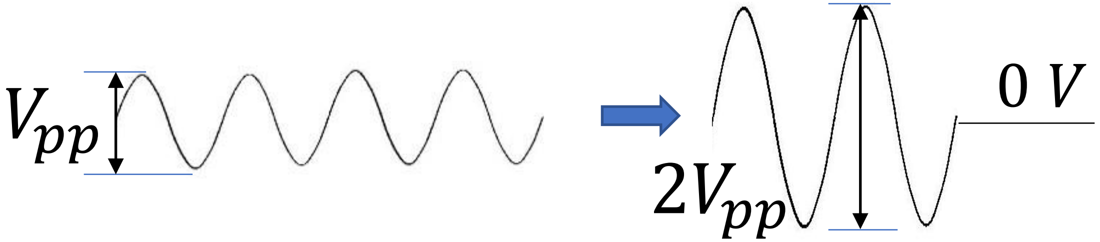
Plasma-Assisted Dry Methane Reforming (PADMR)

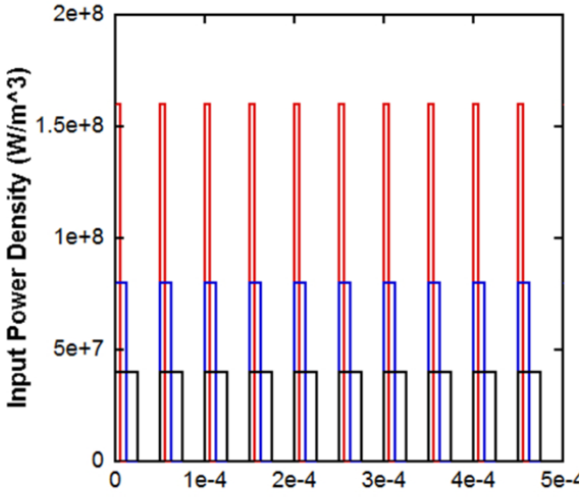
- Cylindrical DBD plasma reactor
- Discharge gap l_g: 0.5–5 mm for packed bed and catalyst loading
- Additional heating and insulation

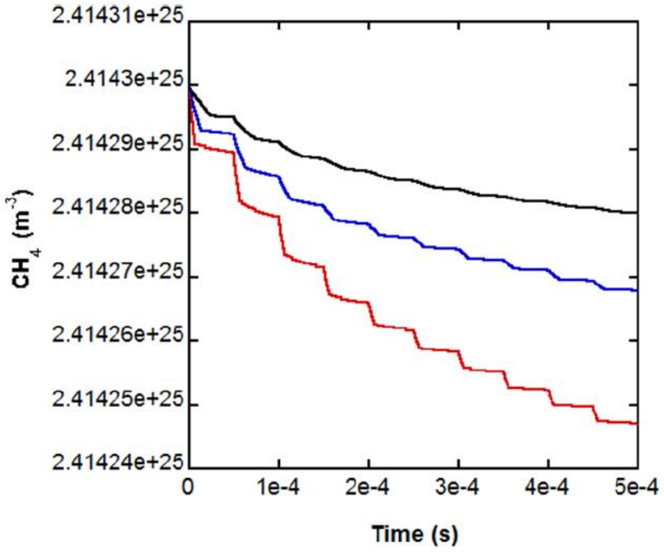
Progress (1/8): Efficiency Enhancement

Cylindrical Reactor Optimization

1. Reduced Gap size l_g: Electric field V/l_g ↑
2. “Burst Mode” power

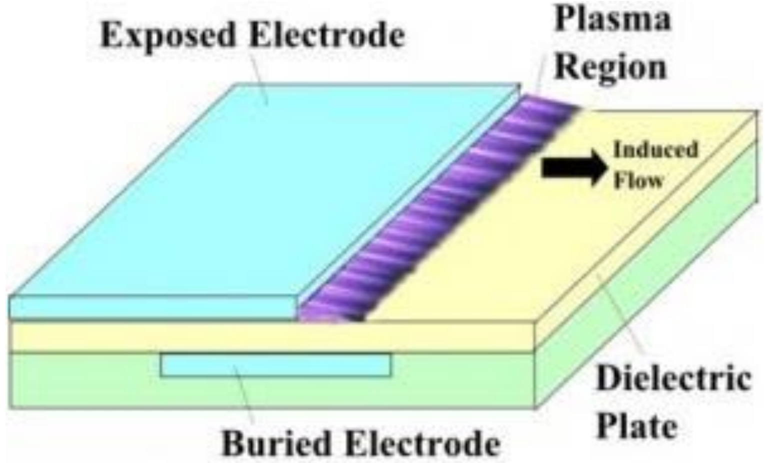






- Same power, duty cycle ↓ , conversion↑

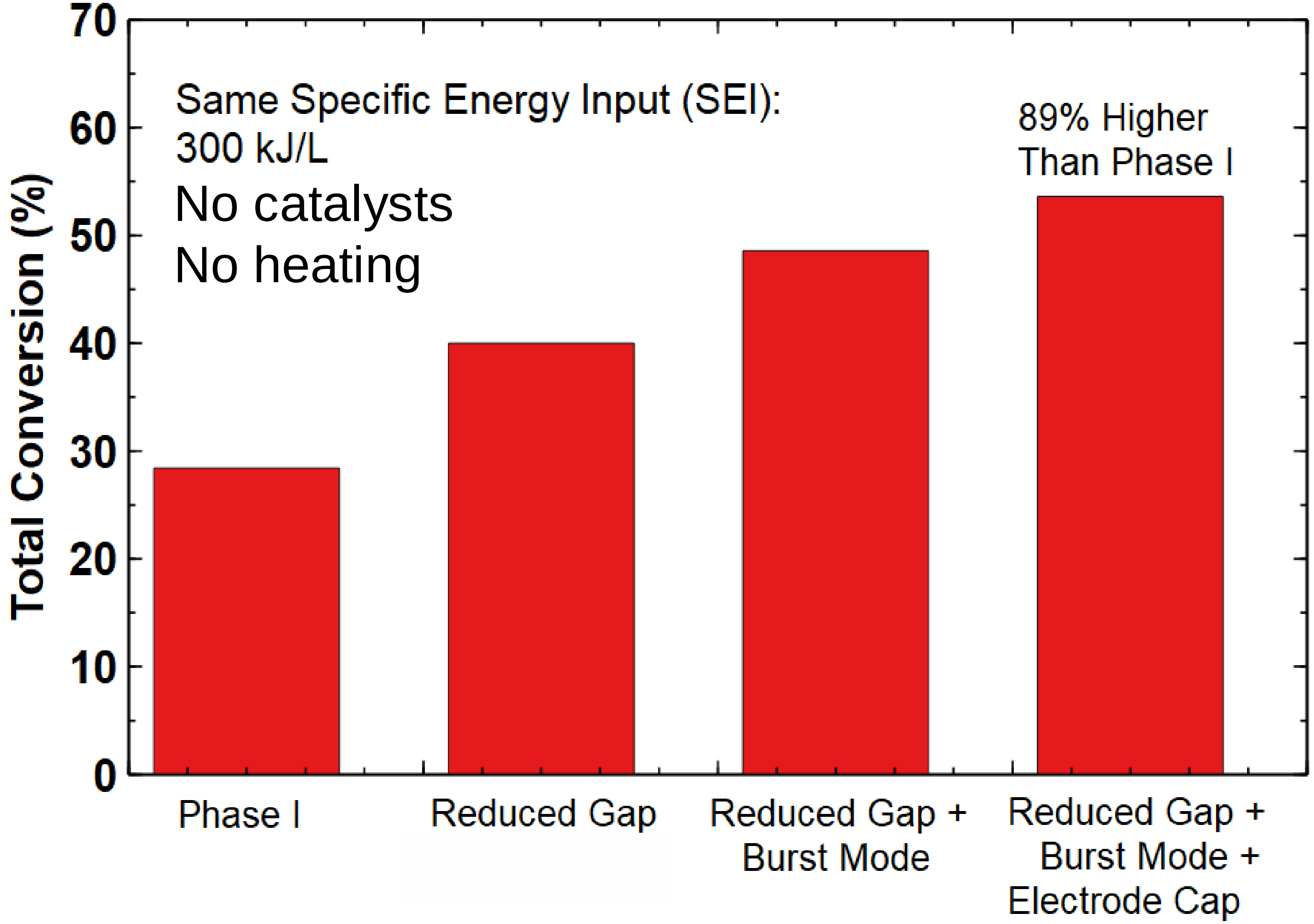
3. Eliminate secondary surface discharge
→ Energy Waste ↓



Progress (2/8): Efficiency Enhancement

Cylindrical Reactor Optimization:

- Room temperature test without catalyst: 89% higher than the end of Phase I (2020).



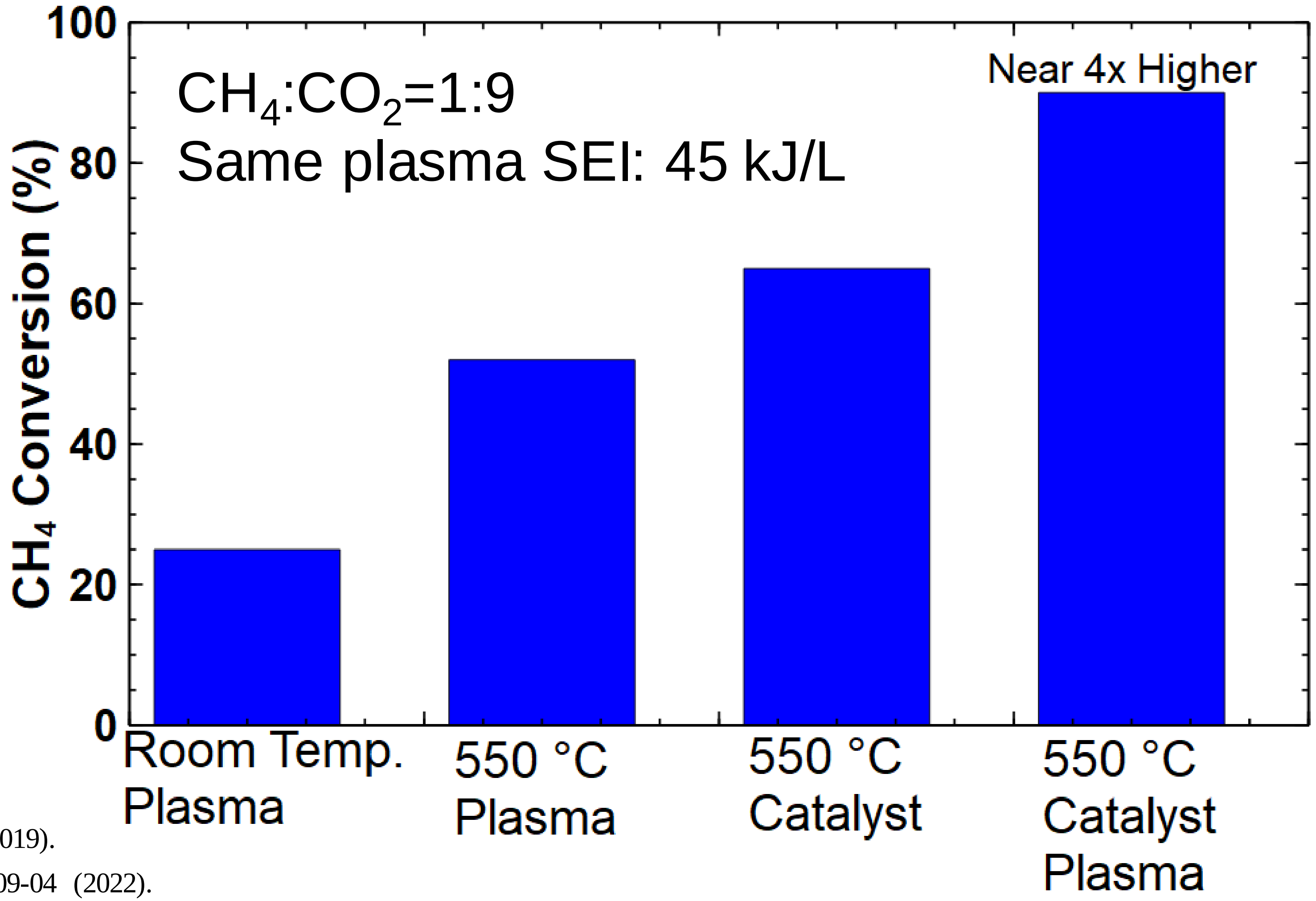
Progress (3/8): Efficiency Enhancement

Advanced catalysts with coke resistance

- $La_{0.9}Ce_{0.1}NiO_3$ perovskite catalyst on CeO_2 support

- Industrial process consideration:
  - Tests with intermediate temperature (up to 550 °C)
  - Maximize CH_4 conversion to eliminate separation

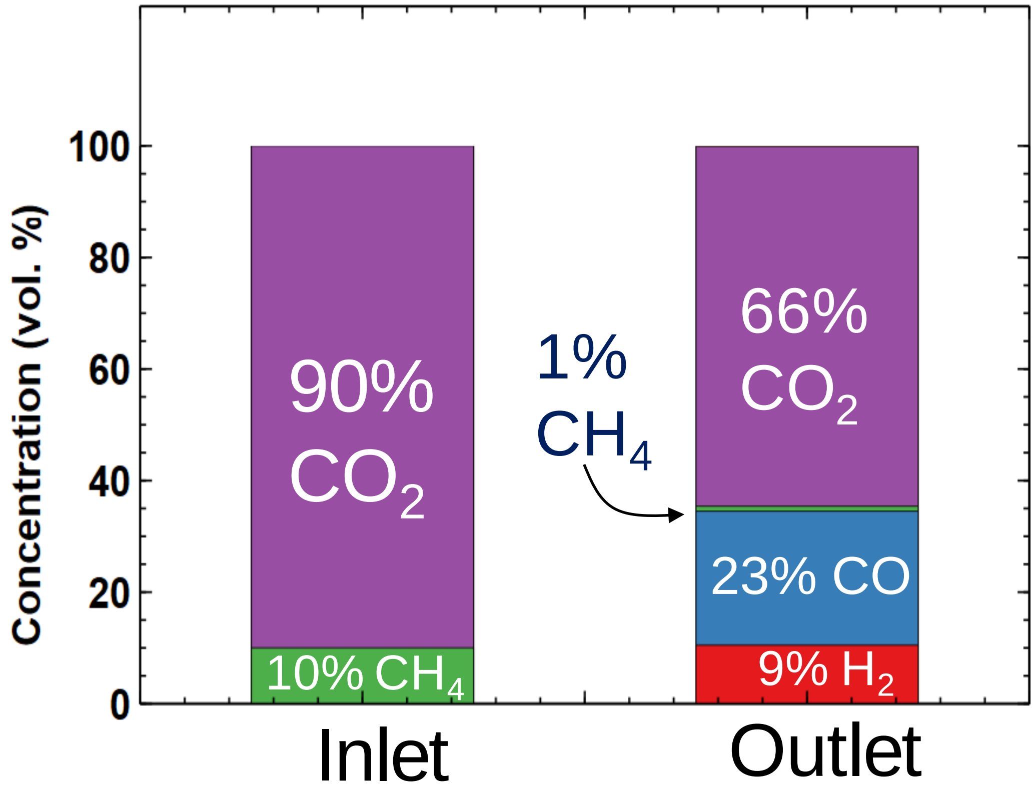
- 90% CH_4 conversion, 16% CO_2 conversion

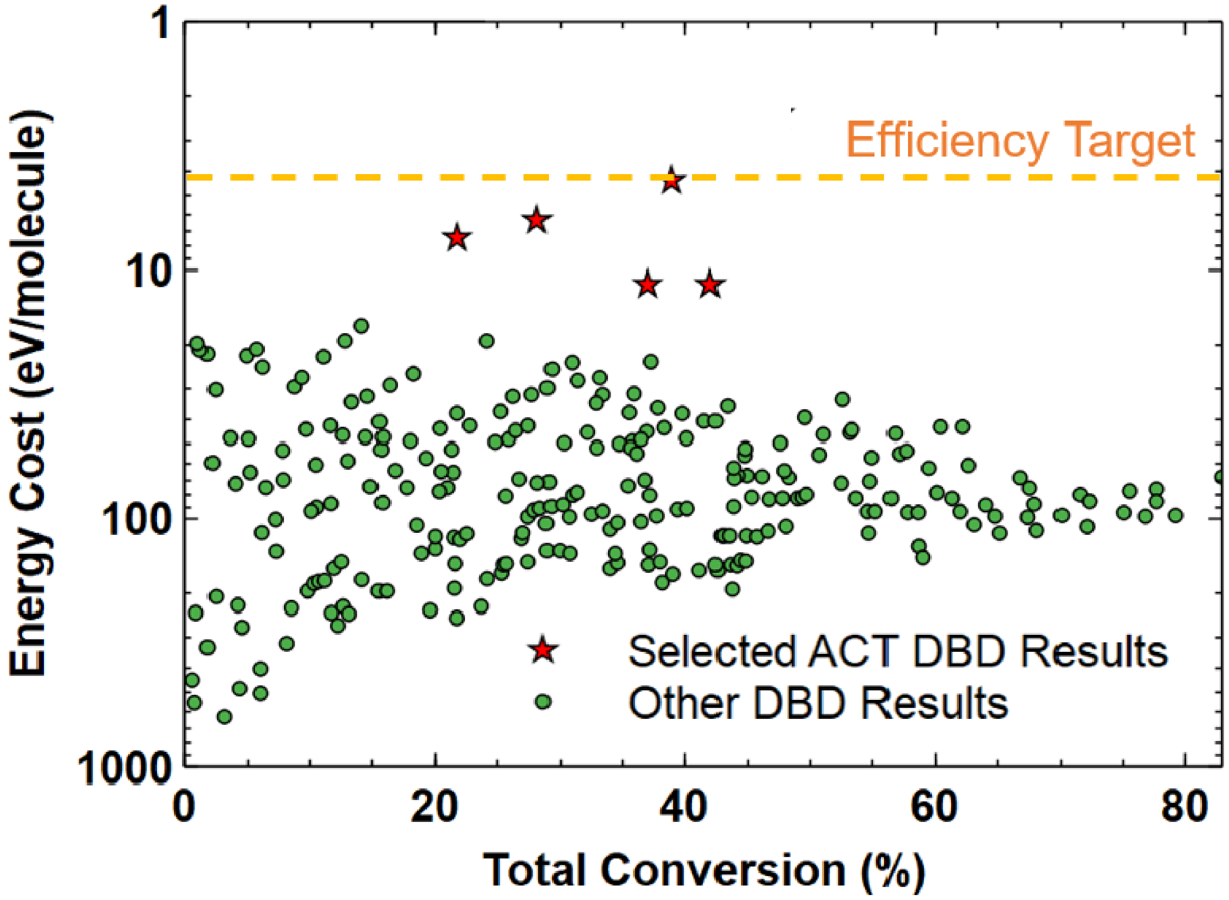


Ranganathan, …**Uddi** et al. *Journal of CO₂ Utilization* ***32*** *11–20* (2019).

Uddi et al. Invited Talk at *23rd Int'l Conf. on Solid State Ionics*, EF09-04 (2022).

Progress (4/8): Efficiency Enhancement





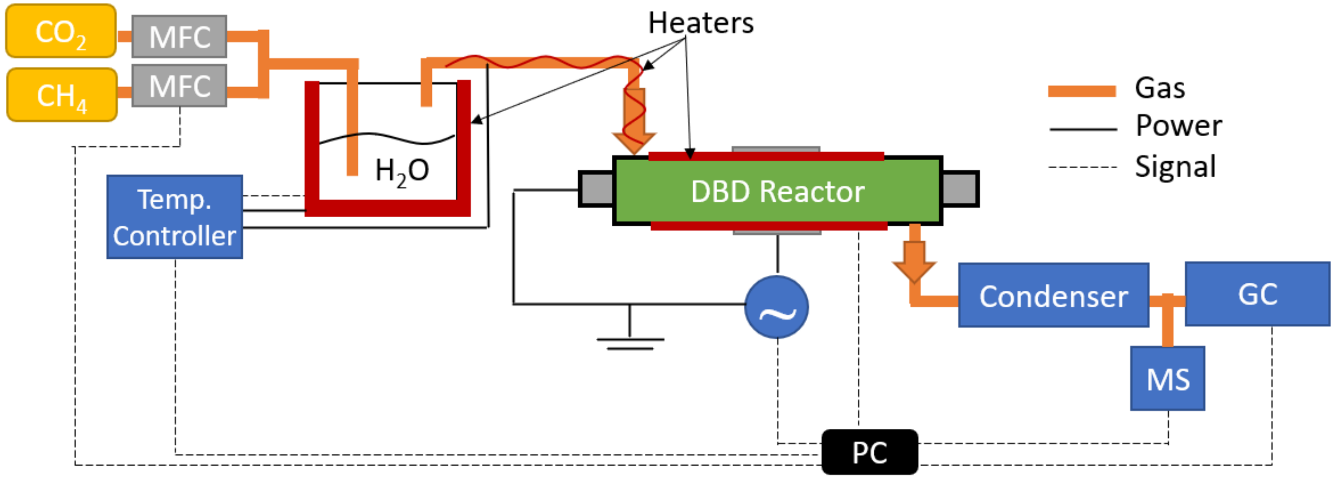
- High CH_4 conversion for industrial process
- Syngas with high CO composition
- Lower energy cost

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

Progress (5/8): Plasma-Assisted Bi-Reforming

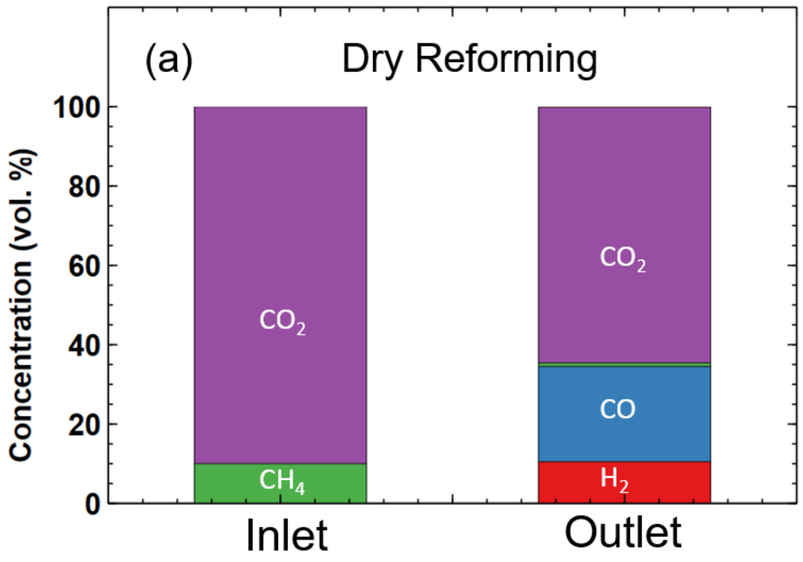
$$CH_4 + CO_2 + H_2O \rightarrow \mathbf{x}H_2 + CO, \quad 1<x<3$$

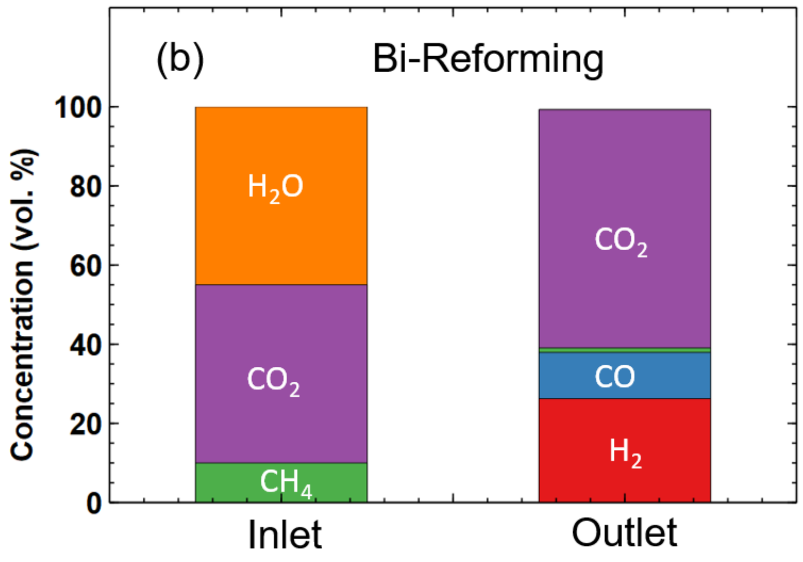
- Complex reactions: DMR, SMR, WGS, etc.
- Syngas directly used for sequential processes
- Commercial interests: Linde's DRYREF bi-reforming pilot plant

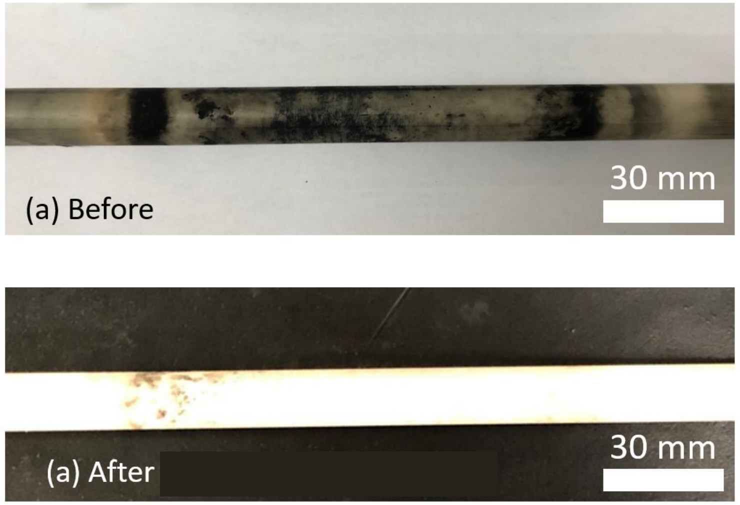


- steam supply line added to the setup

Progress (6/8): Plasma-Assisted Bi-Reforming







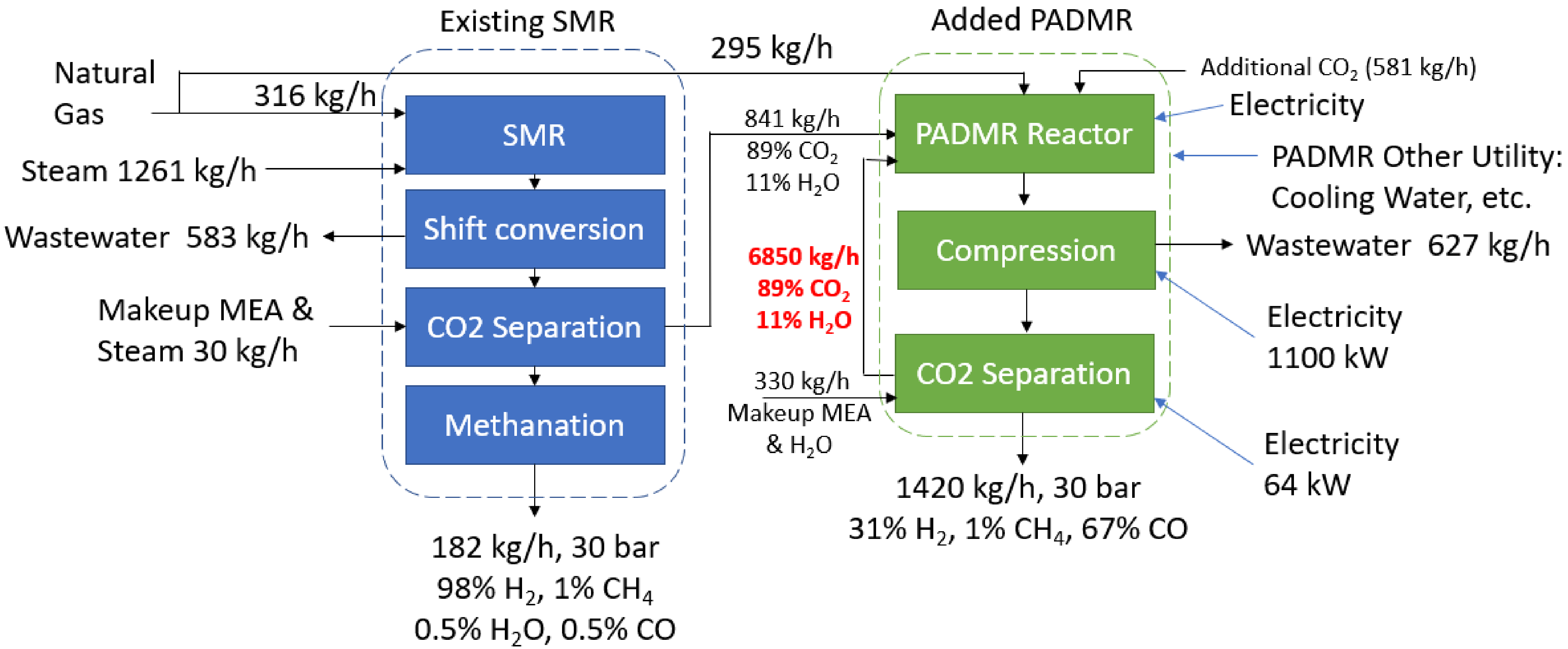
Replace 50% CO_2 with steam, other conditions unchanged:

- Similar ~1% CH_4 composition in outlet gas
- H_2:CO=**2.3** vs. 0.4 in PADMR → direct adoption
- Slightly reduced syngas production (90 vol.% of DMR)
- Much lower CO_2 cycling cost

Excellent decoking with steam gasification:

- Net coke reduction with Steam:Carbon (S:C)=0.81.
- Industry leader: S:C=0.90.

Progress (7/8): Industrial Flow Analysis and TEA



- Industrial process flow modeling on PADMR using ASPEN
- PADMR as an add-on system to SMR hydrogen production plant with 18.5 kmol/h CO_2 emission
- Bi-reforming can largely reduce recirculated CO_2

Progress (8/8): Industrial Flow Analysis and TEA

Major Parameters	Assumptions
SMR Hydrogen Production	4344 kg/day
Corresponding CO2 Emission in Separation	18.5 kmol/hr
Electricity Price	$0.08 kWh
Natural Gas Price	$3/GJ
CO in syngas Price	$300/tonne
H_2 in syngas Price	$1000/tonne
CO_2 Tax Credit	$35/tonne

Estimated Capital Cost (Million $)	8.941
Operation Cost (Million $)	3.133
Product Sales (Million $)	4.215
CO_2 Tax Credit (Million $)	0.263
Total Profit (Million $)	1.299
Return on Capital	**14.5%**

- Conservative estimation of electricity and CO2 tax credit
- 1 eV/molecule syngas production energy cost

- 14.5% Return on Capital (RoC) for PADMR, compared with ~10% for SMR

Future Plan (1/1)

- Synthesize and test high-performance catalysts
- Continue the reactor optimization
- Test with simulated impurities
- System scaling up
- Detailed techno-economic analysis for bi-reforming process

Summary

- High efficiency PADMR at lower temperature (550 °C) with advanced catalyst
- 90% CH_4 conversion to eliminate separation
- Plasma-assisted bi-reforming provides syngas with suitable composition and excellent coke reduction
- Industrial process design showing economical viability

Acknowledgement

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Prof. Jonas Baltrusaitis
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THANK YOU!