A Pressure-Swing Process for Reactive CO_2 Capture and Conversion to Methanol through Precise Control of Co-Located Active Sites in Dual Functional Materials

(FWP-FY21-RCC-LAB-CALL)

Daniel Ruddy

National Renewable Energy Laboratory
(NREL)

U.S. Department of Energy
National Energy Technology Laboratory
Carbon Management Project Review Meeting
August 15 - 19, 2022

Participants and Roles

Overall Project Performance Dates: Oct 1, 2021 – Sept 30, 2024

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

- $2,670k over 3 years
- Lead DFM **Characterization**
  - *Wilson McNeary*
- Lead **performance** testing for CO_2 to MeOH
  - *Anh To*
- Lead process modeling, **techno-economic and life cycle analyses** (TEA, LCA)
  - *Jennifer King*
- Project Management
  - *Dan Ruddy*

Boulder

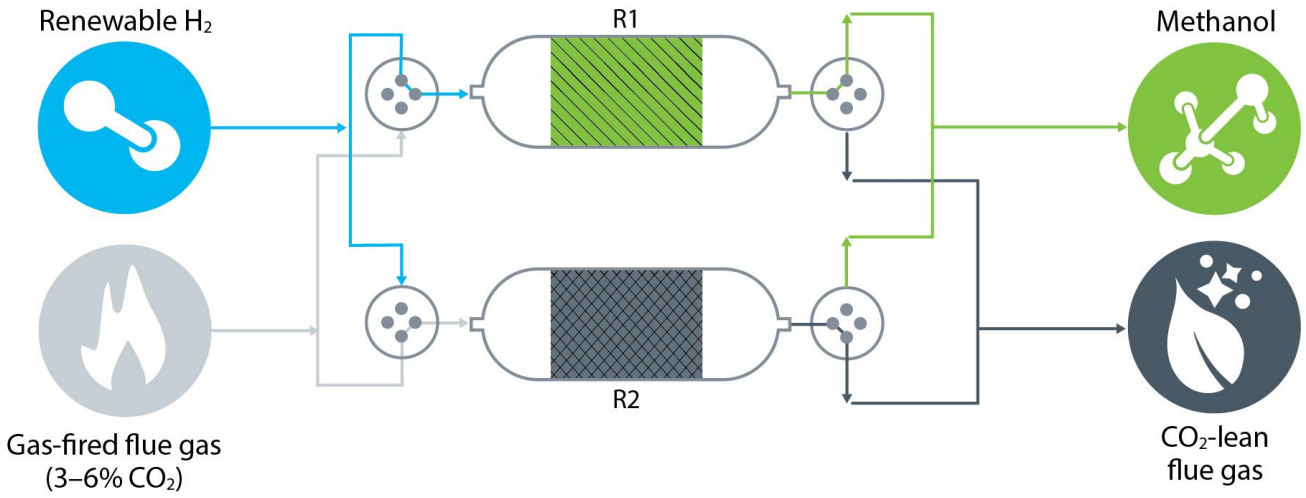
- $283k over 3 years
- **Lead synthesis** of dual-function materials (DFMs)
  - *Prof. Al Weimer*
- Atomic layer and molecular layer deposition (**ALD, MLD**)
- Assist DFM characterization

FORGE NANO

- $35k in year 3
- **Assist technology maturation** for DFM scalability via ALD/MLD
  - *Arrelaine Dameron*
  - *Staci Moulton*

Project Objective

- This project will **design and develop tailored dual-function materials (DFMs) and the accompanying pressure-swing process** for reactive capture and conversion (RCC) of CO_2 to directly produce **methanol**
- This will *favor lower capital and operating expenses and offer compatibility with a dynamic energy grid* to provide favorable process economics



Task Structure and Key Personnel

A Pressure-Swing Process for CO_2 RCC to Methanol through Precise Control of Co-Located Active Sites in DFMs

Task 1: DFM Synthesis and Characterization

Task Leaders: Wilson McNeary (NREL) and Alan Weimer (CU)

Key Personnel: Susan Habas (NREL), Hailey Loehde-Woolard (CU)

Task 2: RCC Evaluation

Task Leader: Anh To (NREL)

Key Personnel: Martha Arellano-Trevino (NREL), Wilson McNeary (NREL)

Task 3: Process Modeling and Scale-up

Task Leader: Jennifer King (NREL)

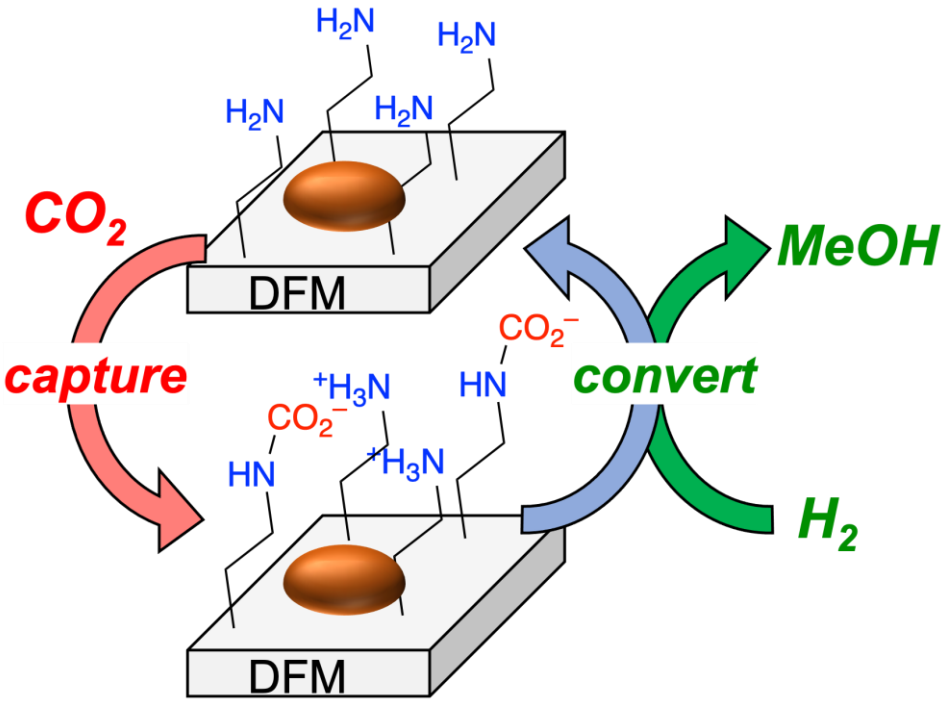
Key Personnel: Jonathan Martin (NREL), Eric Tan (NREL), Staci Moulton (FN)

Task 4: Project Management and Planning

Task Leader: Dan Ruddy (NREL)

Key Personnel: Alan Weimer (CU), Arrelaine Dameron (FN)

How the chemistry works



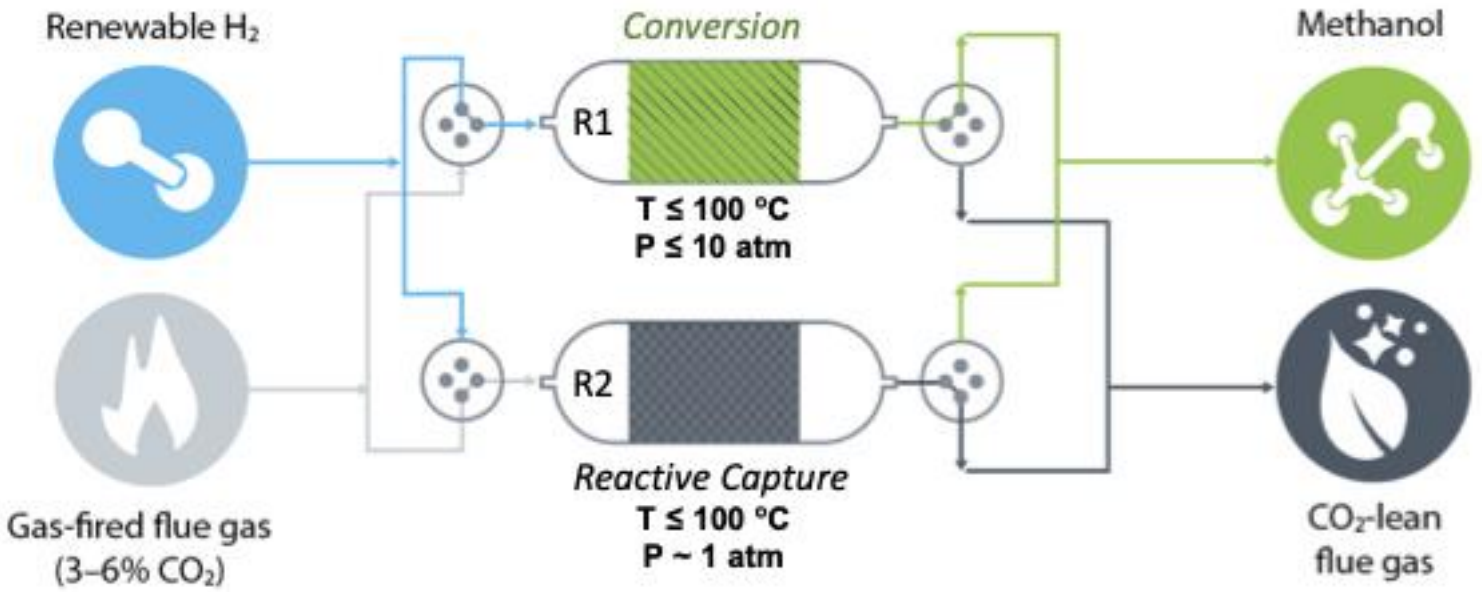
2-step capture-convert chemistry

- Amine binding of CO_2 followed by introduction of H_2 with increased pressure
- Constant temperature, targeting operation near 100 °C
- Metal species chosen to favor methanol production (e.g., Pd, Cu)

Key Challenges

- Capture capacity and efficiency
- Selectivity to methanol
- Stability

How the process works



- Multi-bed pressure-swing capture-conversion system

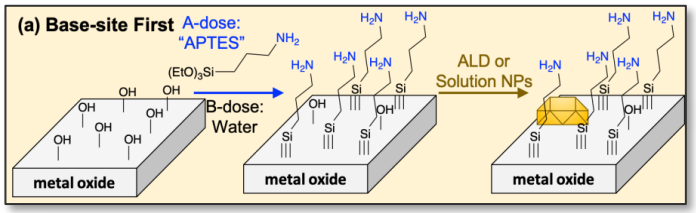
Key Challenges

- Capture AND conversion rates – cycle time dictates production rate
- Separations and purity of methanol product

Unique Aspects of this Project

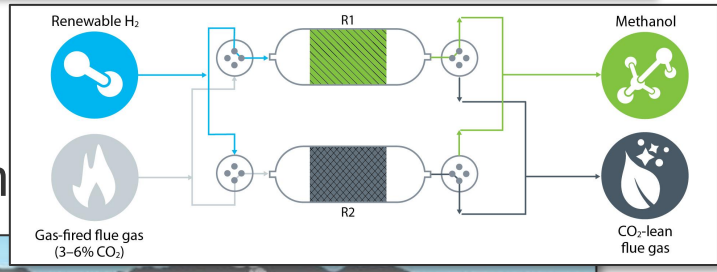
Materials Chemistry

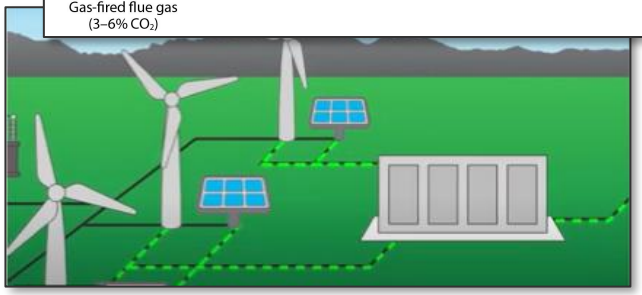
- Precise ***control*** of base and metal sites



Catalysis

- Pressure-swing reactor for ***low temperature*** conversion (< 100 ºC)
- Avoids high-T costs compared to methanation
  - capex, opex, low product value

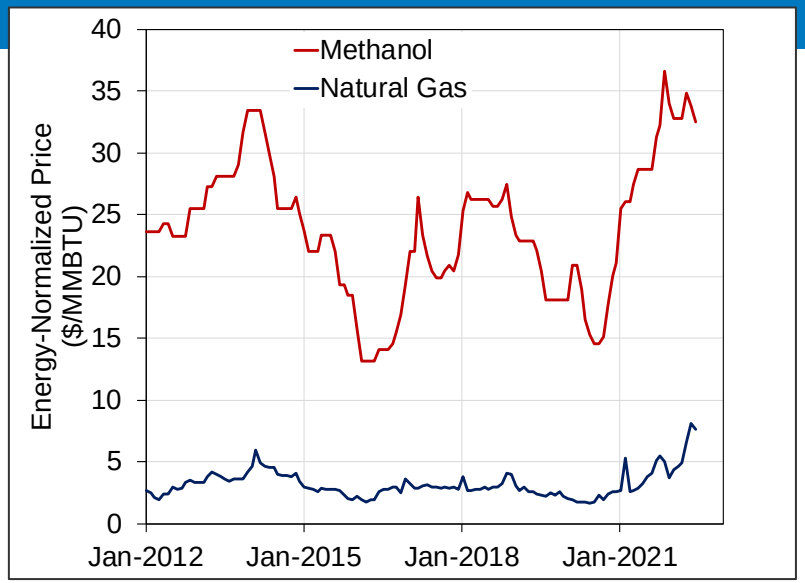


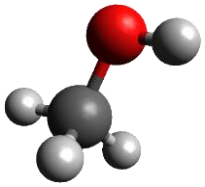


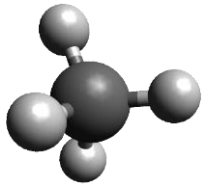
Process Design and LCA

- ***Static and dynamic*** energy grid situations
  - DFM stability during periods of inactivity,
  - Modular process design to match energy demand and availability
  - CO_2 conversion step using renewable H_2

Advantages, by the Numbers







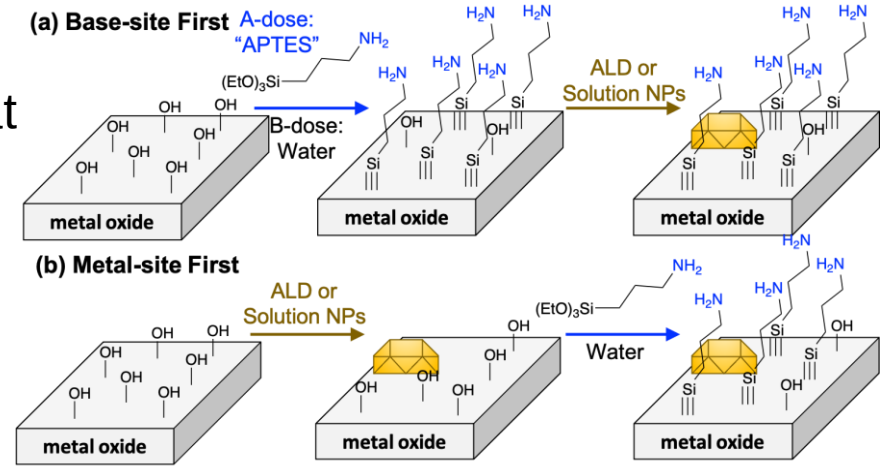
- ***Methanol vs Methane***
  - 5-10X difference in value
  - Versatile precursor in fuel/chemical markets

- ***Why an RCC approach at gas-fired power plants?***
  - CO_2 capture costs of $43-89/ton
  - Carbon capture rate (0.47 MMT_{CO2}/year/plant) matches well with RCC scale
    - Does not require a "giant" first RCC installation
    - 5–7 cylindrical reactors of 5m dia. x 10m height; 375-560 t_{DFM}/site
  - High number of plants (>1100)
  - Can ***equal current annual production of renewable MeOH*** (0.2 MMT/year) with the 1st installation

Experimental Design

DFM Synthesis and Characterization

- MLD and ALD are *scalable technologies* that provide needed **control over base and metal sites**
- Structural and active site characterization
- CO_2 chemisorption and thermogravimetric analysis – capacity, rate, strength
- H_2 chemisorption – capacity and rate



RCC Evaluation

- **0.5 – 2.0 g-scale** single-bed system for the 2-step capture-convert process
- **Tailored gas compositions** (%CO_2, H_2) and ability to study the effects of impurities in later-stage R&D

NREL's HOPP tool (hybrid optimization and performance platform) for renew. H_2

- **Establish model** for wind+solar PV, battery storage, H_2 production and storage, RCC co-located with the gas-fired power plant
- **Optimize this hybrid system** *down to the component level* for each technology to maximize operational efficiency and cost-effectiveness of the overall system

Project Schedule and Key Milestones

Milestones at 6-month intervals (8 total over 36 months)

- 03/22: **Synthesize and characterize** at least 12 first-generation DFMs
- 09/22: **Evaluate RCC performance** of DFMs at bench scale, targeting 80% MeOH selectivity
- 03/23: Achieve **stable RCC performance** over 20 cycles
- 03/23: Build initial **process model with TEA, LCA**
- 09/23: Evaluate **top 3 DFMs with simulated flue gas** containing oxygen, water, impurities
- 03/24: **Identify critical hurdles** to DFM and process scale-up
- 03/24: Evaluate best performing DFM(s) for **100 RCC cycles**
- 09/24: **Final report** with process model, TEA, LCA

Success Criteria: Go/No-Go Decision Points

- 03/23: Using TEA and LCA, **determine performance metrics needed to achieve favorable carbon intensity and economics** versus baseline methanol production with and without CCS. Achievable performance results in a 'go'.
- 03/24: Demonstrate **stability over 100 cycles**. 90% of original activity results in a 'go'.

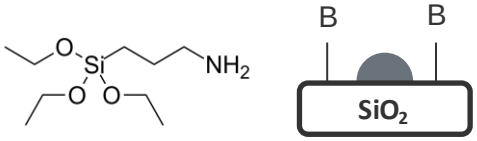
Risks and Mitigation

Risk	Mitigation
DFMs do not remain **stable** under repeated reaction cycles.	Utilize **multiple amine precursors** for MLD with previously-demonstrated stability under relevant temperatures. Test stability of top-performing DFMs under simulated flue gas containing oxygen, water vapor, and impurities.
Sufficient **catalytic activity and selectivity to methanol** is not obtained under proposed range of operating conditions.	Examine **multiple synthetic approaches of DFMs and a range of candidate metal species (Cu, Pd, Ru) in BP1**. Expand operation conditions (increase reaction temperature and/or pressure) of the reactive conversion of adsorbed CO_2.
Mismatch in kinetics between CO_2 capture and reactive desorption steps	**Tuning basic/metallic ratio** of the catalysts to adjust rate of CO_2 capture and reactive desorption steps.
Proposed process does not meet **carbon intensity and economic** metrics in TEA/LCA.	**Engage TEA team early in BP1** to evaluate high-performing DFMs in TEA/LCA and make adjustments in synthesis if necessary.

Task 1: DFM Synthesis and Characterization

Goal: Synthesize DFMs with a range of base/metal site ratios (B/M) targeting 1-25 mol/mol

Add catalytic metal → **Add base sites** → **Characterize**



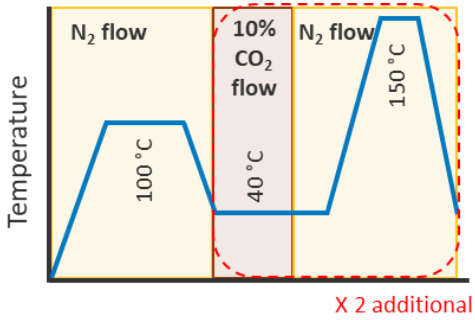
Methods:
Atomic layer deposition
Incipient wetness

Metals: Pd, PdH, PdCu, Cu, CuZnO/Al_2O_3 (CZA)

Methods:
Molecular layer deposition
Solution grafting, Incipient wetness

Bases: APTES, TMPTA
Alkali (Na, K)

TGA cycling of DFMS



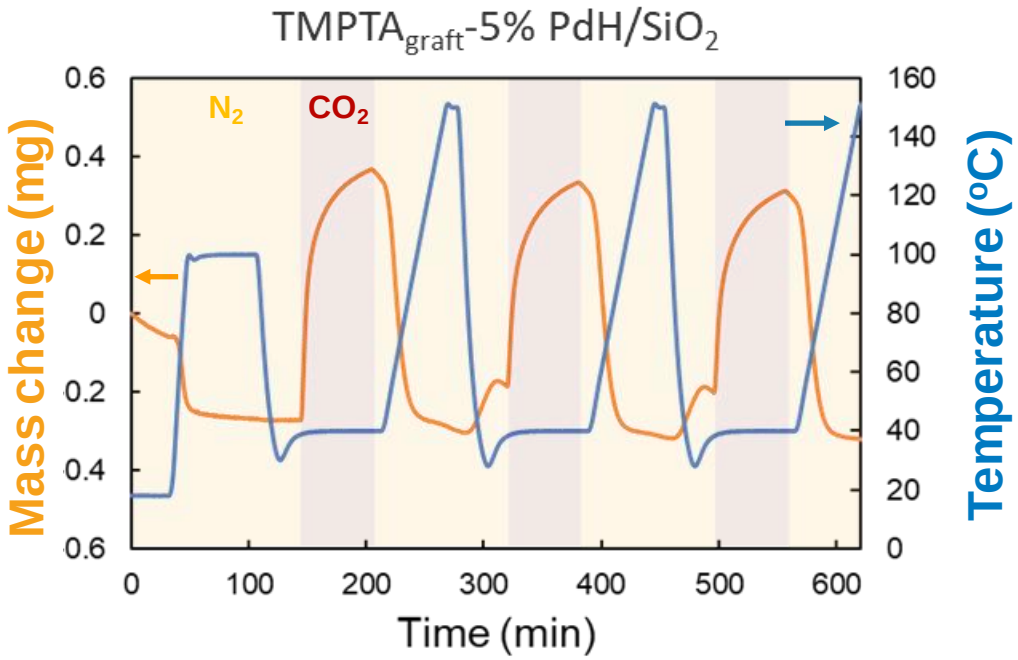
Methods:
TGA-IR, CHN,
Chemisorption

DFM	B/M_{surf}	CO_2 uptake (mmol/g)
$TMPTA_{graft}$-5% Pd	114	2.4
$APTES_{graft}$-5% Pd	88	1.8
$TMPTA_{graft}$-5% PdH	–	1.7
$TMPTA_{graft}$-1% Pd	42	1.2
$TMPTA_{graft}$-1% PdH	–	1.2
K_{IW}-CZA	1	1.1

Exceeded the target range for accessible B/M site ratios

+ 16 additional DFMs

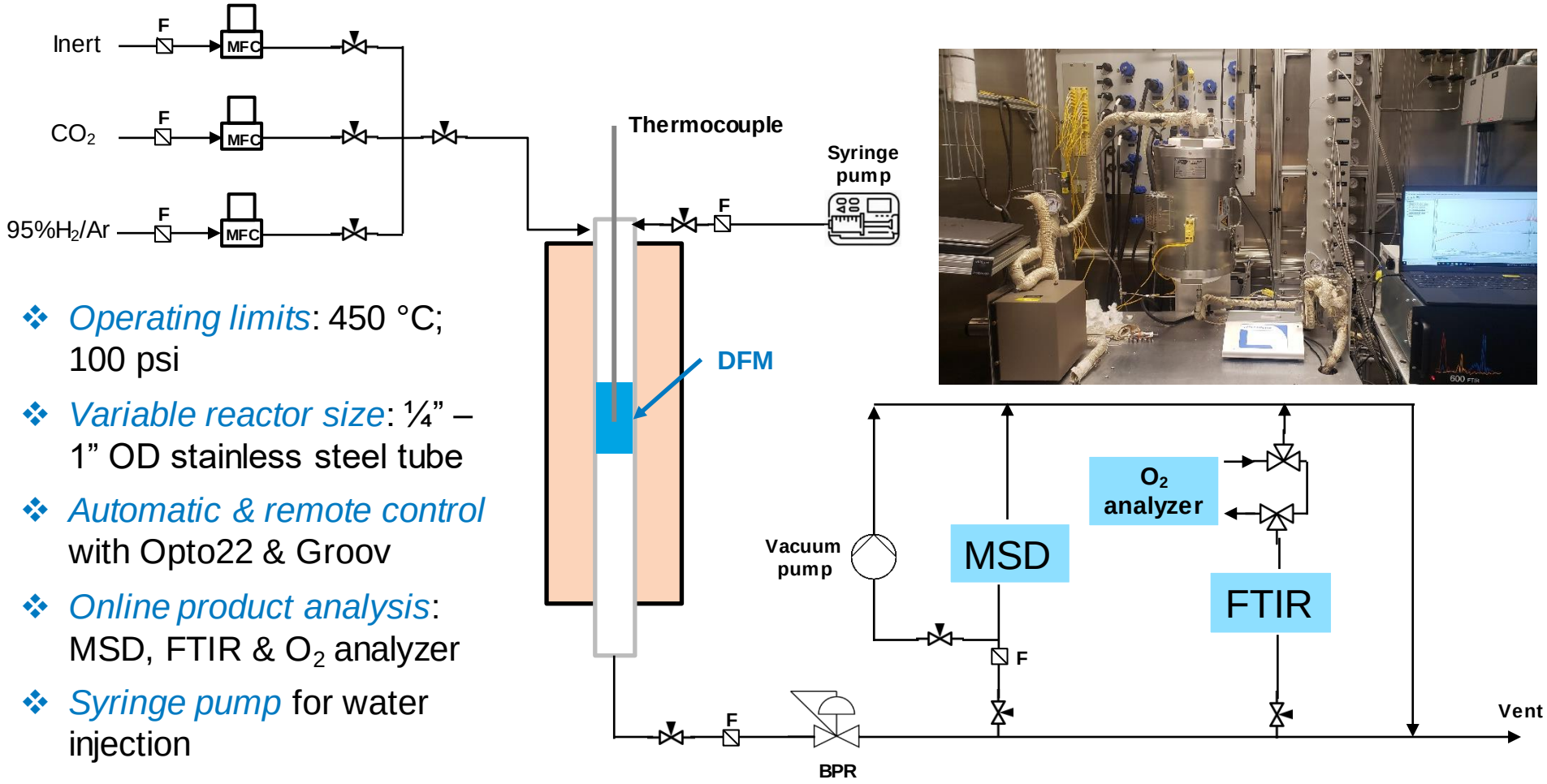
Task 1: CO_2 Adsorption-Desorption TGA Cycling



- **Thermal cycling used to assess stability**
- **TMPTA-5% PdH/SiO_2 DFM retained > 90% starting capacity**
- **Future DFMs will be investigated in isothermal adsorption/hydrogenation RCC cycles**

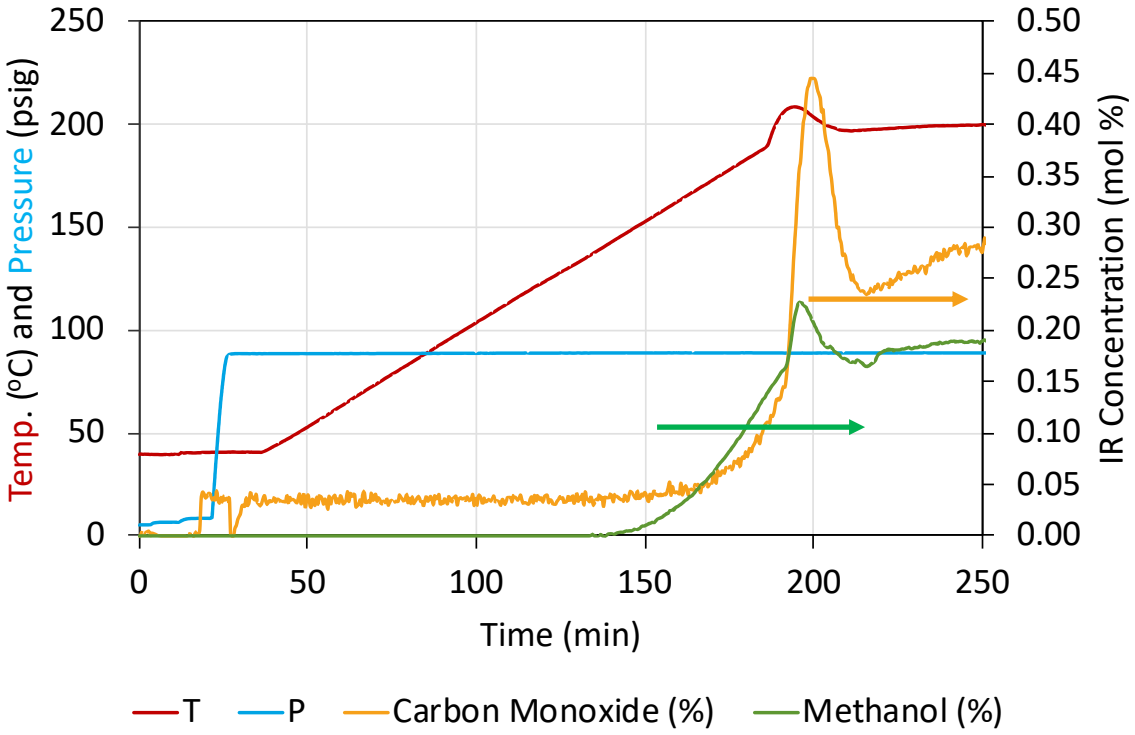
Task 2: DFM Performance Testing

Schematic of RCC Reactor System



- *Operating limits*: 450 °C; 100 psi
- *Variable reactor size*: ¼" – 1" OD stainless steel tube
- *Automatic & remote control* with Opto22 & Groov
- *Online product analysis*: MSD, FTIR & O_2 analyzer
- *Syringe pump* for water injection
- *Variable gas supply*

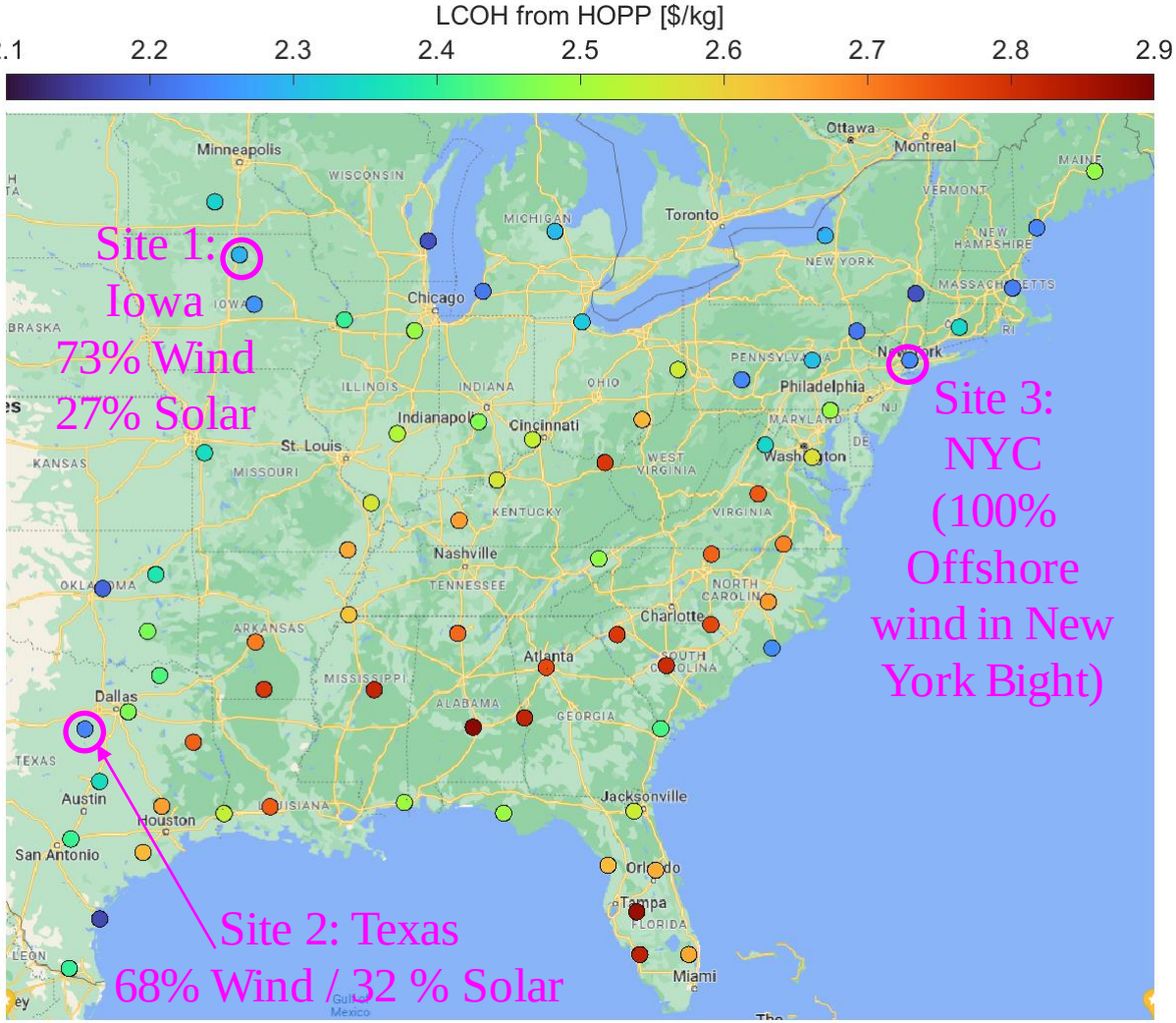
Task 2: Commissioning of RCC Reactor



- **Baseline CO_2 hydrogenation using benchmark CuZnO-Al_2O_3**
- **Not RCC, light off temp ca. 135 ºC**
- **Goal is decreased light-off T with amine capture**

Task 3: Techno-economic Analysis – Site Selection

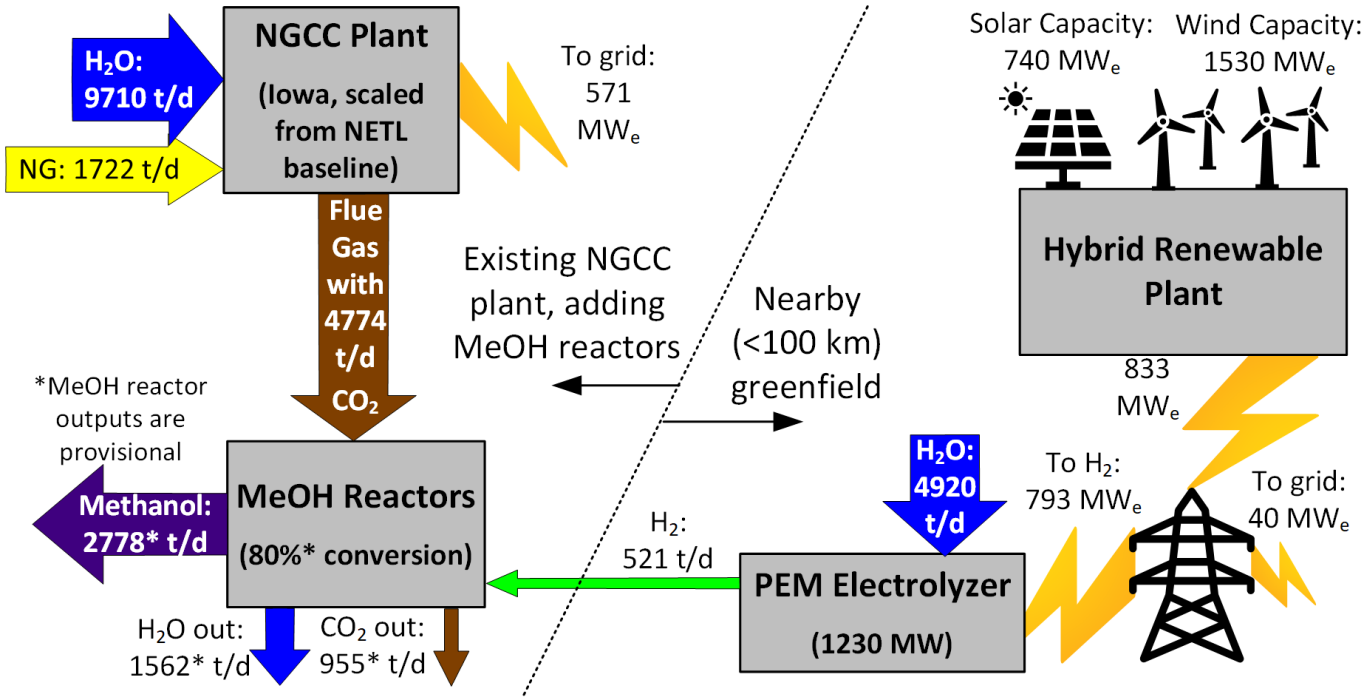
- H_2 generated by new wind/solar hybrid plants built near existing NGCC plants
- **Scouted sites near all existing 500 MW+ NGCC plants in the eastern US**
  - Excluded the west - H_2O scarcity
- **Metric**: Levelized Cost of Hydrogen (LCOH) [$/kg]
  - Color of circle = LCOH
  - Location of circle = Existing NGGC plant
- **Tool**: NREL's "HOPP" (Hybrid Optimization and Performance Platform)
- **Calculates wind/solar ratio to minimize cost**



Identified 3 sites with promising co-location opportunity based on cost of renewable H_2 production from wind+solar

Task 3: Techno-economic Analysis – Levelized Cost of Methanol

- Levelized Cost of Methanol (LCOM) for pure CO_2/H_2 process: \$0.57/kg[1]
- **PROVISIONAL** LCOM for our flue gas/H_2 process: **\$0.53/kg**
- \$0.43/kg – H_2 production: **hard calculation** – using existing HOPP model
- \$0.10/kg – RCC retrofit for NGCC flue gas: **provisional** – building ASPEN models



[1]doi.org/10.3389/fenrg.2019.00081

Framework to determine LCOM is ahead-of-schedule

Next Steps

Task 1: DFM Synthesis & Characterization

- Determine **CO_2 adsorption modes** with FTIR spectroscopy
- Tune synthesis parameters to **maximize M-B co-location** based on initial RCC data outcomes

Task 2: RCC Evaluation

- Develop CO_2 RCC procedure to identify temperature, pressure, cycle time
  - Baseline and benchmark against commercially available catalysts (CuZnO)
- **Study cycle performance** of initial suite of DFMs
- *in-situ* FTIR spectroscopy to **identify intermediates** during CO_2 adsorption on DFMs and identify **species that limit RCC performance**

Task 3: Process Modeling and Scale-up

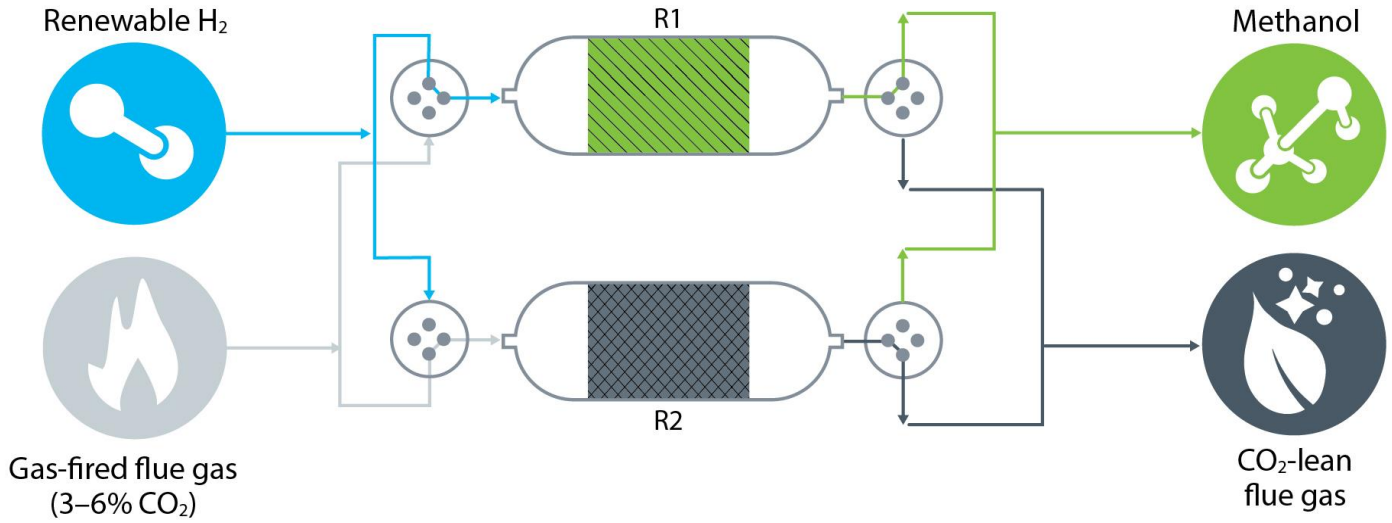
- ASPEN modeling of flue gas decontamination and RCC reactors
- **Cradle-to-gate Life Cycle Analysis** (LCA) using OpenLCA software
  - Carbon intensity (CI) for standard methanol: 1.13 kg CO_2e/kg MeOH
  - *Provisional* CI for our RCC process with assumptions: 1.26 kg CO_2e/kg MeOH
- **Scale–up**: Engage ForgeNano in Years 2 and 3

Next Steps: Stakeholder Engagement

- Getting **industry input and feedback on assumptions** in our TEA/LCA to ensure highest impact and market readiness
- **Seeking strategic partnerships and co-operative R&D** opportunities with methanol producers looking to reduce carbon intensity and grow the bio-methanol market

Summary

- **Tailored DFMs** and the **accompanying pressure-swing process** for RCC of CO_2 to methanol with renewable H_2
- **Rigorous RCC evaluation** including stability testing and scale-up consideration
- Process modeling with **comparative** TEA and LCA



Team Members

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Dan Ruddy
Wilson McNeary
Anh To
Martha Arellano-Treviño
Susan Habas
Nicole LiBretto
Eric Tan
Jennifer King
Jonathan Martin

Boulder

Alan Weimer
Hailey Loehde-Woolard

FORGE NANO

Arrelaine Dameron
Staci Moulton

Appendix

- These slides will not be discussed during the presentation but are mandatory.
- Organization Chart
- Gantt Chart
- Additional materials provided
- ALD/MLD reactor at CU-Boulder
- Schematic of ALD/MLD process chemistry
- PID for commercial ALD from ForgeNano

Organization Chart: Task Structure and Key Personnel

A Pressure-Swing Process for CO_2 RCC to Methanol through Precise Control of Co-Located Active Sites in DFMs

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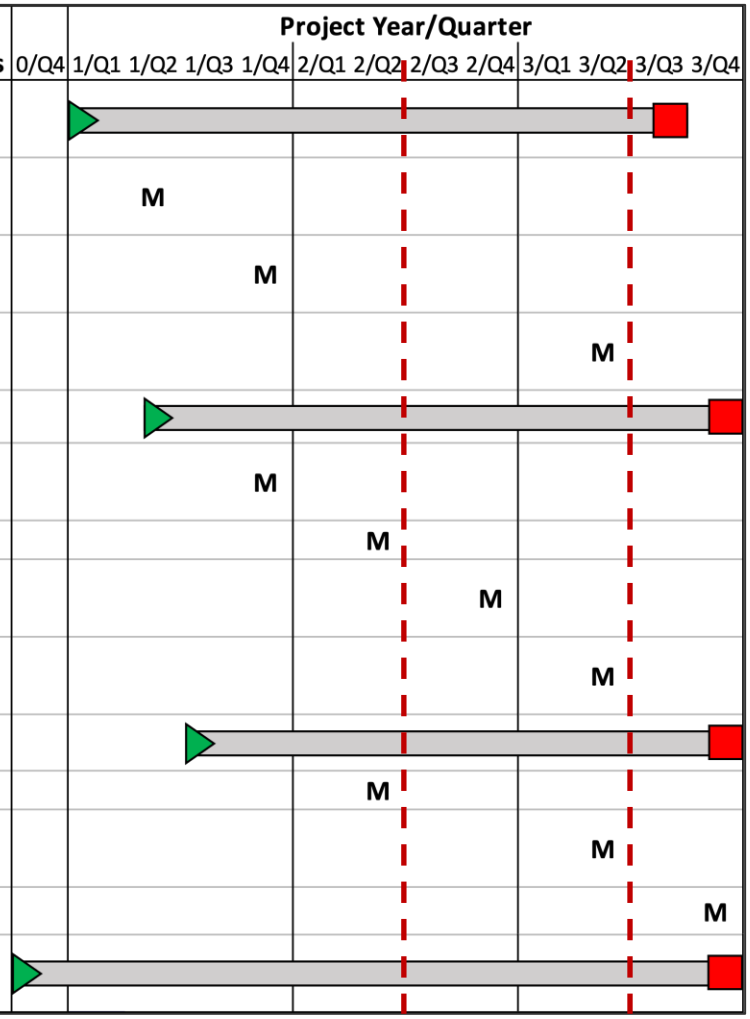
Task 4: Project Management and Planning

Task Leader: Dan Ruddy (NREL)

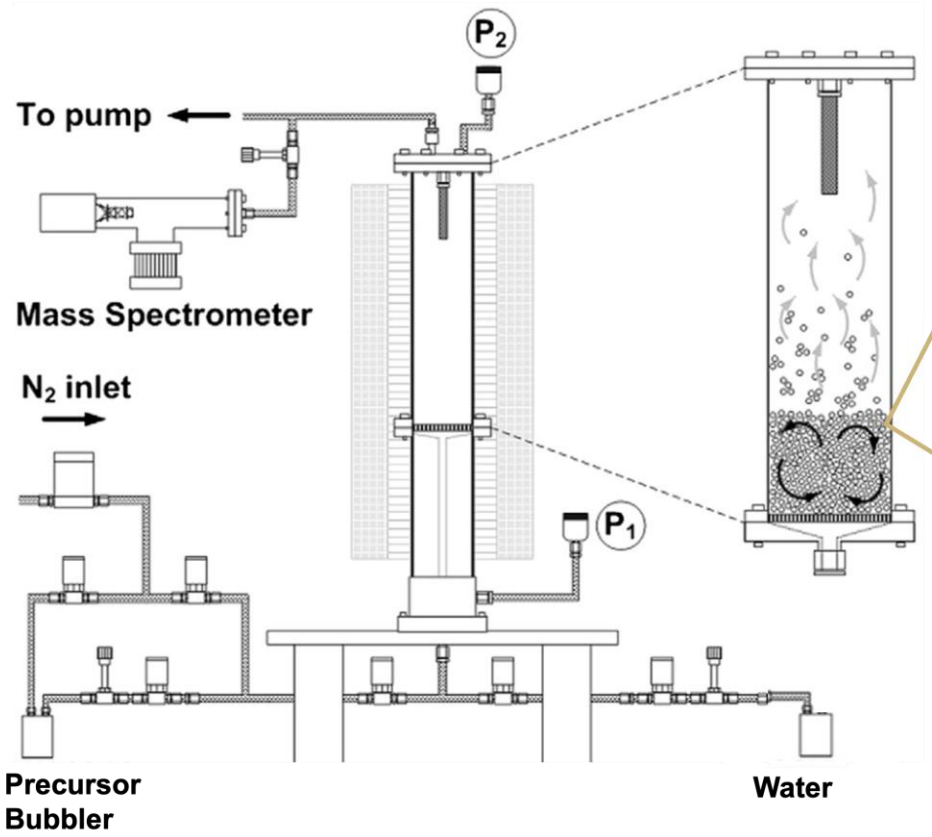
Key Personnel: Alan Weimer (CU), Arrelaine Dameron (FN)

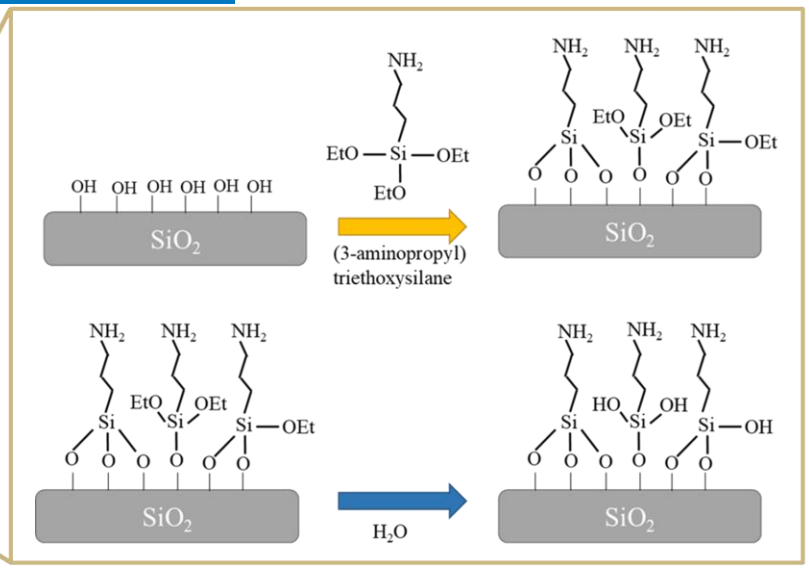
Gantt Chart

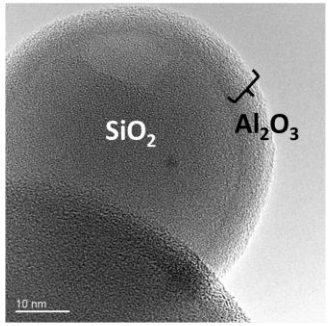
Task Name	Assigned Resources
Task 1.0 - DFM Synthesis and Characterization	Wilson McNeary; Alan Weimer
Milestone : DFM synthesis and characterization	Wilson McNeary; Alan Weimer
Milestone : DFM performance in RCC	Wilson McNeary; Anh To
Milestone : Demonstrate stable RCC performance under practical conditions	Wilson McNeary; Anh To
Task 2.0 - RCC Evaluation	Anh To
Milestone : DFM performance in RCC	Wilson McNeary; Anh To
Milestone : DFM stability	Anh To
Milestone : RCC process evaluation with simulated flue gas	Anh To
Milestone : Demonstrate stable RCC performance under practical conditions	Wilson McNeary; Anh To
Task 3.0 - Process Modeling and Scale-up	Dan Ruddy
Milestone : Initial TEA/LCA model	Eric Tan
Milestone : Identify critical hurdles	Arrelaine Dameron; Dan Ruddy
Milestone : Final report	Dan Ruddy
Task 4.0 - Project Management and Planning	Dan Ruddy



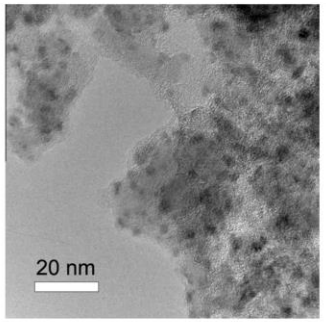
ALD/MLD Reactor at Univ. of Colorado-Boulder







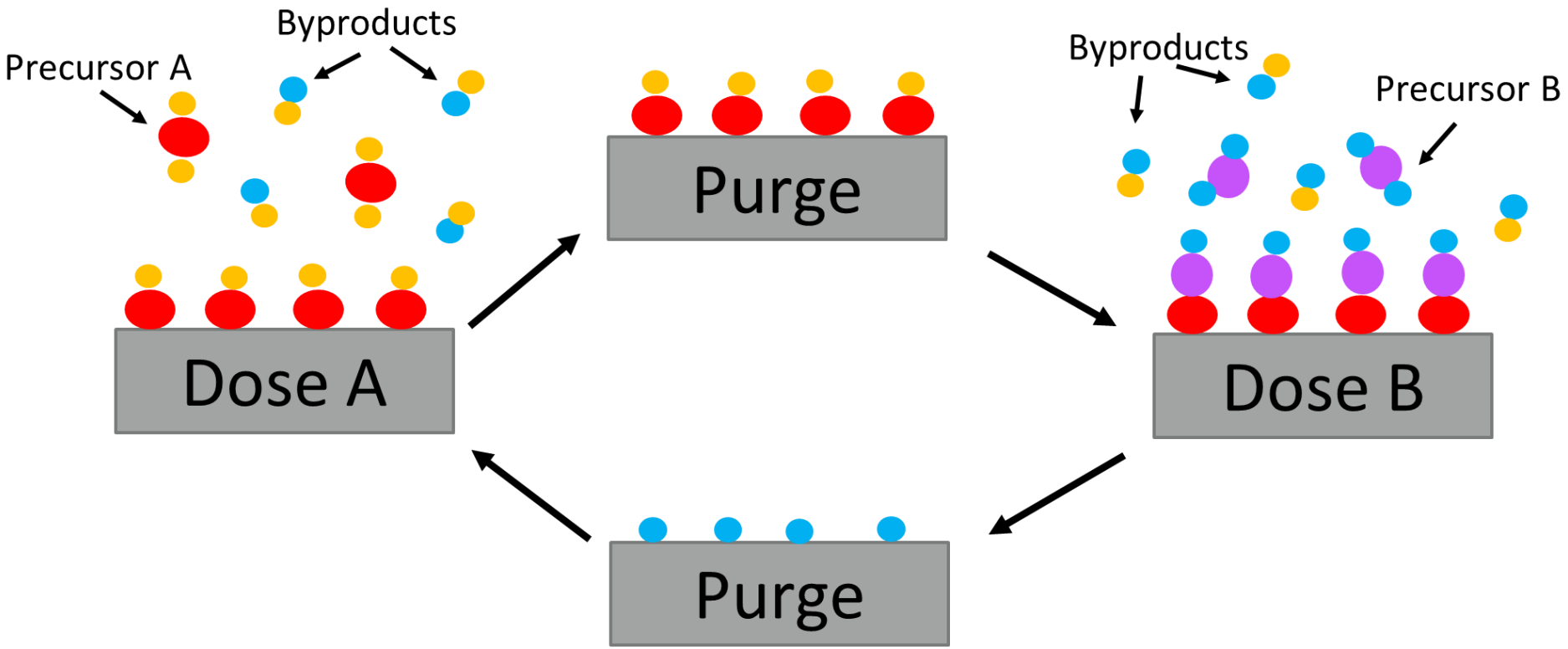
Al_2O_3 film on SiO_2



Ni particles on Al_2O_3

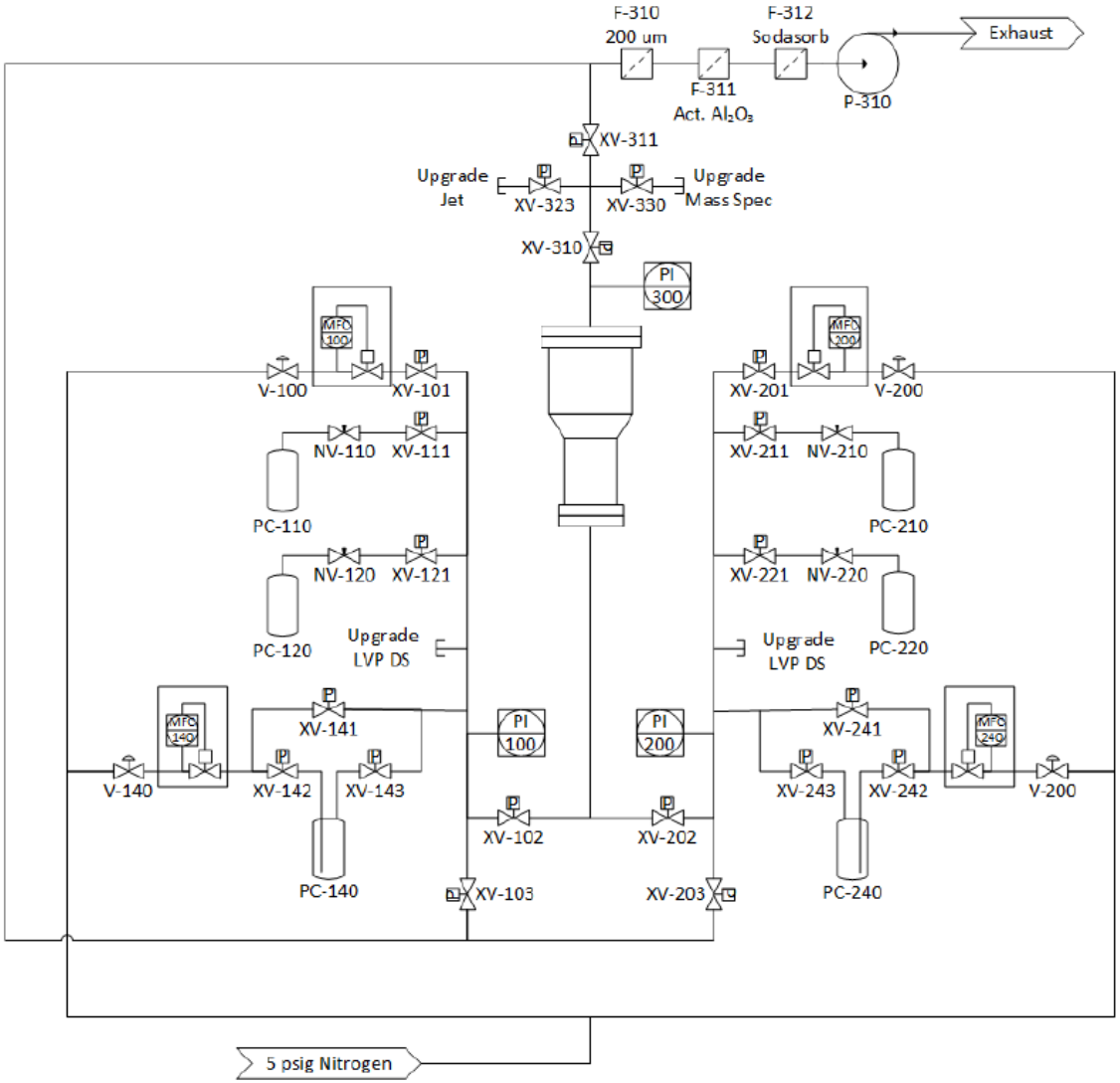
Adapted from Scheffe, J. et al. Thin Solid Films. 517, 1874-1879 (2009)
Hakim, L.F. et al., Chem. Vap. Deposition, 11, 420 (2005)
Gould, T. et al. Journal of Catalysis, 303, 9-15 (2013)
Lai*, A., Loehde-Woolard*, H. et al. Chem. Eng. Sci. 245, 116954 (2021)

Schematic of ALD/MLD Process Chemistry



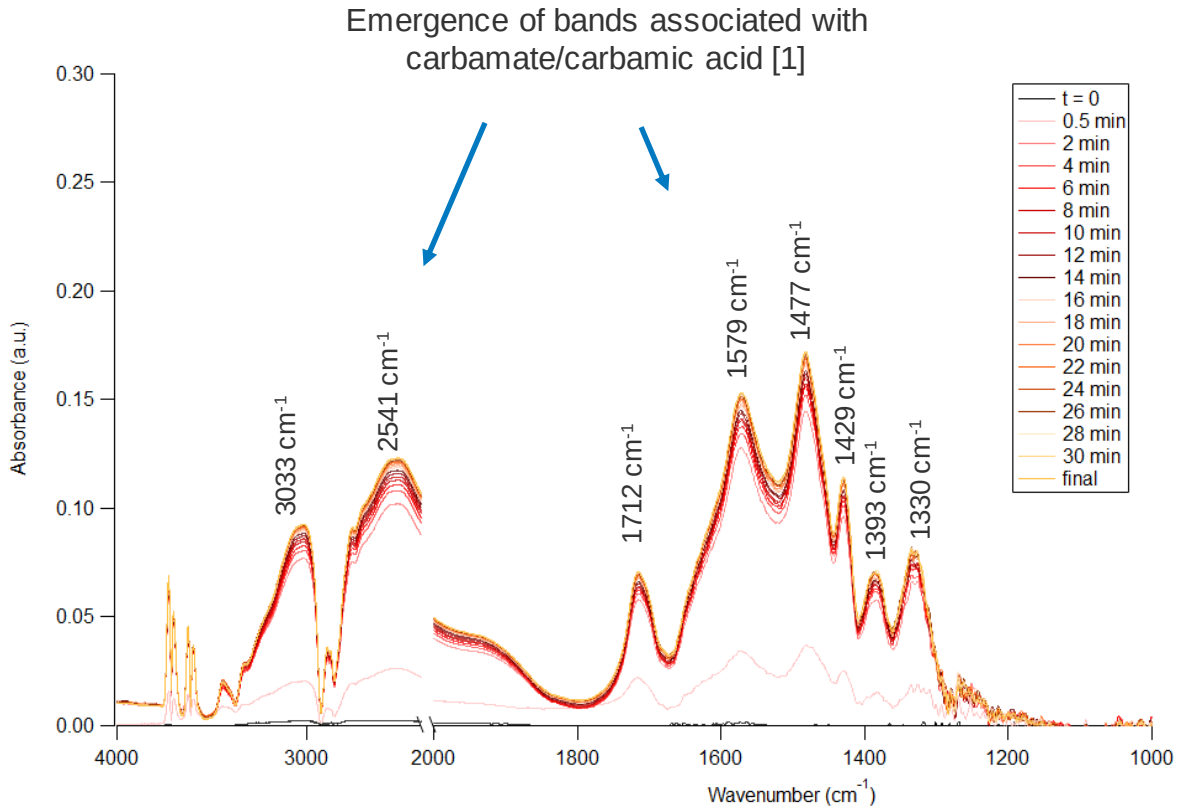
Start-Stop Point of Cycle

PID for Commercial ALD/MLD from ForgeNano



DRIFTS (CO_2 adsorption)

$APTES_{graft}$-5% Pd/SiO_2
DRIFTS cell at 70 °C
10 sccm CO_2
90 sccm N_2

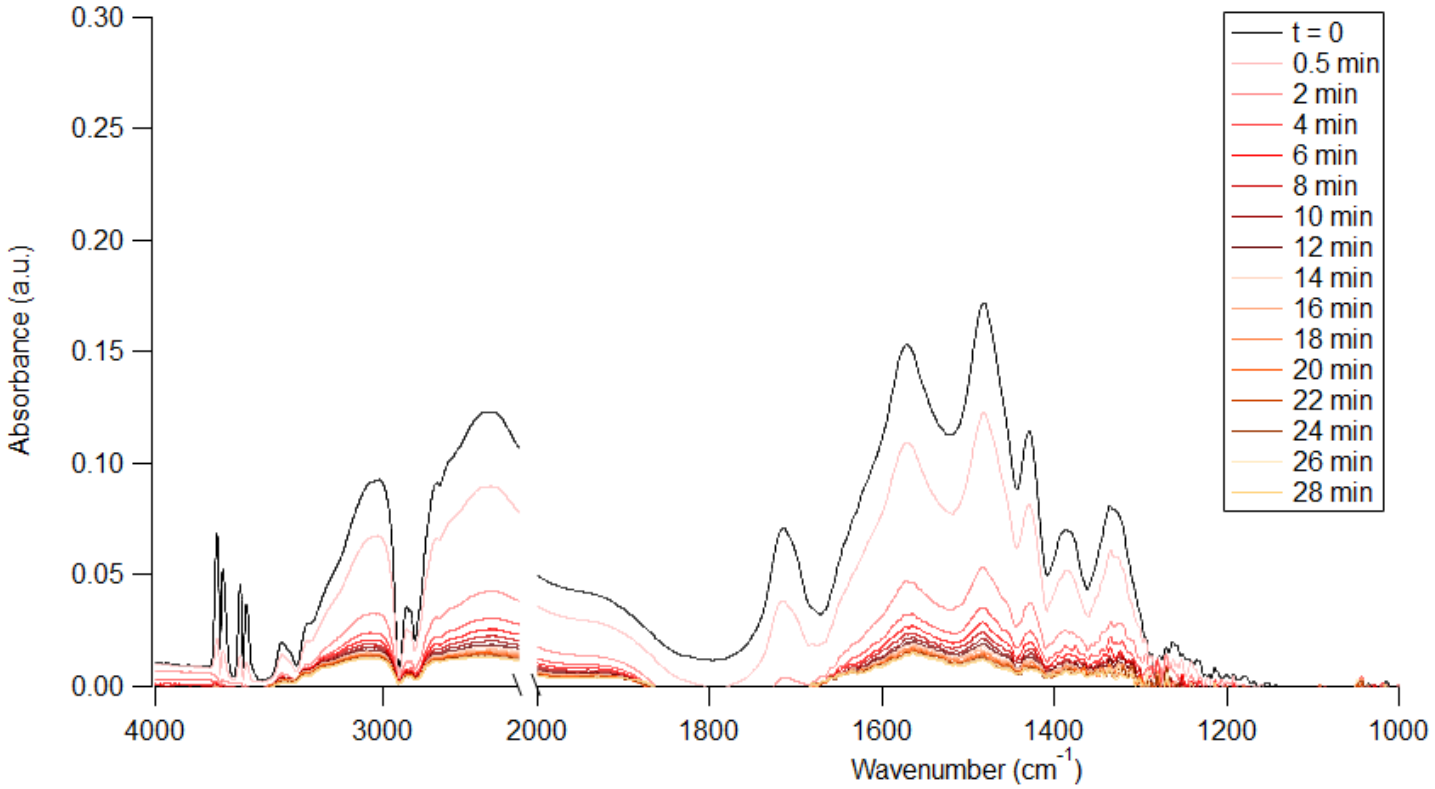


[1] Pazdera, J.; Berger, E.; Lercher, J. A.; Jentys, A. Conversion of CO2 to Methanol over Bifunctional Basic-Metallic Catalysts. *Catalysis Communications* **2021**, *159*, 106347. https://doi.org/10.1016/j.catcom.2021.106347.

DRIFTS (N_2 purge)

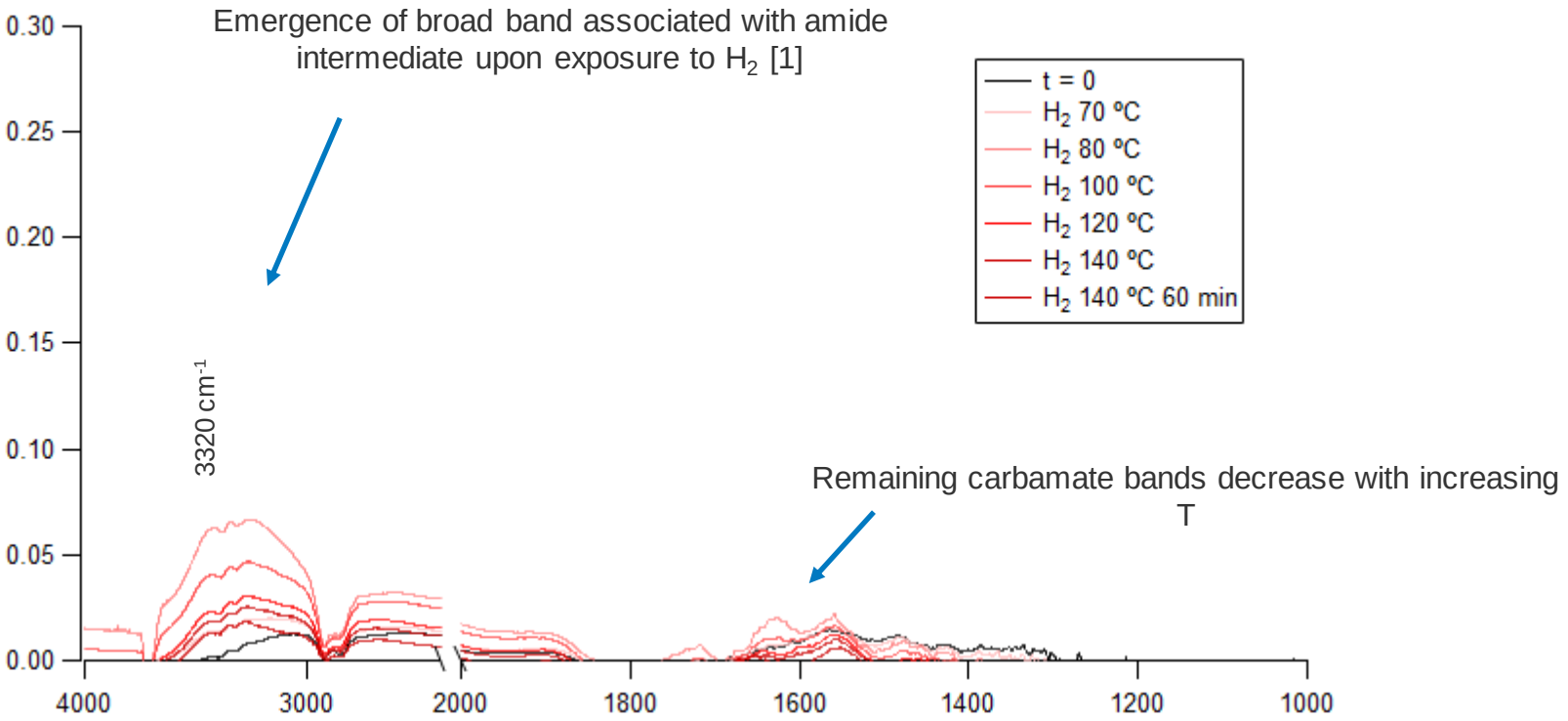
$APTES_{graft}$-5% Pd/SiO_2
DRIFTS cell at 70 °C
100 sccm N_2

Band intensity decreases during purge



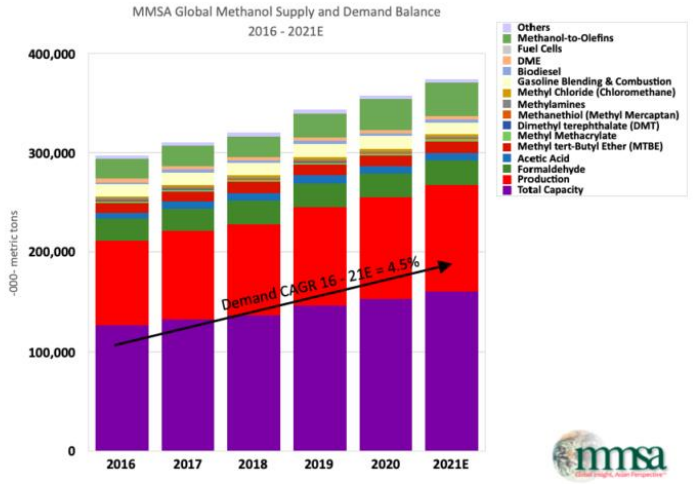
DRIFTS (T ramp under H_2)

$APTES_{graft}$-5% Pd/SiO_2
DRIFTS cell at 70 °C, ramp 5 °C/min
50 sccm N_2
50 sccm H_2



Opportunity for RCC Deployment

- **Methanol: vital precursor in the chemical market and intermediate to fuels – gasoline, diesel, marine, and jet**
  - Production: 100 MMT/y; 0.2 MMT/y renewable
  - *Huge opportunity for low-carbon intensity MeOH*
- **Demand is rising world-wide**
  - Opportunity to increase US MeOH production
  - Near-term opportunity for new technologies (RCC) to *co-locate with new facilities*
  - Take advantage of logistical synergies, energy and off-take of low-C intensity MeOH



from methanol.org