DE-FE-0031867

Modular System for Direct Conversion of Methane into Methanol via Photocatalysis

PI : Arun Majumdar

Presenter : Gang Wan

Stanford University

DOE/NETL Program Manager : Frances Toro

Outlines

- Project Overview and Technology Background
- Technical Approach and Current Status
- Future Development Plan
- Summary

Project Overview

Title	A Modular System for Direct Conversion of Methane into Methanol via Photocatalysis
Award No.	DE-FE0031867
Period of Performance	10/01/2020 – 09/30/2024
Project Funding	DOE: $1,000,000 Cost-Share: $250,000
Overall Project Goal	Develop a liquid phase photocatalytic process for direct conversion of methane in flare gas into methanol.
Project Participants	Stanford University, Susteon Inc., Casale SA
DOE/NETL Project Manager	Frances Toro

Organization Chart

Integrating Catalyst Development, Separation, Scale-up and Reactor Design

Arun Majumdar

Principal Investigator

Gang Wan (Research Scientist)

Max Kessler (graduate student)

Richard Randall (graduate student)

Raghubir Gupta

Vasudev Haribal

Ermanno Filippi

Michal Bialkowski

Pierdomenico Biasi

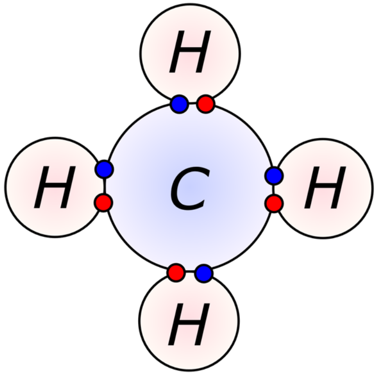
Stanford

Experiments; Modeling

Susteon and Casale

Tech-Economic Analysis

Technical Background – Grand Challenge



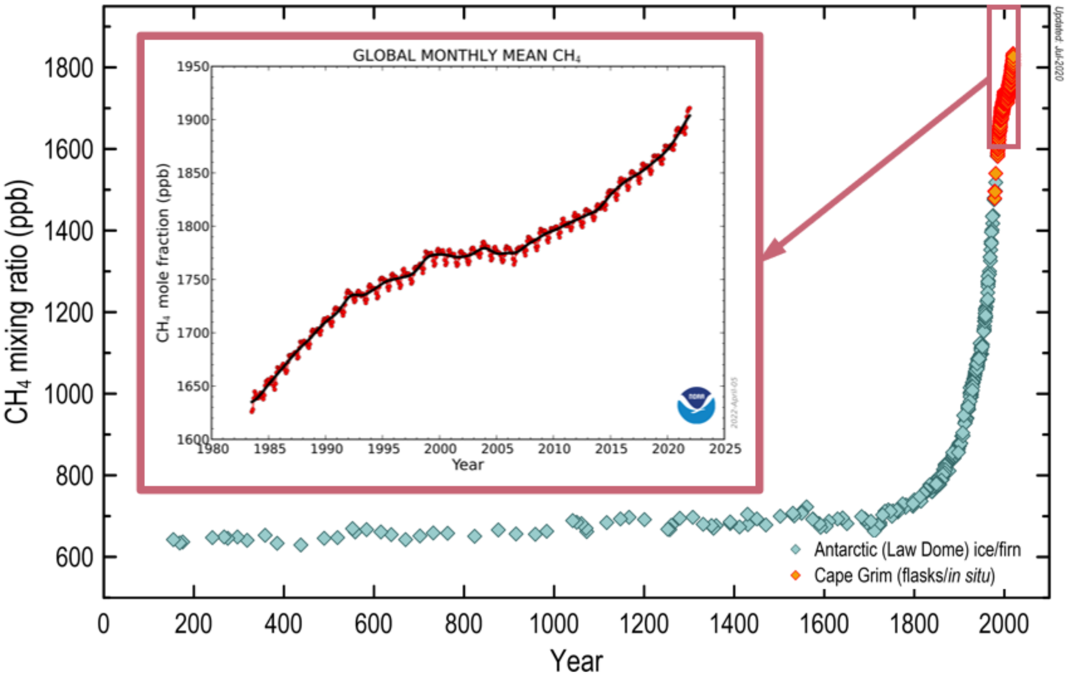
U. S. Methane

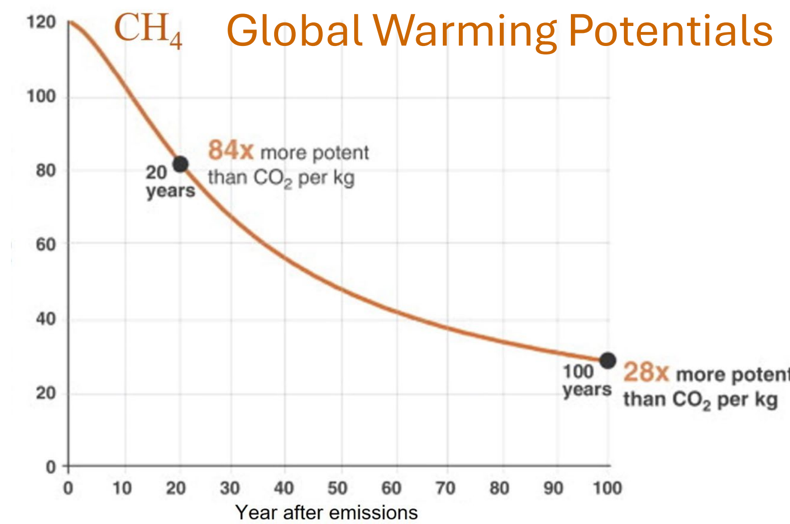
Reduction Action Plan

From U. S. Department of Energy

& U. S. Environmental Protection Agency

Technical Background - CH_4 Pollution



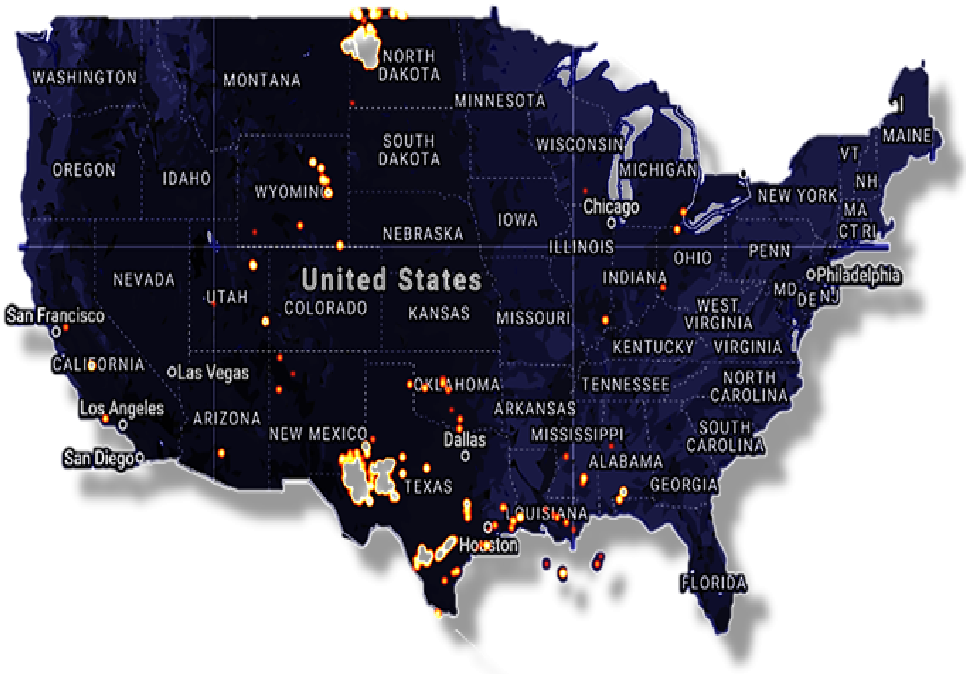


- ➢ Atmospheric concentration - rapidly rising
- ➢ Contributed to ~ 30% of warming temperatures

Atm. Environ. **2010**, 44 (27), 3343

Phil. Trans. Roy. Soc. A **2022**, 380 (2215), 20210108

Technical Background - CH_4 Flaring Issue



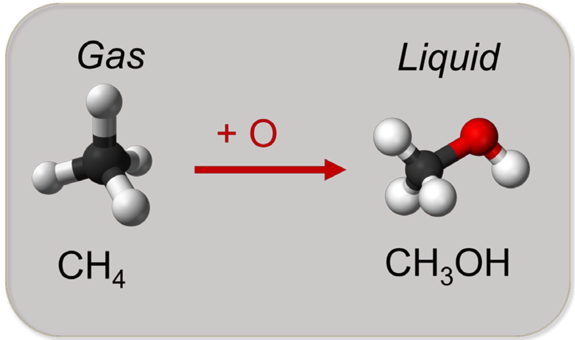
Contribute 1% of global CO_2 emissions

One Solution - Upgrade Methane to Methanol

Concentrated

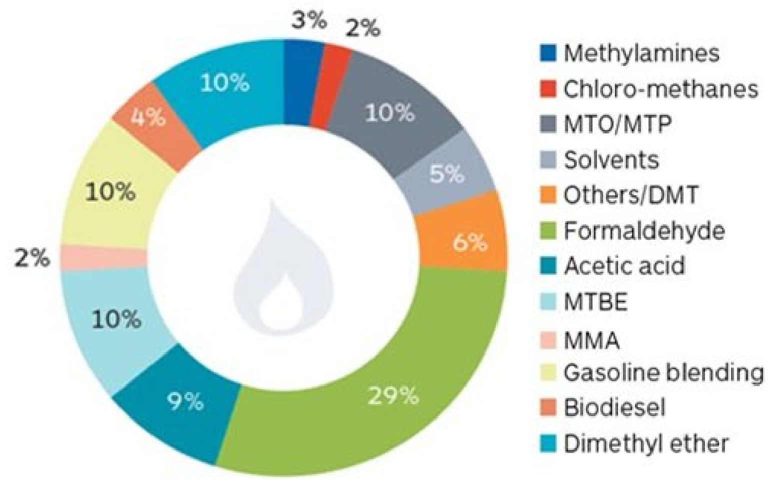
Methane

(Point sources)



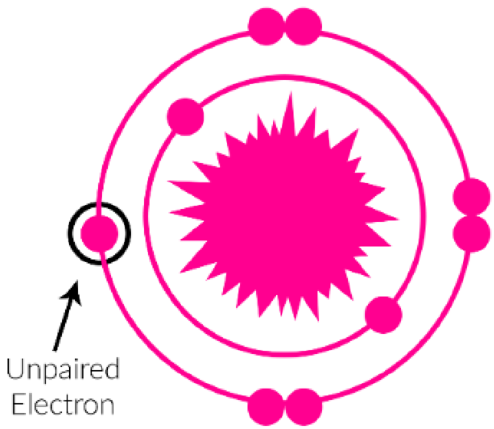
~ 61.7 billion $ by 2030

Worldwide Demands

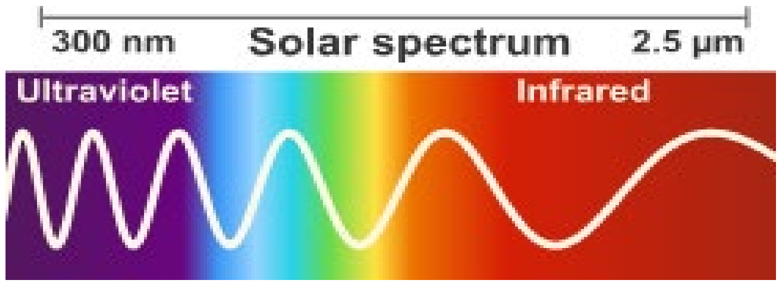


Key Feedstock

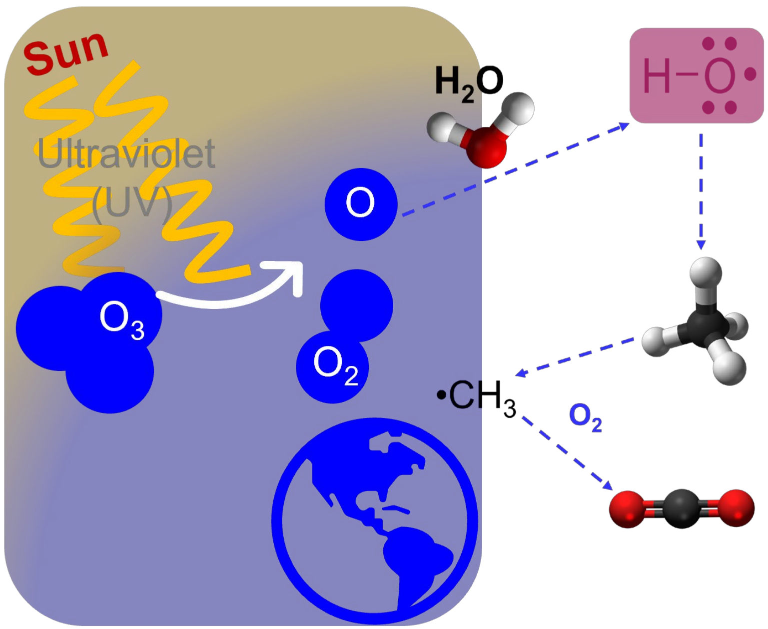
One Solution from Nature



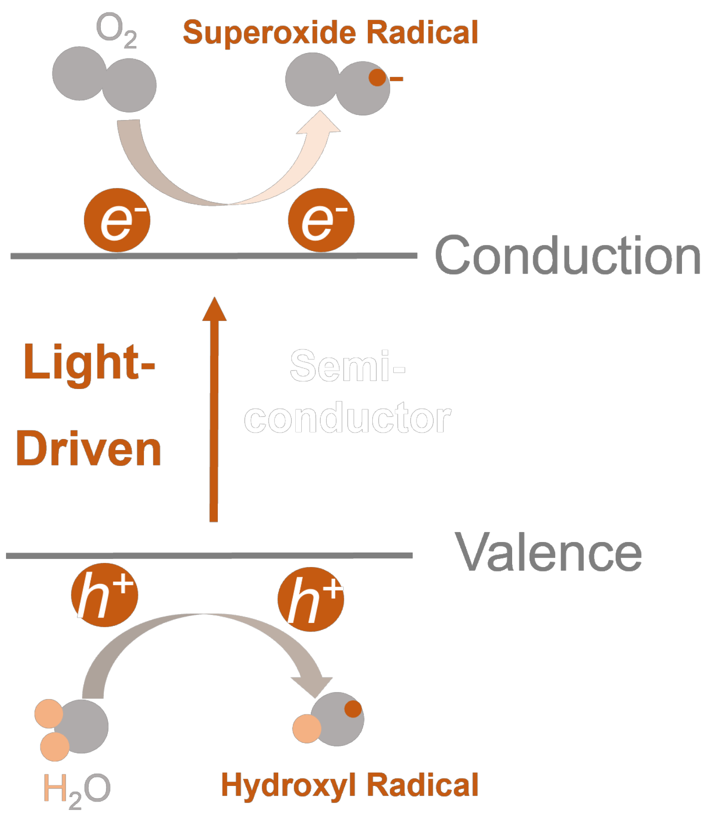
FREE RADICAL



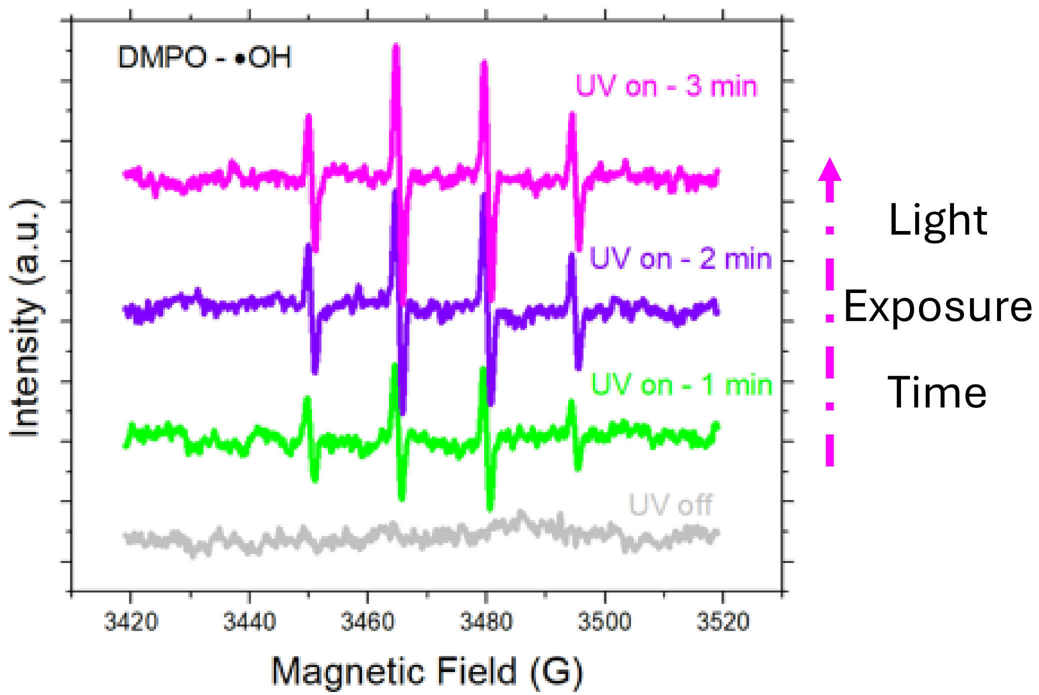
Free-Radicals Pathway



Technology Approach - Free Radicals from Photocatalysis



Free-radical formation



Two Interconnected Goals using Free Radicals

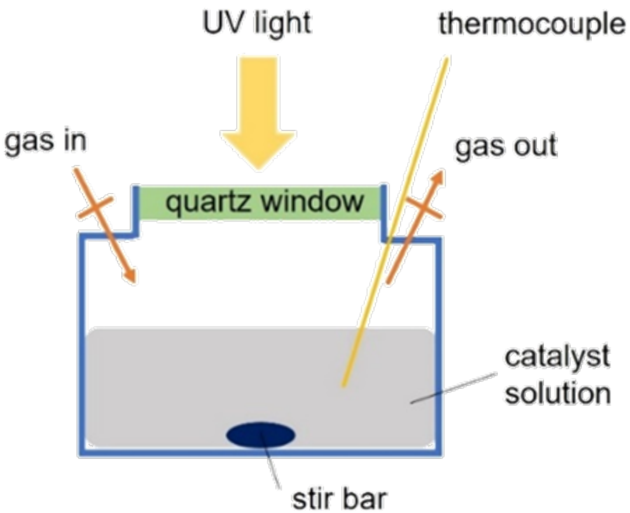
- 1) Methane Upgrading to Methanol

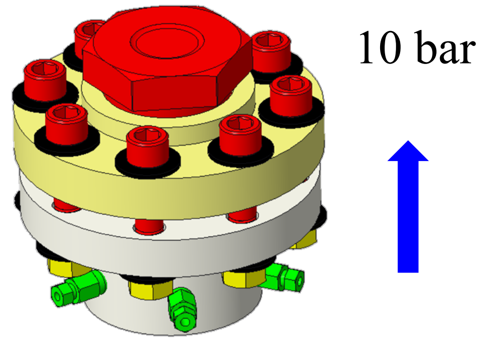
  (Concentrated Emission Source)

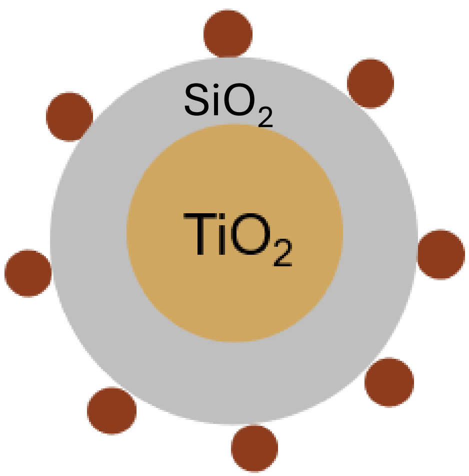
- 2) Environment Methane Removal

  (Dilute Emission Source)

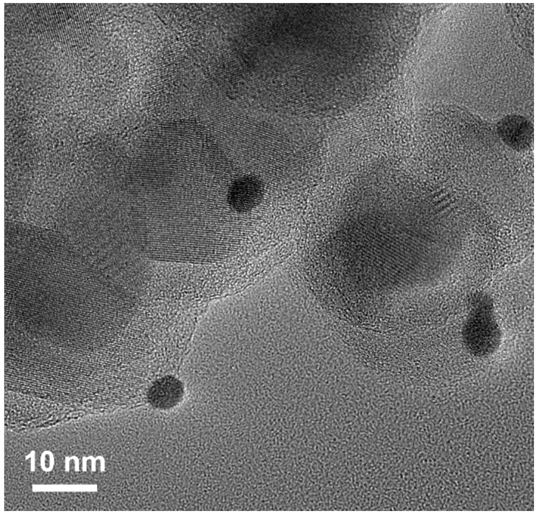
Technology Approach - Experimental Set-up and Materials

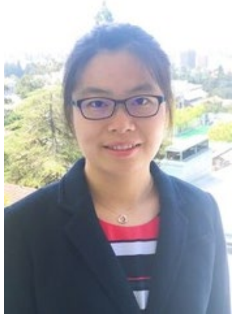






Electron Microscopy Image





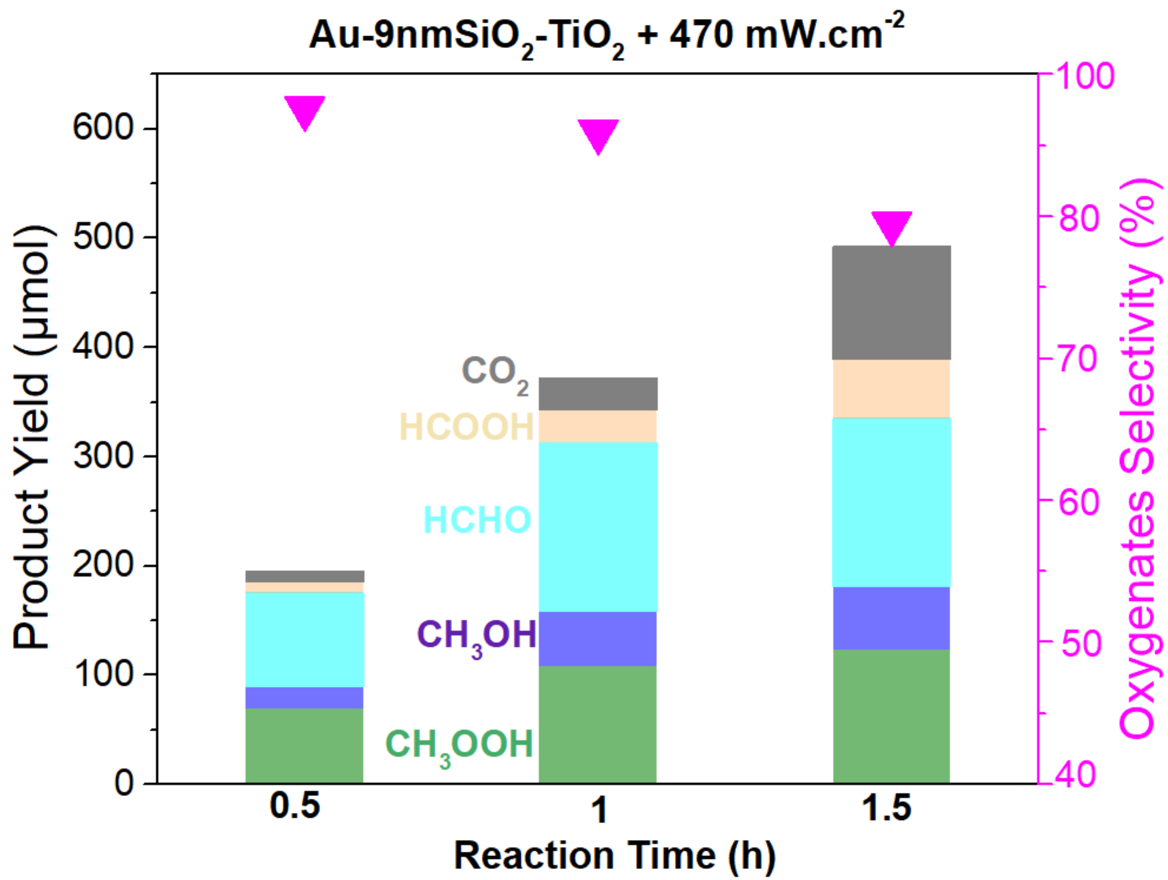
Chenlu Xie

Eddie Sun

Nano Letters, **2023**, 23 (5), 2039–2045

Current Status – Methane Conversion

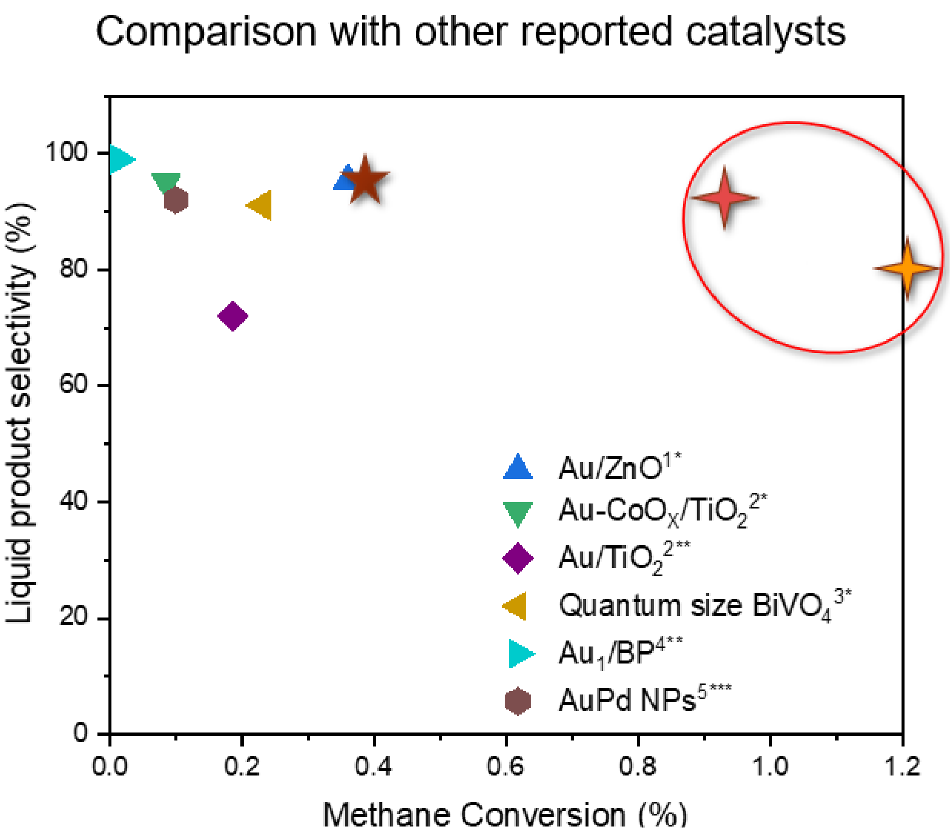
Methane Conversion Ratio (~1 %) + Liquid Product Selectivity (~90%)



Reaction conditions: 10 mg catalysts, 100 mL H_2O, 6.89 bar CH_4, 2.76 bar O_2,

1 h reaction time, reaction temperature: 25 ± 3 °C, light source: 365 nm UV LED

Current Status – Breaking the Trade-off



One of the Best Combinations of **Methane Conversion** and **Liquid Product Selectivity**

What we learned

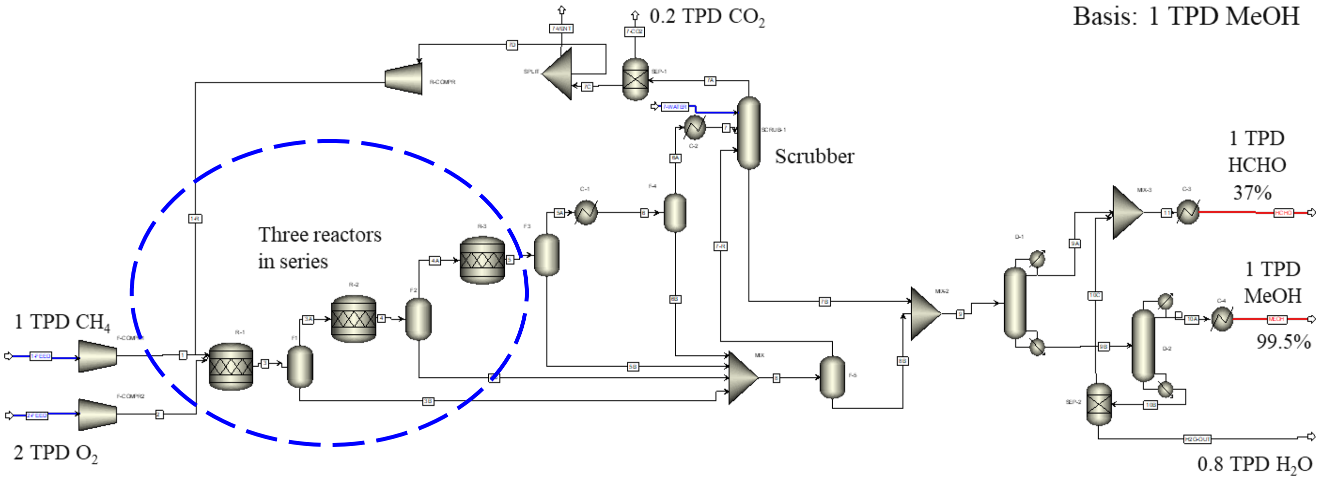
- ❑ The quantum efficiency is low (~1%)
- ❑ Most of the photon flux turned into heat

[1] *JACS*, **2019**, 141, 20507−20515 [2] *ACS Catal*. **2020**, 10, 14318−14326 [3] *Nat. Sustain.* **2021,** 4, 509–515;
[4] *Nat. Commun.* **2021,** 12, 1218 [5]*Science*, **2017**, 358, 223–227

Current Status – Techno-Economic Analysis

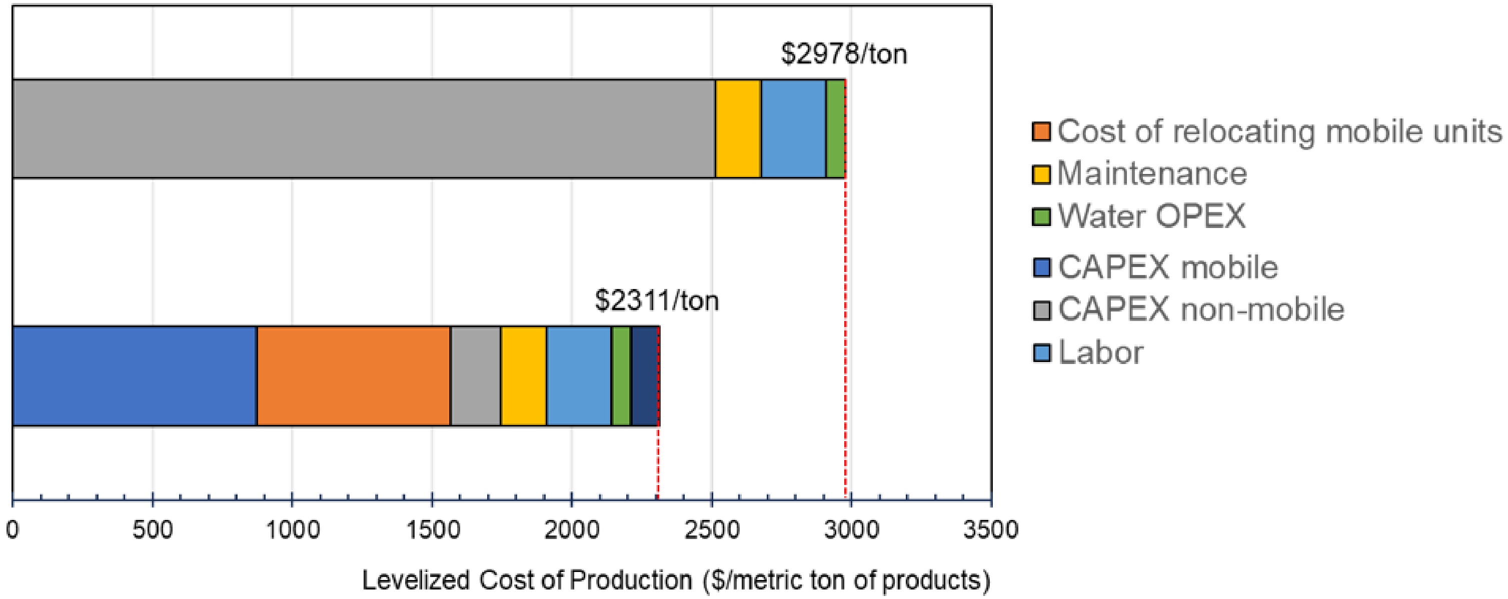
Reactors

In Tandem



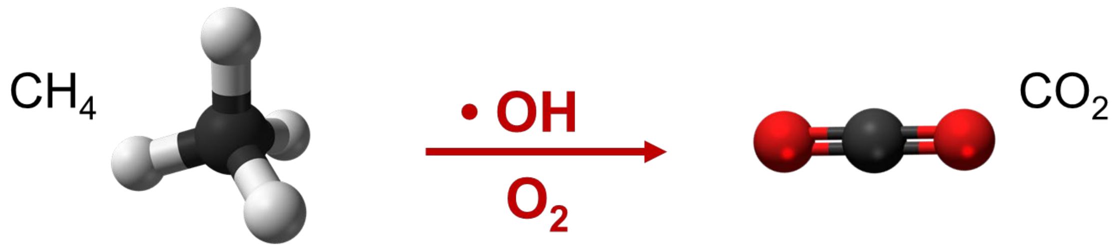
Production

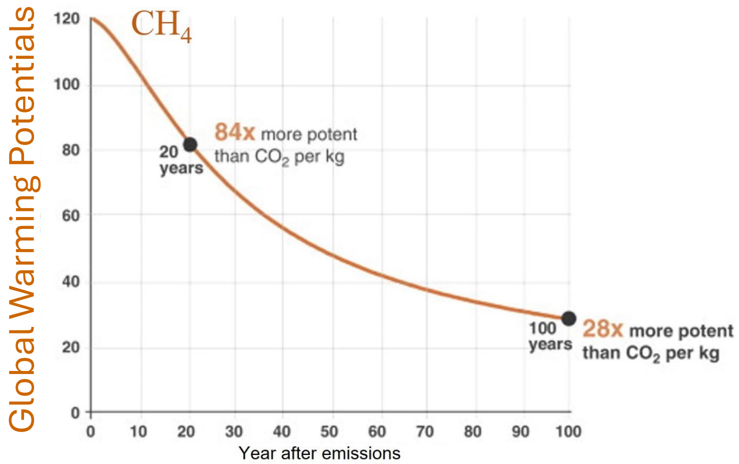
Cost

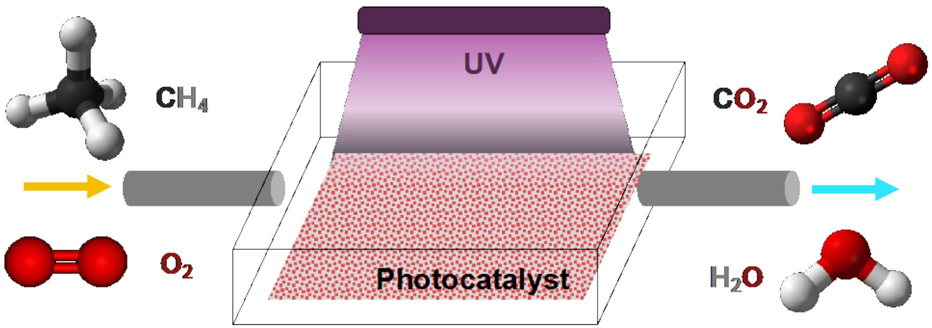


Another Solution to Convert Methane

Mimic how nature does

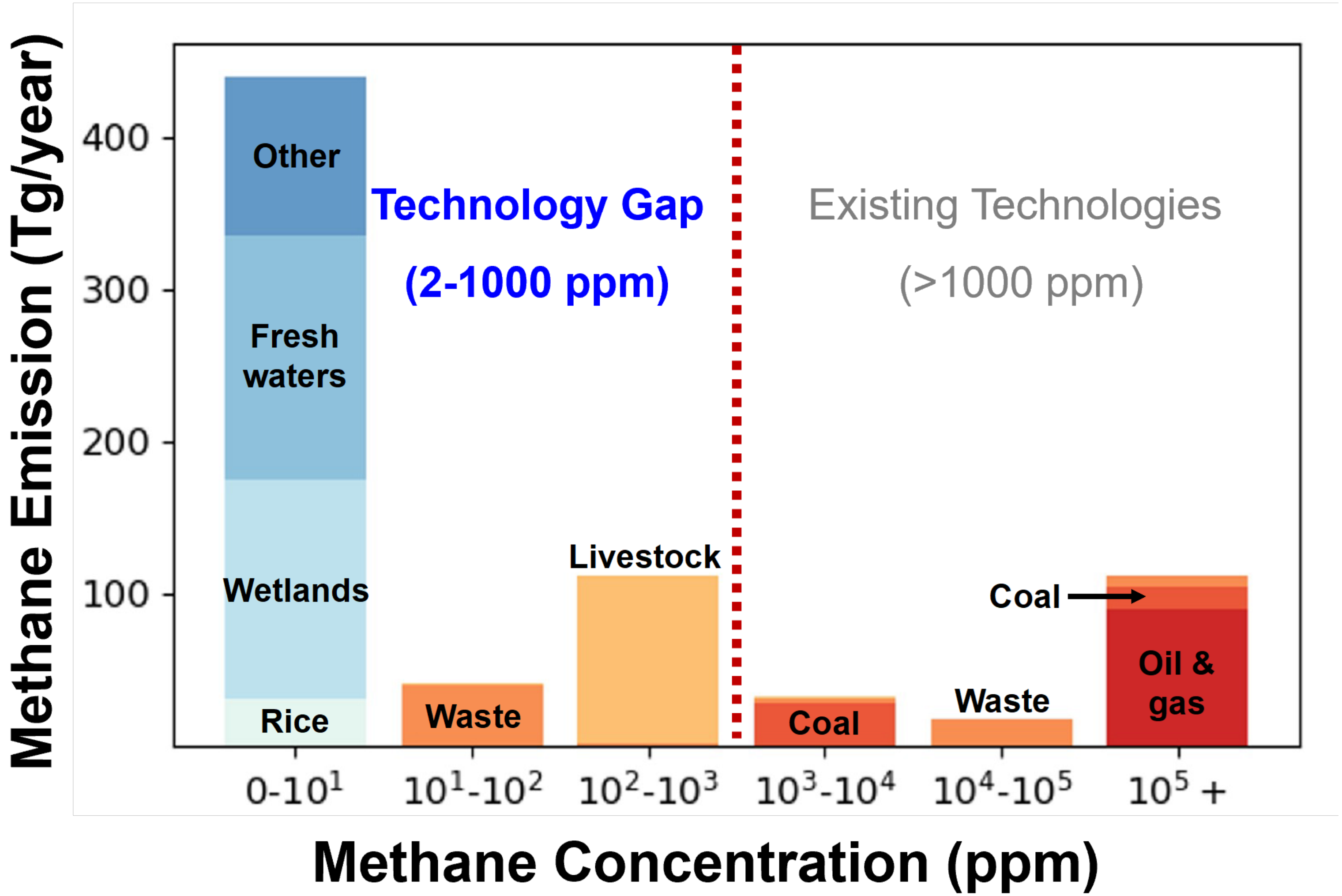






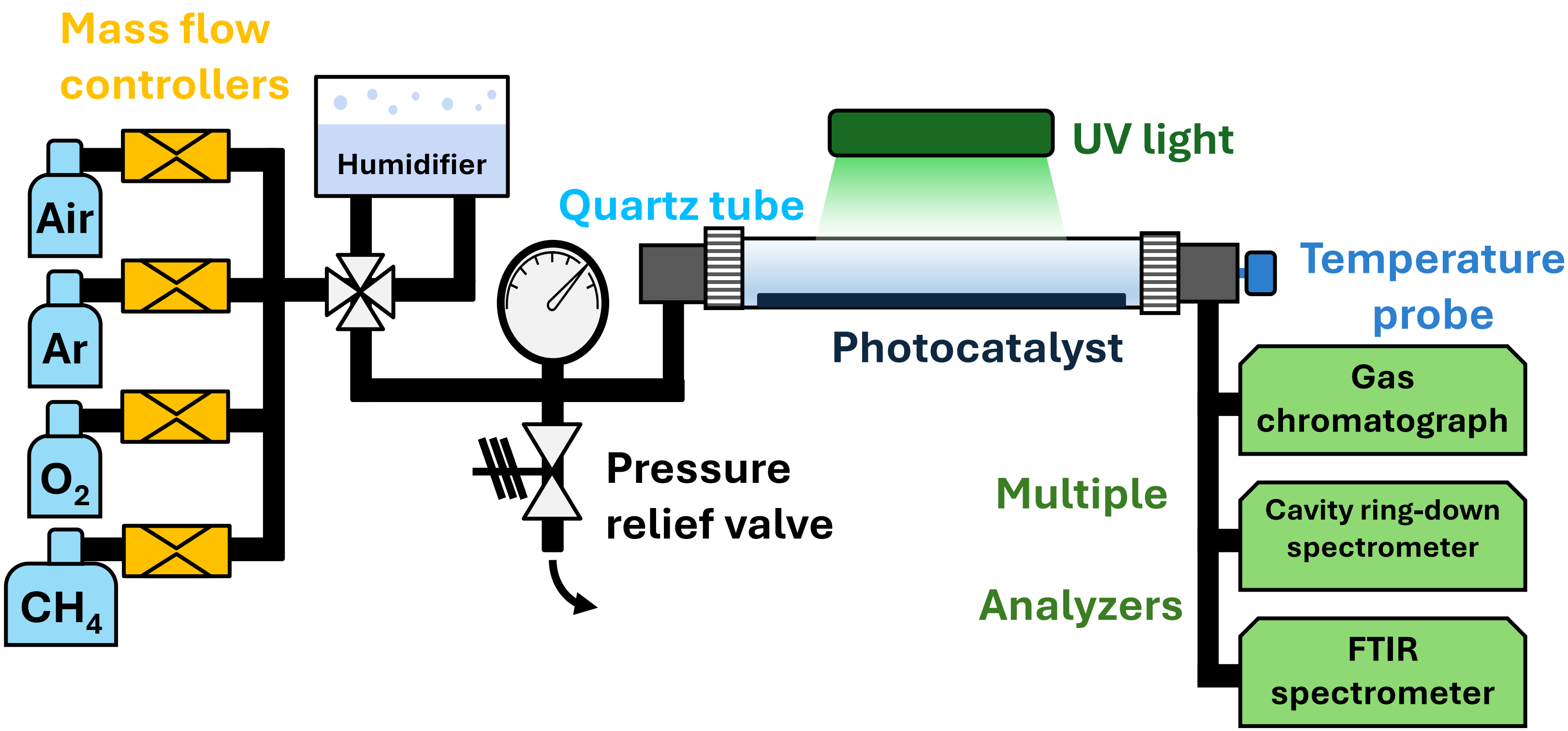
Promising solution to reduce methane's 20-year global warming impact by 99%

The Gap of Dilute Methane Removal



Environmental Research Letters 2023, 18 (9), 094064

Our Experimental Platform for Methane Removal



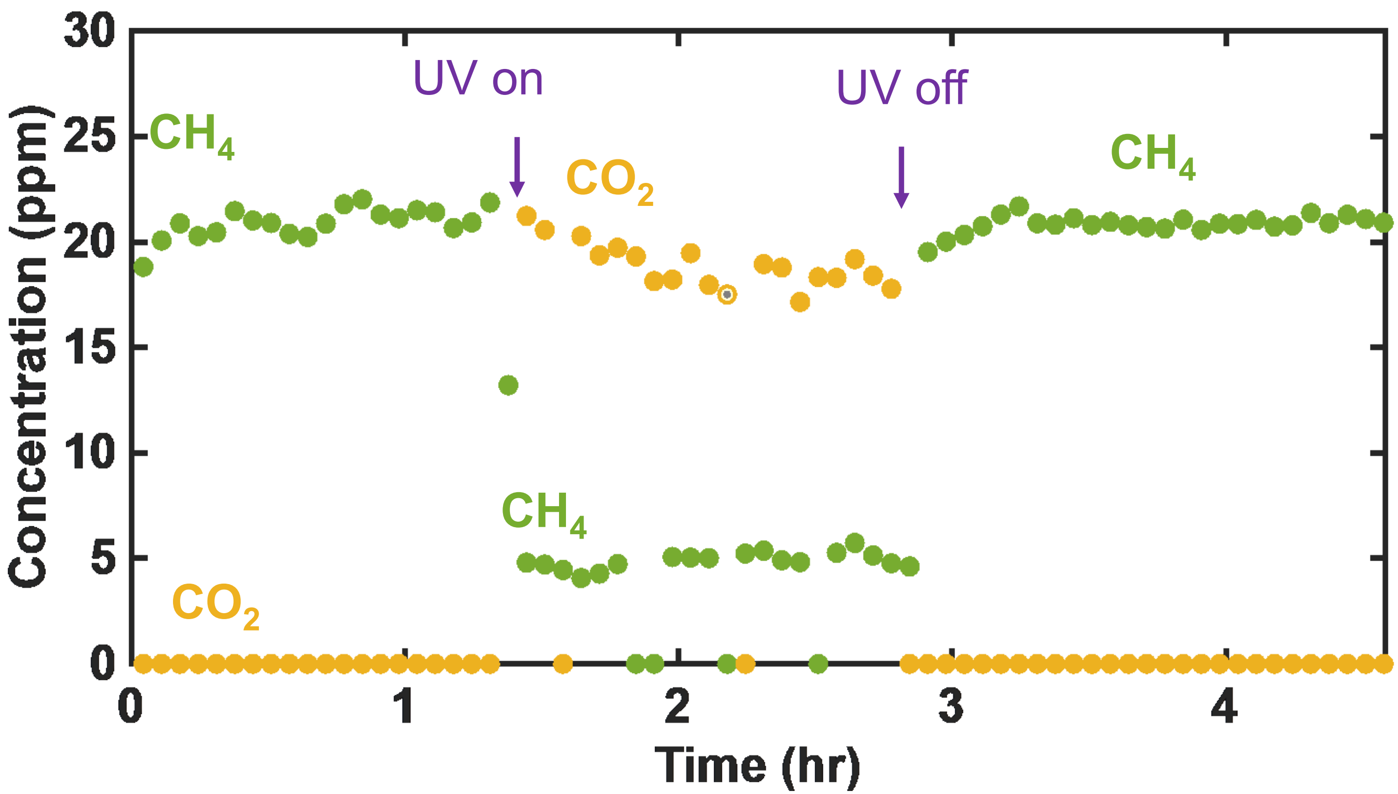
Precisely control gas input,

and quantify the products


Max Kessler

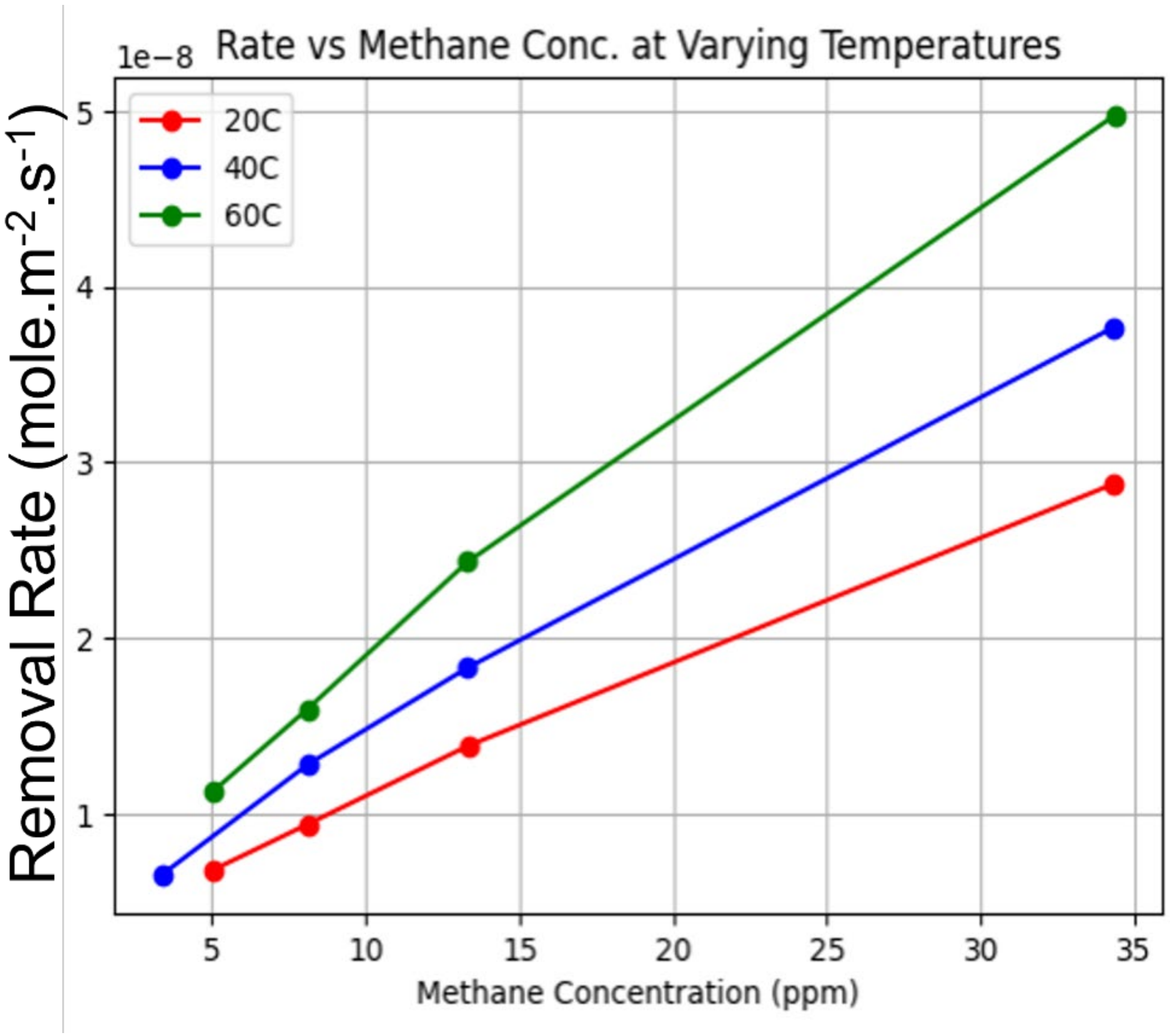

Richard Randall

Progress – Removing 20 ppm



Photocatalysis enables high conversion of CH_4 to CO_2

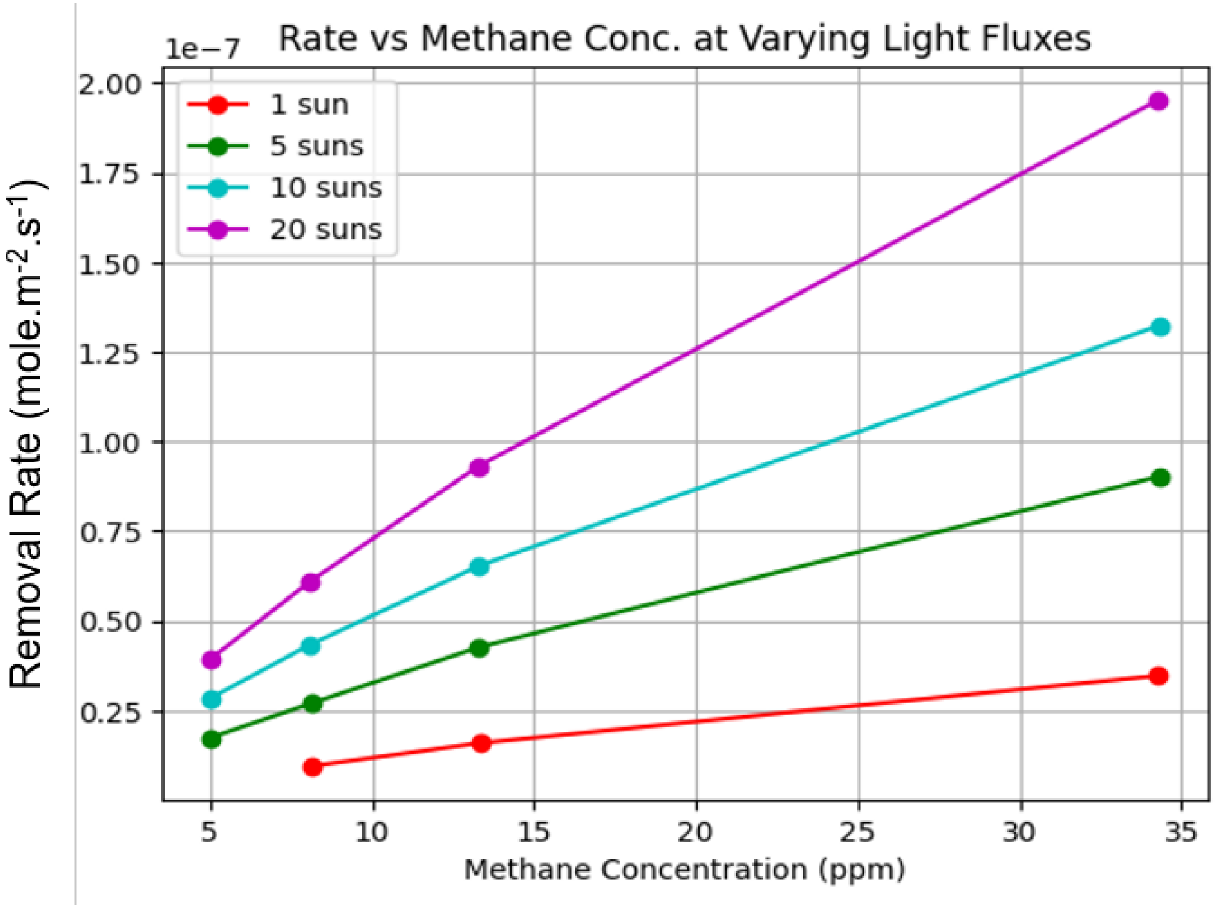
Progress – Temperature Effect



Elevated temperatures slightly boost photocatalytic methane removal

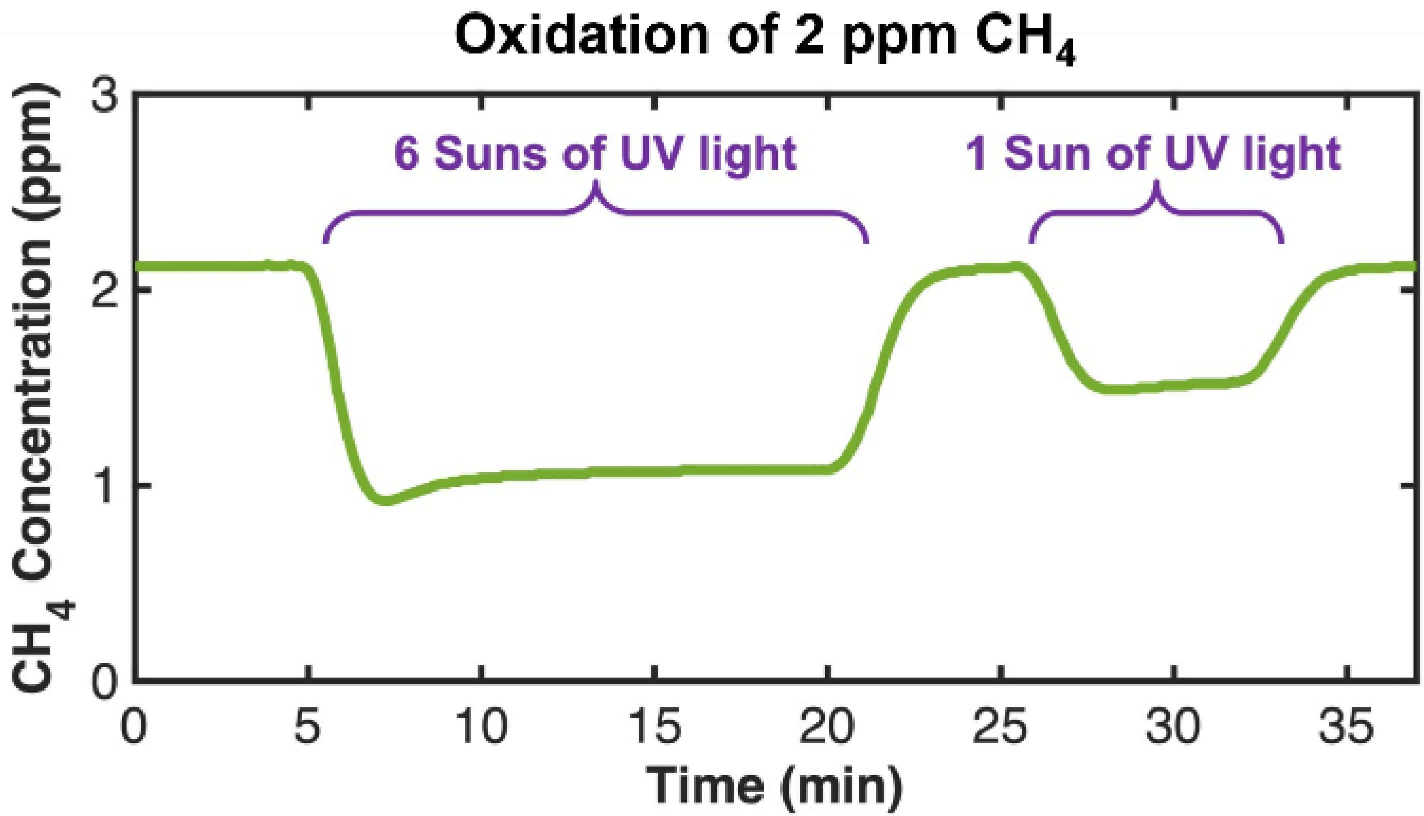
At kinetically controlled regions

Progress – UV Flux-driven Methane Removal



- UV flux significantly impacts the rate of methane removal
- Quantified the reaction rate spanning various concentrations

Progress – Atmospheric Concentration



Existing studies are largely limited to concentrations > 100 ppm

Project Schedule

Task/Subtask	Key Milestone	Planned Completion Date
Task 1	Kickoff meeting and submission of revised **project management plan** (PMP), technology maturation plan and techno-economic analysis	04/01/2020 ✓
Task 2	Successful demonstration of the ability to **incorporate the co-catalyst** clusters and molecular complexes with the semiconductor catalyst while controlling co-catalyst loading and proximity to semiconductor sites.	01/31/2021 ✓
Task 3	Successful optimization of semiconductor material and synthesis conditions for maximizing **hydroxyl radical** production.	01/31/2021 ✓
Task 4	Successful optimization of a **bifunction photocatalyst** with a capable of converting methane into methanol with high selectivity and yield.	09/30/2021 ✓
GO/NO-GO Decision	**Test results** show approaching 7-10% methane conversion with 80-90% methanol selectivity under commercially reasonable operating conditions.	09/30/2021 ✓
Task 5	Complete one final iteration for **optimizing bifunctional catalyst** for methane to methanol conversion and potential for future catalyst scaleup and large-scale production.	03/31/2022 ✓
Task 6	Obtain **key operating catalyst performance data** under realistic conditions with simulated natural gas for commercial application.	06/30/2022 ✓
Task 7	Identification of effective **reactor configuration** to optimize methane transfer onto the catalyst surface across the aqueous media.	09/30/2022 ✓
Task 8	Demonstrate production of photocatalytic methane to methanol conversion using H_2O as reagent for **hydroxyl radical production**	09/30/2022 ✓
Task 9	Demonstration of activation of methane or CO_2 in a mixture with other gases	09/30/2024
Task 10	**Pilot plant design** for modular operation	07/30/2023 ✓

Future Development Plan

- Water (moisture) on methane removal
- Co-feeding gases (e.g., hydrogen, ammonia, carbon monoxide)
- Stability of the photocatalysts
- Other gas-phase reactions

Summary

- Generation of Free Radicals for Methane Activation via Photocatalysis

- Point Emission Source (Concentrated Methane) CH_4 to CH_3OH

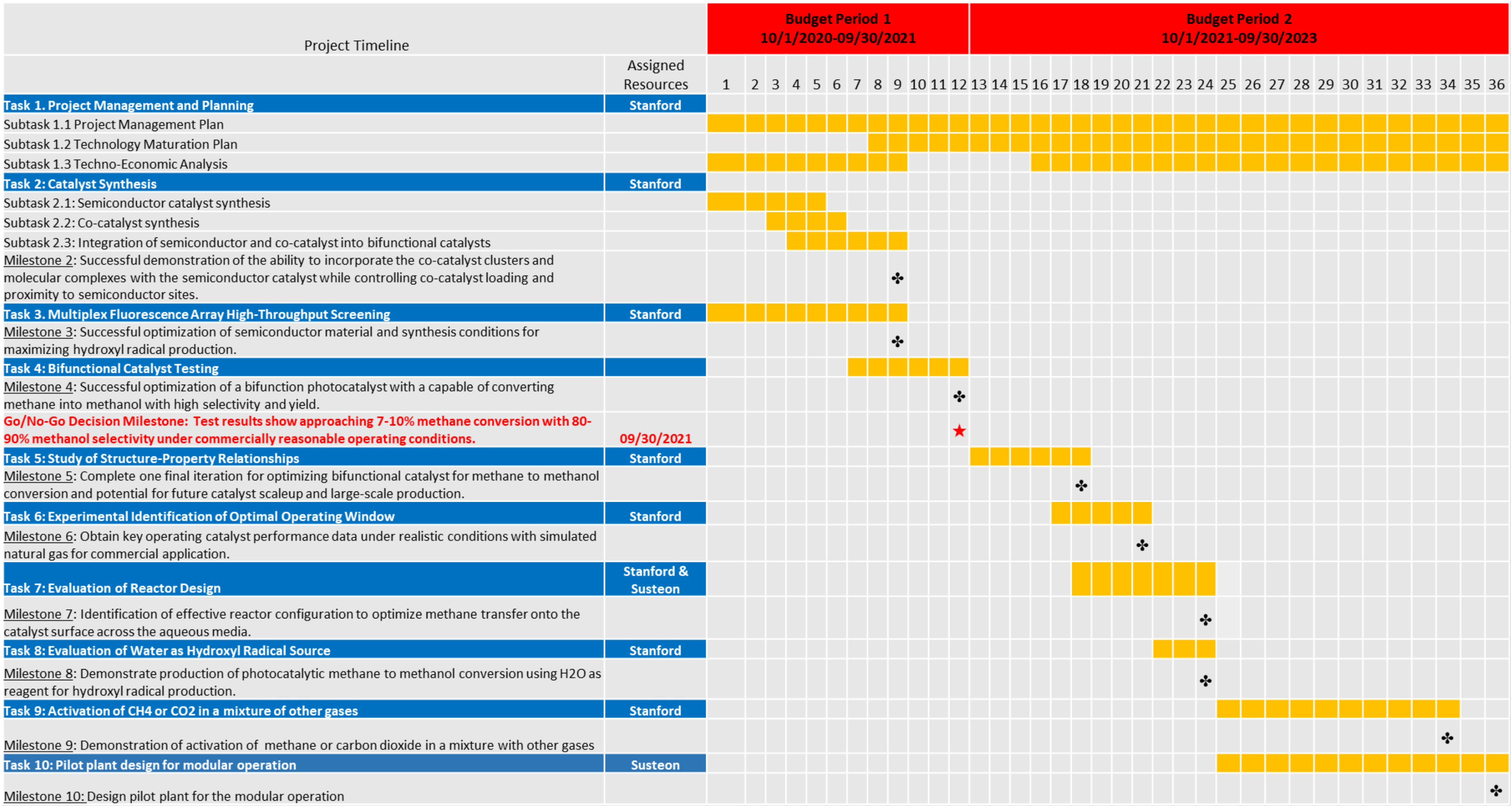
  Benchmarking the Performance for Methane Upgrading to Methanol

- Dilute / Environmental Methane Removal CH_4 to CO_2

  Leveraging Free Radicals for the Removal of 2 ppm Methane

Appendix

Gantt Chart



With an extension to 09/30/2024