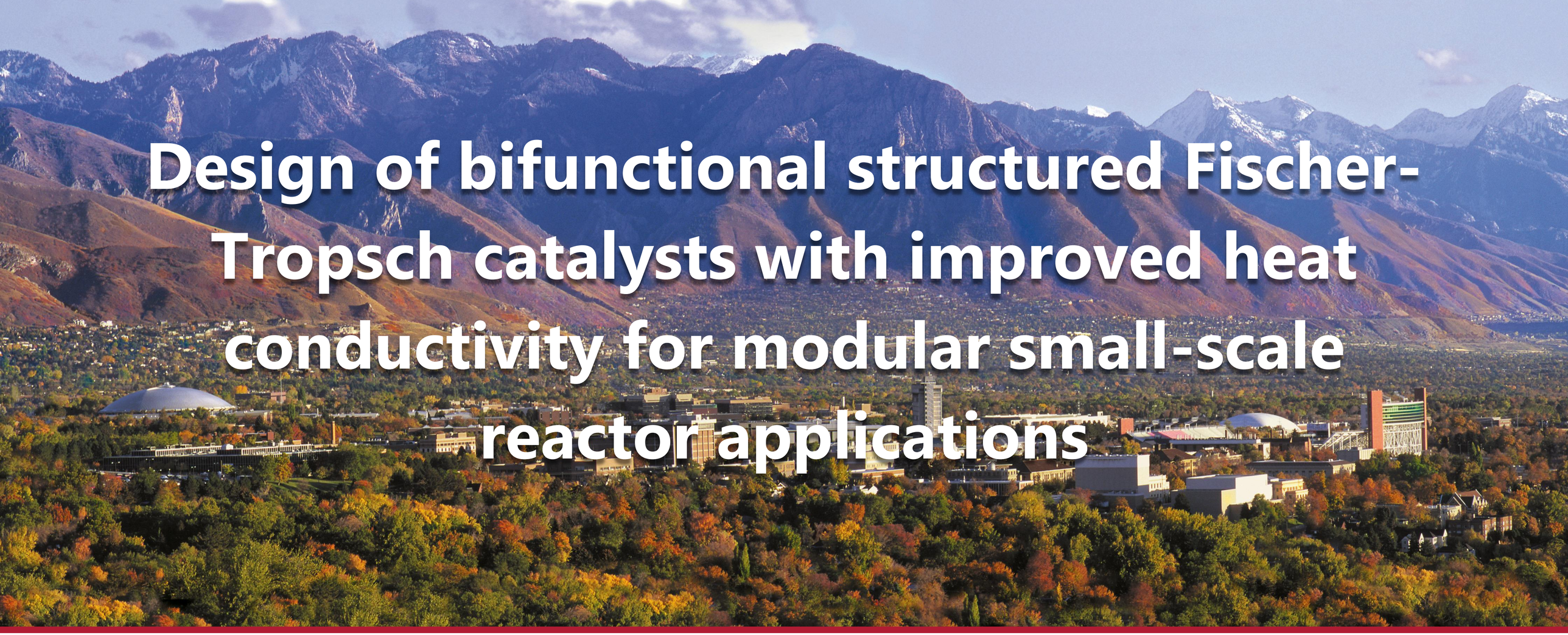

Design of bifunctional structured Fischer-Tropsch catalysts with improved heat conductivity for modular small-scale reactor applications

Luis Caballero, Joe Brindle, Bobby Mohanty, Eric Eddings, Kevin Whitty, Michael Nigra

Monday, May 2, 2022

THE UNIVERSITY OF UTAH®

University of Utah Team Overview

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PI

Dr. Bobby Mohanty
Co-PI

Dr. Eric Eddings
Co-PI

Dr. Kevin Whitty
Co-PI

Luis Caballero and Joe Brindle (Ph.D. Students)

Outline

- **Motivation**
- Materials design and synthesis
- Reactor testing
- Kinetics and CFD Modeling

Overall goal

- This project develops new structured Fischer-Tropsch catalysts which have **improved heat conductivity** and **higher selectivity** for the formation of long chain hydrocarbon products.

Fischer-Tropsch Synthesis (FTS)

- Reaction: $CO + H_2 \longrightarrow C_1 + C_2 + \ldots + C_{30}$
- Typical catalysts are supported Co and Fe.
- Operates at 10-60 bar and temperatures between 200-350°C
- Highly exothermic reaction: $\Delta H = -165$ kJ/mol CO.
- **Need strategies to manage heat from reaction!**
- Product distribution and catalyst deactivation rate are highly sensitive to temperature.

Critical need and hypothesis

- **Critical need:** Rapid removal of heat generated by reaction.
- **Hypothesis:** By designing a support with better heat transfer properties, hotspots can be minimized and deactivation can be slowed.
- **Novelty:** First structured TiO_2 nanotube supported FTS catalyst with controlled acidity.

Expected outcomes

- New FT catalysts that exhibit enhanced thermal conductivity, activity, and selectivity.
- Environmentally-responsible utilization of coal with positive economic impact.

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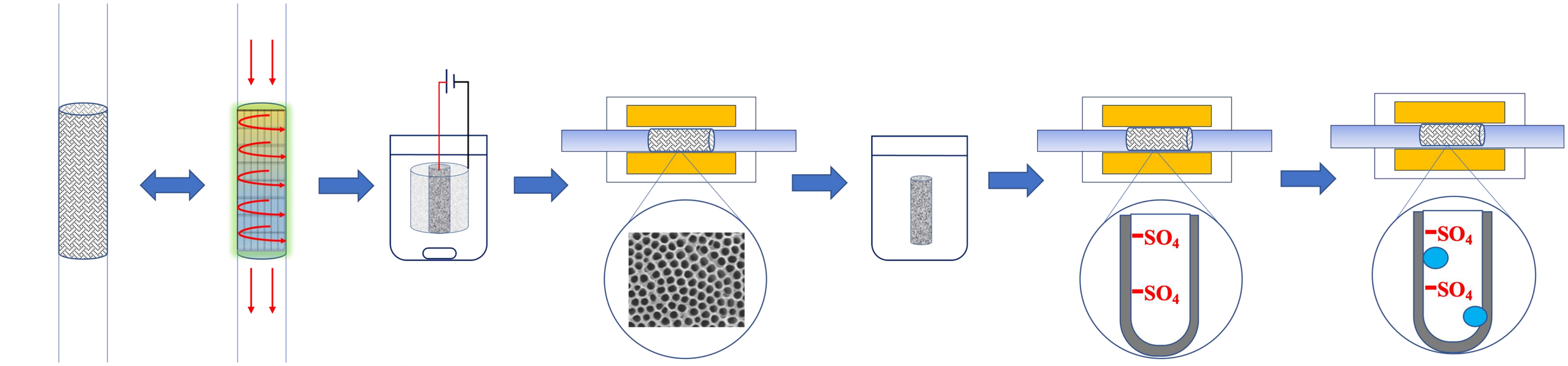
New conductive bi-functional catalytic materials

- **Solution:** 3-dimensional structured catalyst with conductive materials (**Ti** or graphite support) with FeCo nanoparticles.
  - FeCo was chosen because it performs better than Fe in H_2 lean feedstocks from coal or biomass.
  - Support will be functionalized with acid groups to perform both hydrocarbon grown and hydrocracking/isomerization processes simultaneously.
  - Two types of supports: **Ti-based** and C-based.

Materials summary

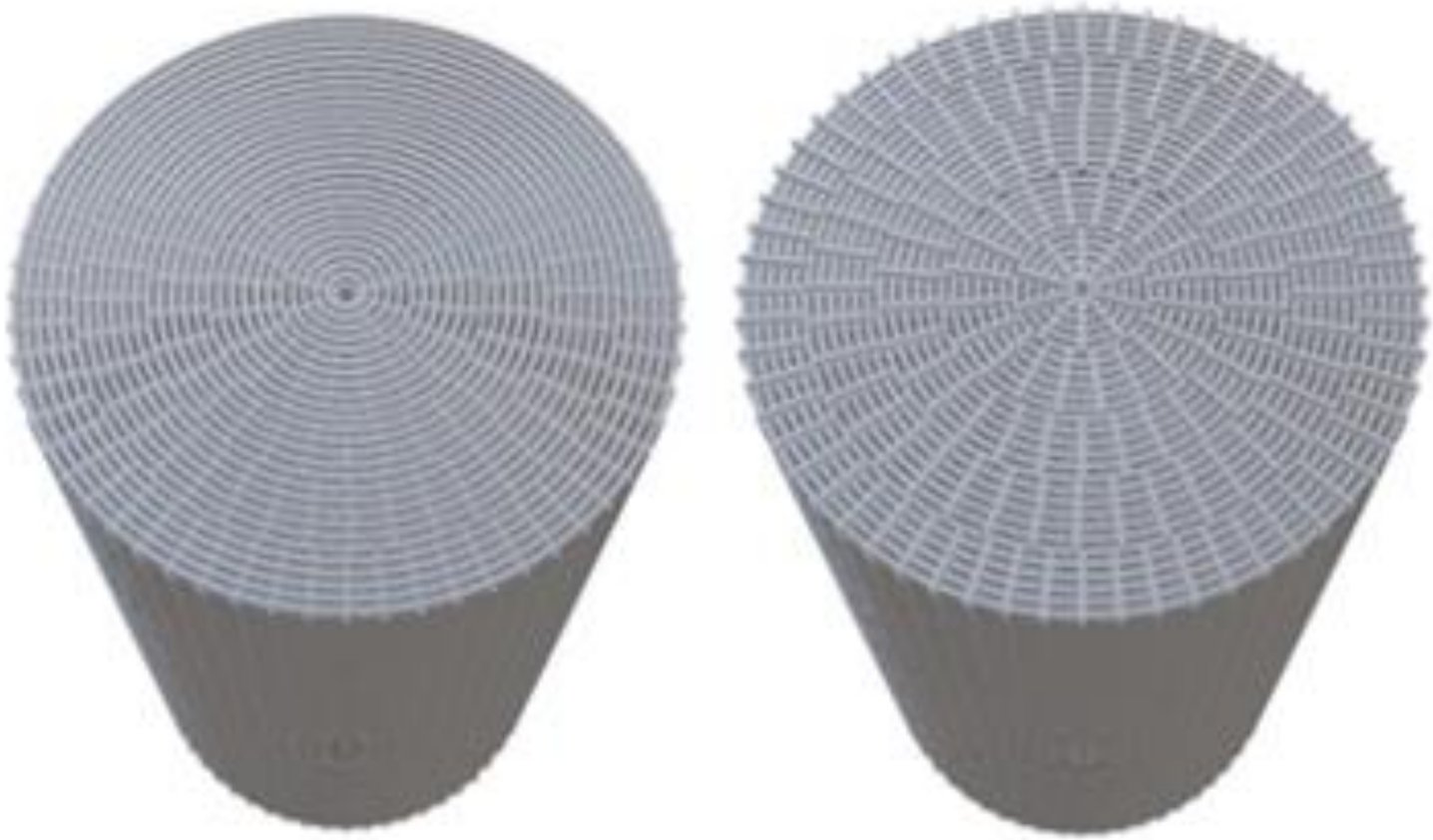
- New materials will consist of structured, bifunctional catalysts for FTS.
- 3-D printing techniques will allow for flexibility in design of catalyst.
- Improved **heat transfer** by:
  - Using a structured catalyst
  - Using a conductive support material.

Preparation of Ti-based materials



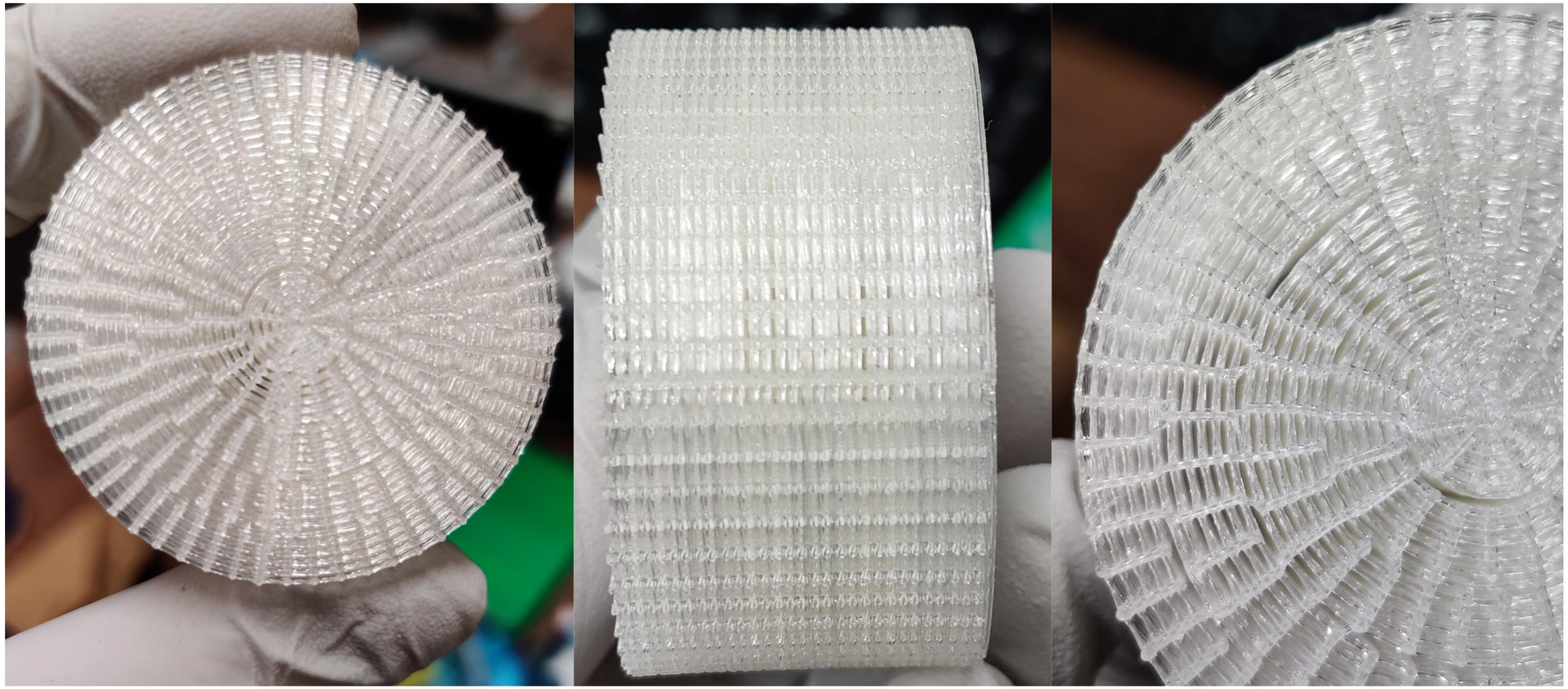
Proposed structure for Ti-based support materials

- Structure is designed to enable heat transfer away from active sites.



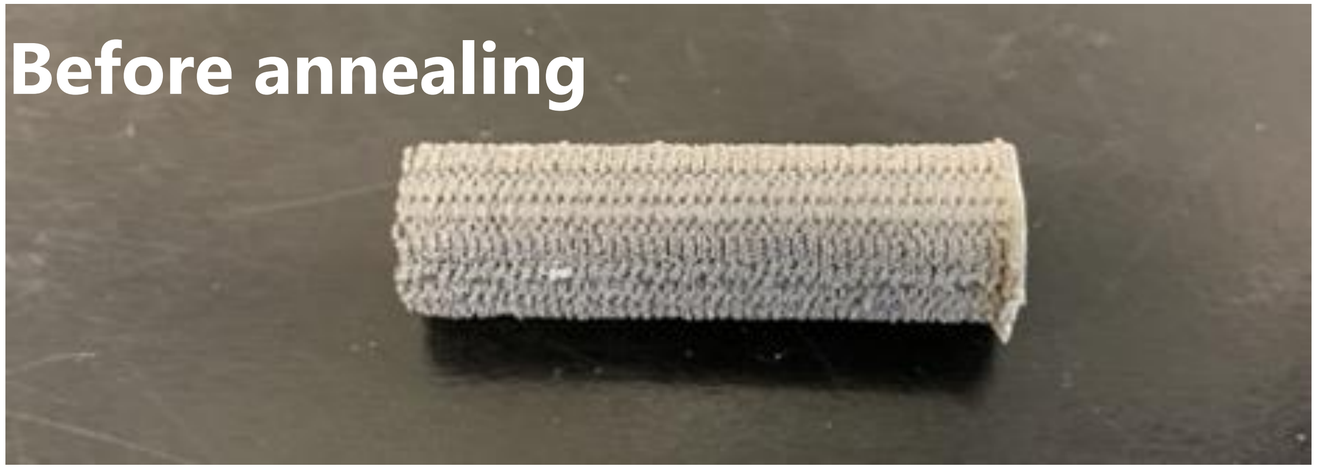
Materials synthesis—3D printing model structures

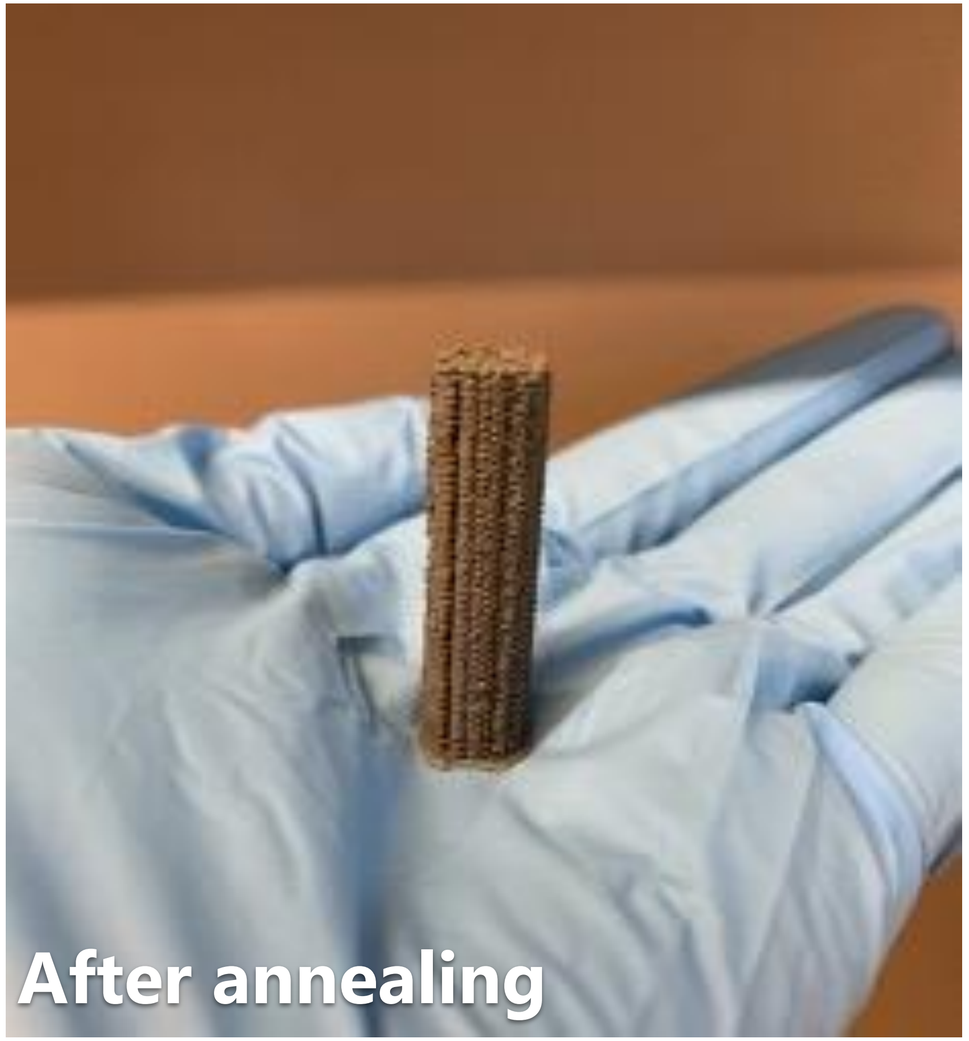
- Test printing with PLA polymer before using Ti.



3D-printing with optimized printing parameters

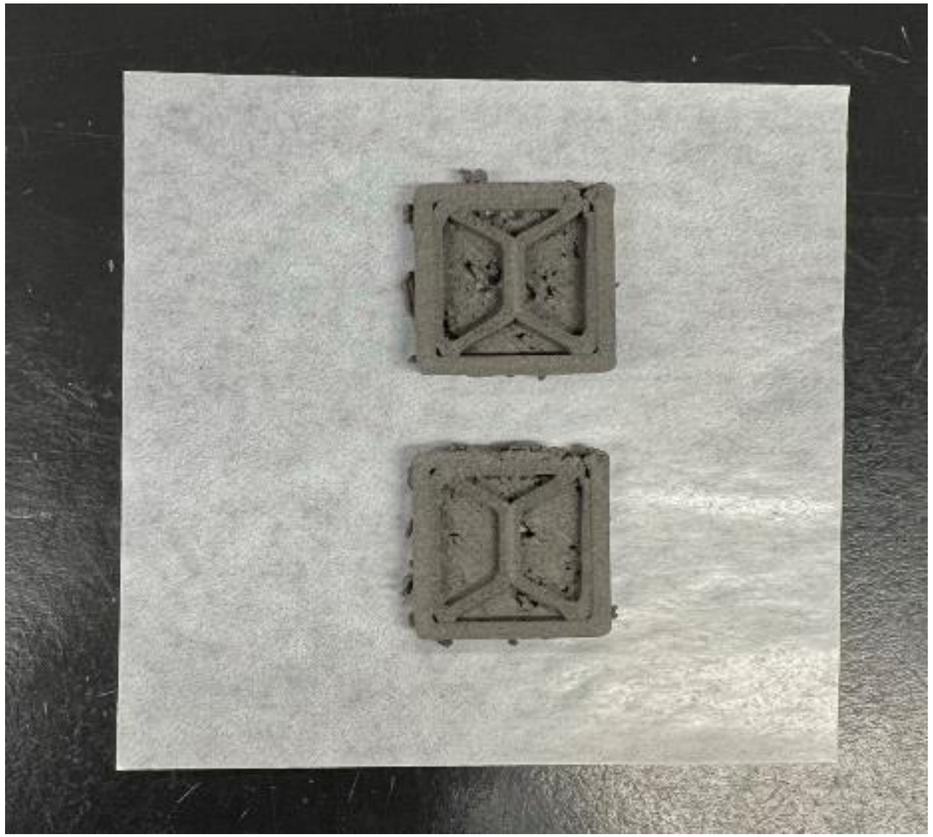
- Example of Ti 3D-printed structured material.

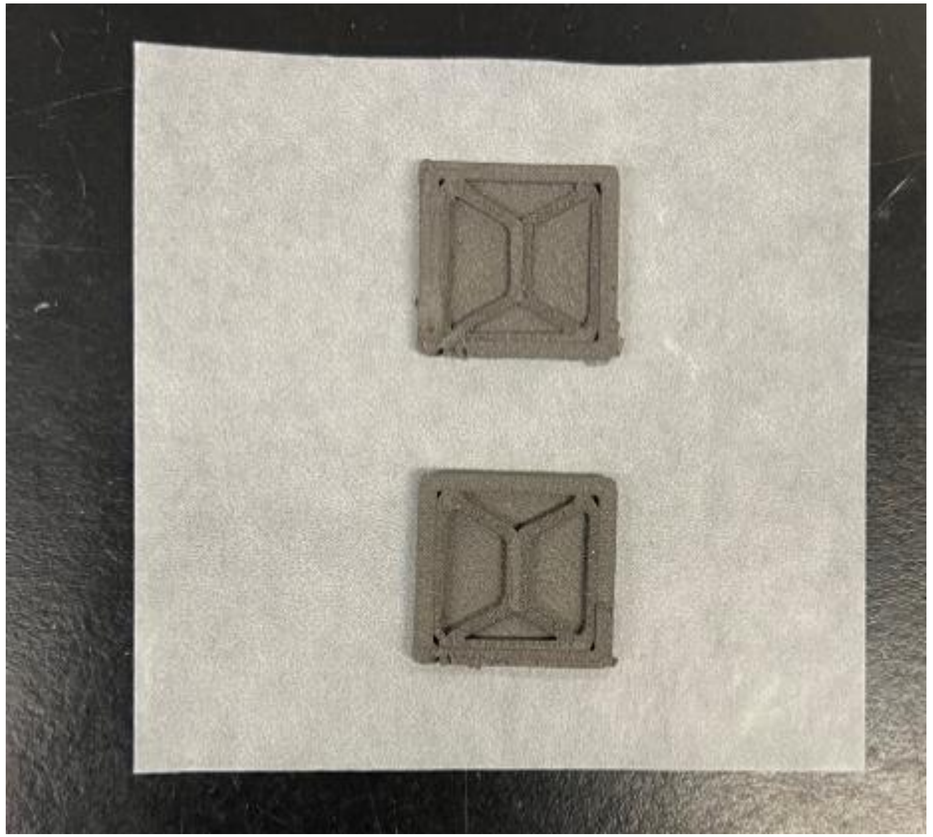




3D-printing with optimized printing parameters

- Example of Ti 3D-printed structured materials.
- Left sample printed at 260°C, right at 265°C





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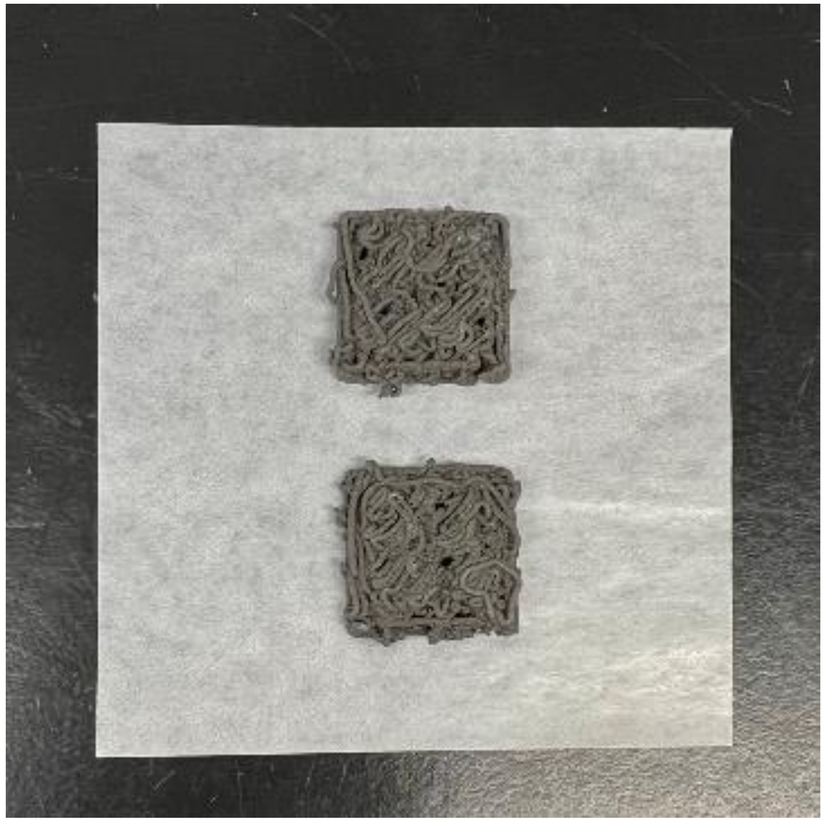
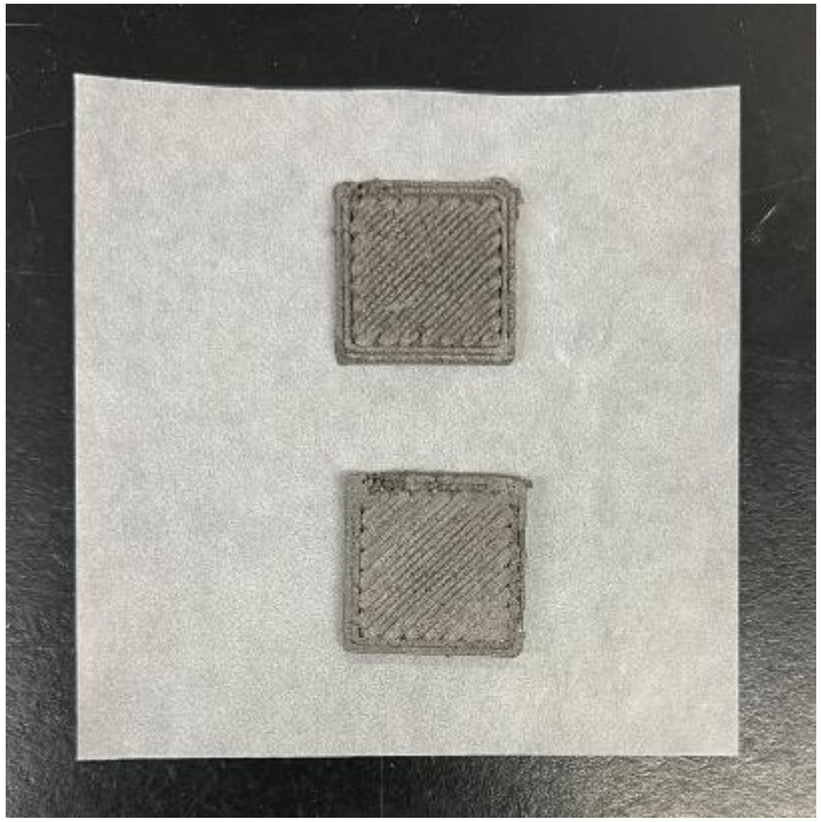
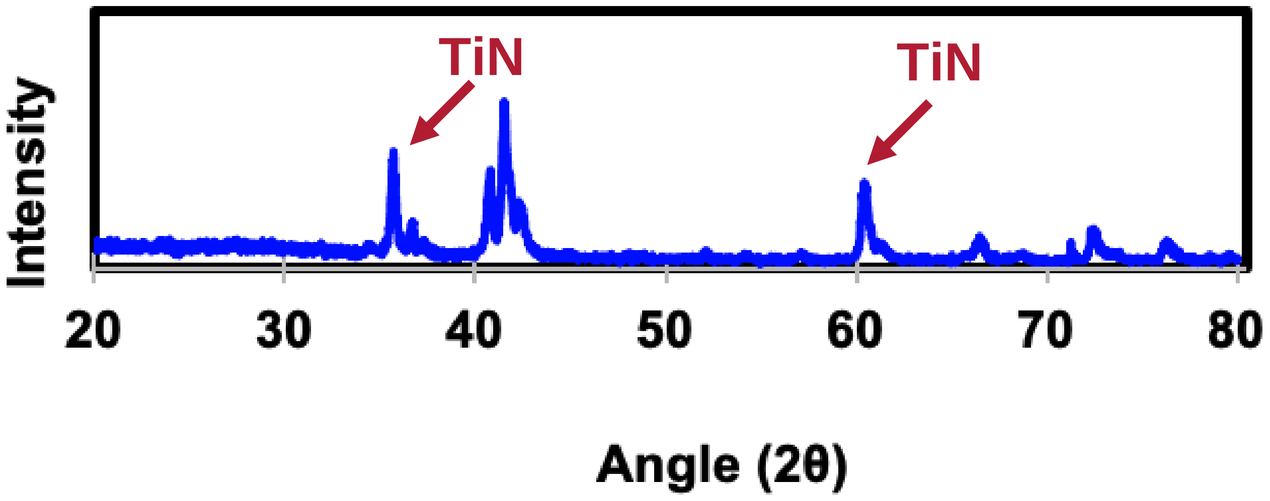
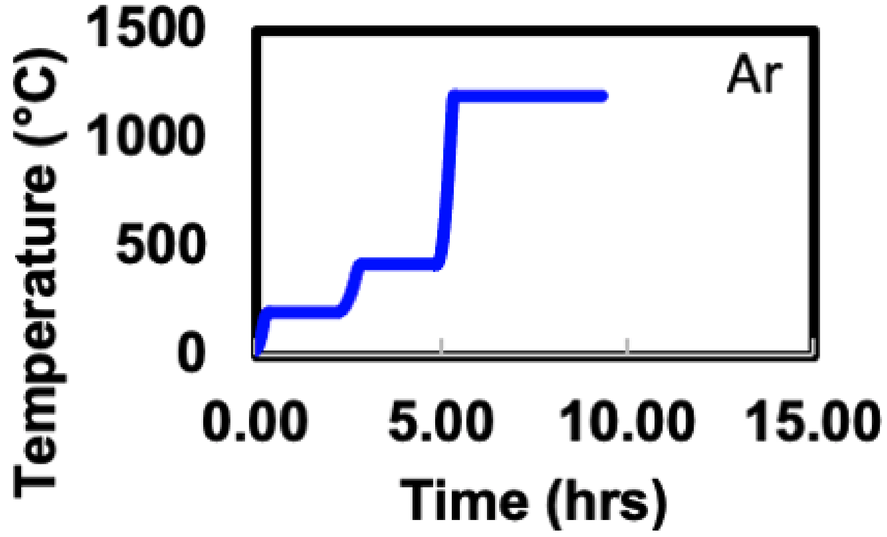




Annealing yields surprise appearance of TiN

- After annealing in Ar, we found that there was titanium nitride in the sample.
- Nitrogen does not appear to be coming from PLA polymer.





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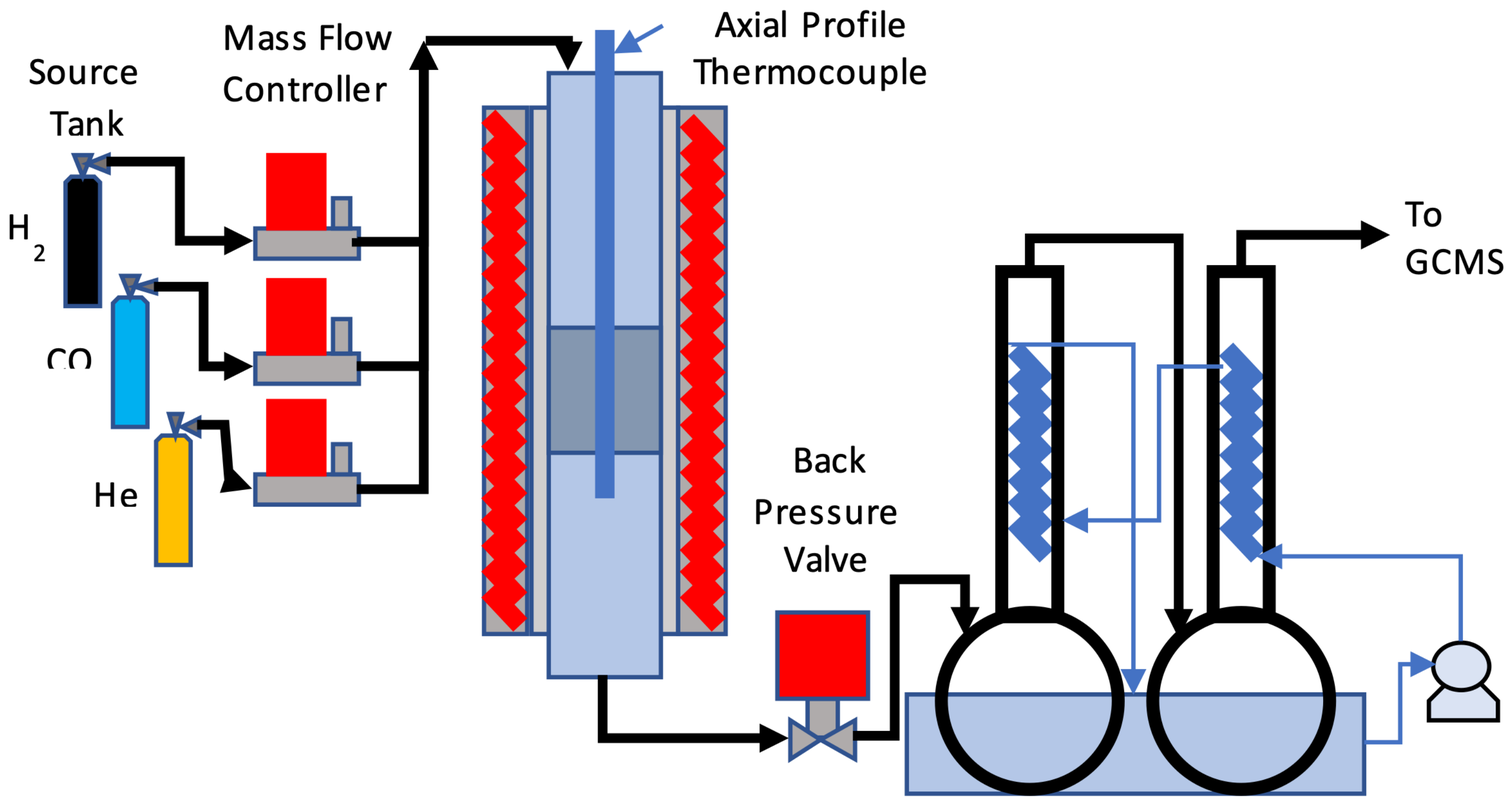
- **Reactor testing**
- Kinetics and CFD Modeling

Reactor set-up

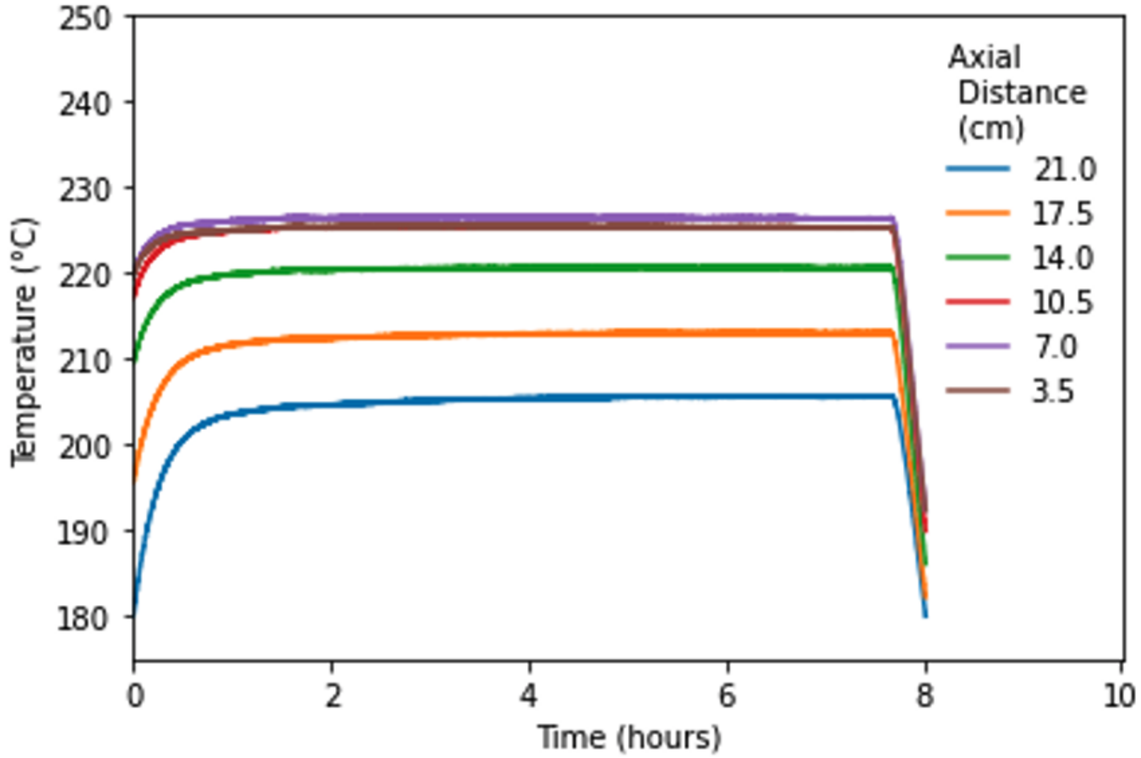


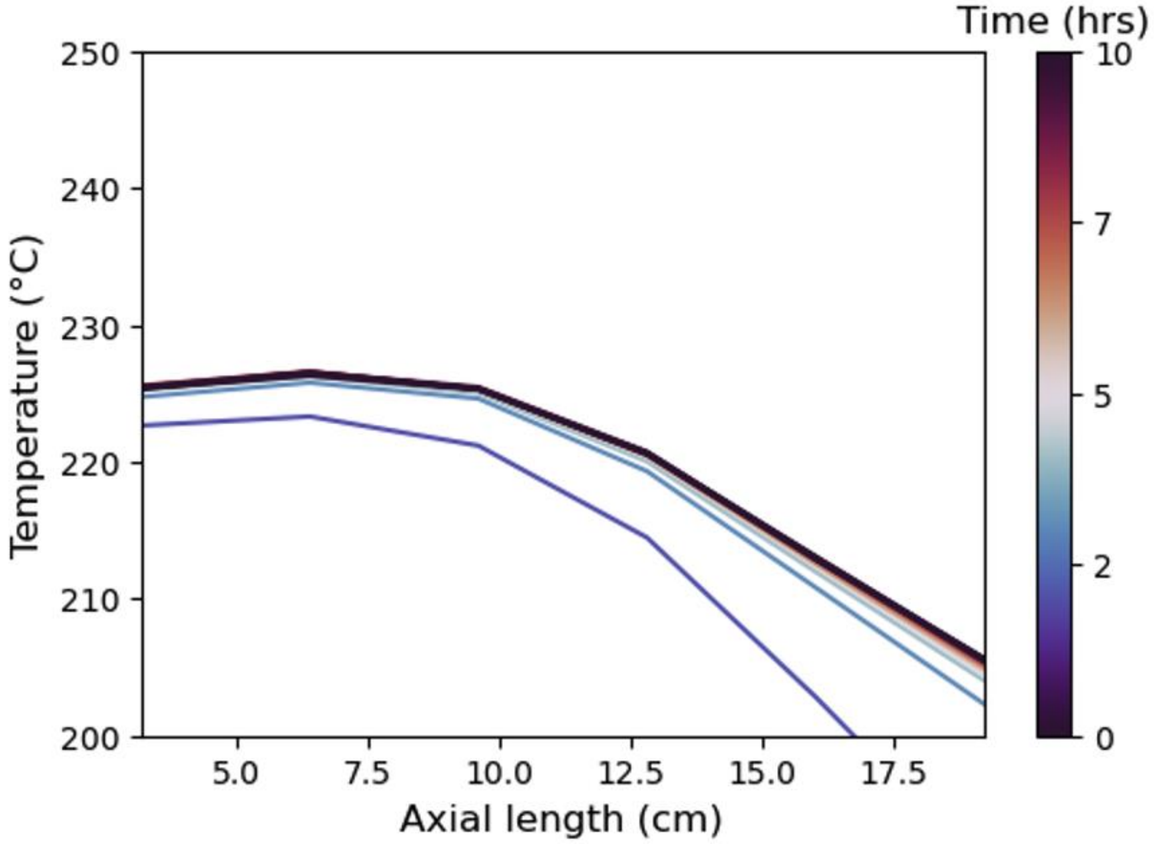
Reactor diameters: 1.77 in. and 0.37 in.

Baseline catalytic testing

- Prepared unstructured catalytic materials supported on P25 TiO_2 and activated carbon.
- Fe and FeCo (1:1 ratio) nanoparticles supported on TiO_2 or C.
- Full characterization of these materials was completed.

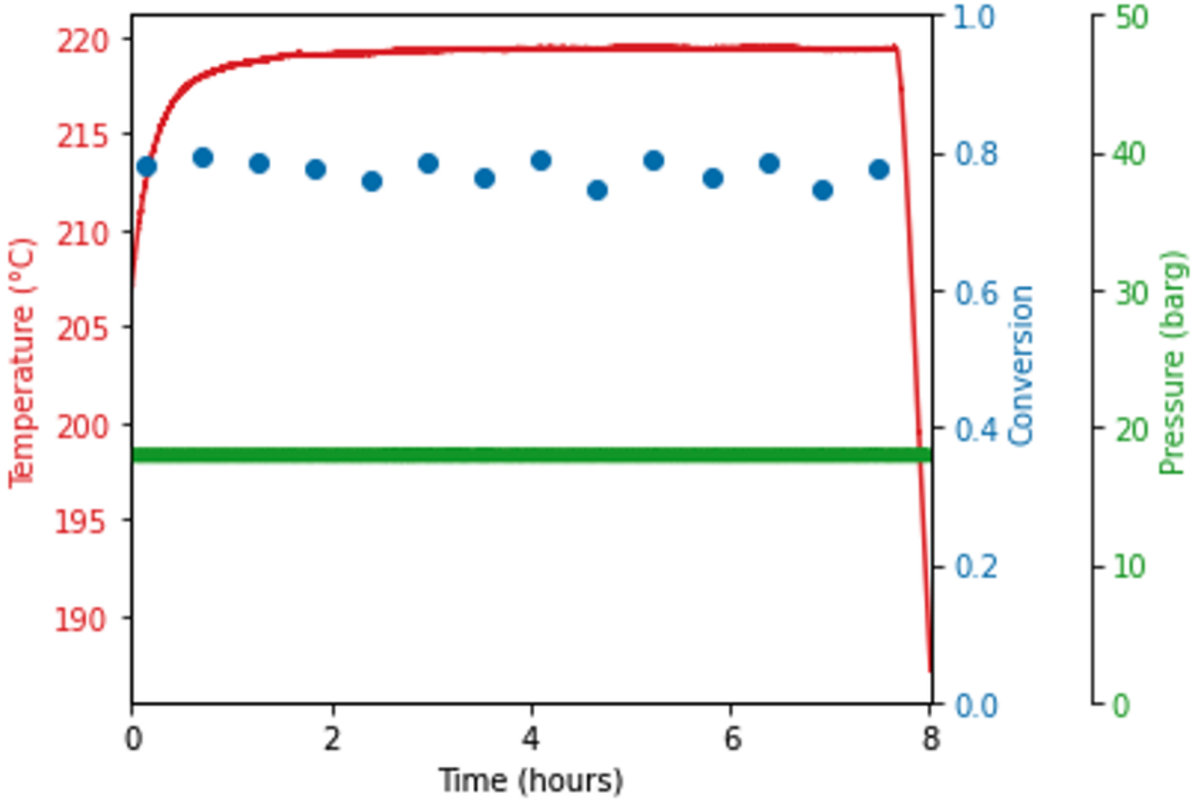
Baseline catalytic testing—
Transient temperature profiles

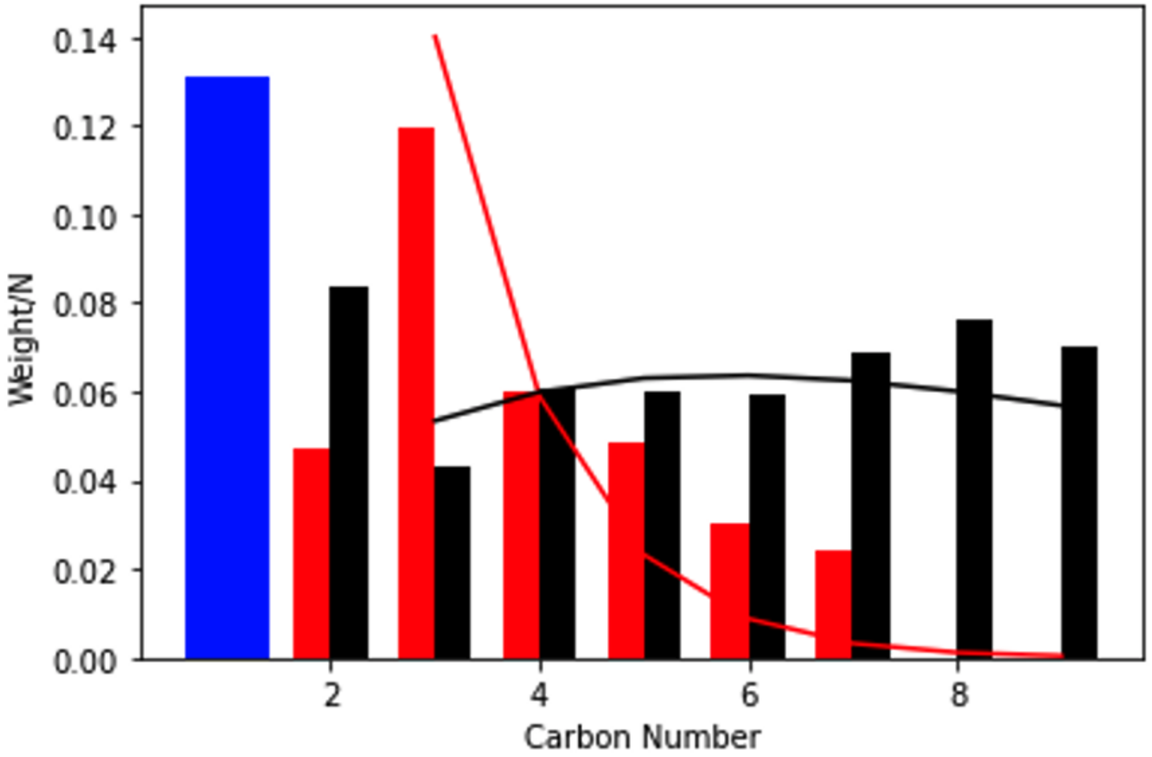




Reaction conditions: pressure: 18 barg, gas flow: 175 SCCM (50 SCCM H_2, 25 SCCM CO, 100 SCCM He, temperature set point: 250°C.

Baseline catalytic testing—Catalyst performance





- Measurements taken over the reaction time of 8 hours.
- Alpha value is measured from C_3 and greater.

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Kinetic modeling

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CO-insertion mechanism based kinetic model of the Fischer–Tropsch synthesis reaction over Re-promoted Co catalyst

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[a] *Chemical Engineering Program, Texas A&M University at Qatar, PO Box 23874, Doha, Qatar*
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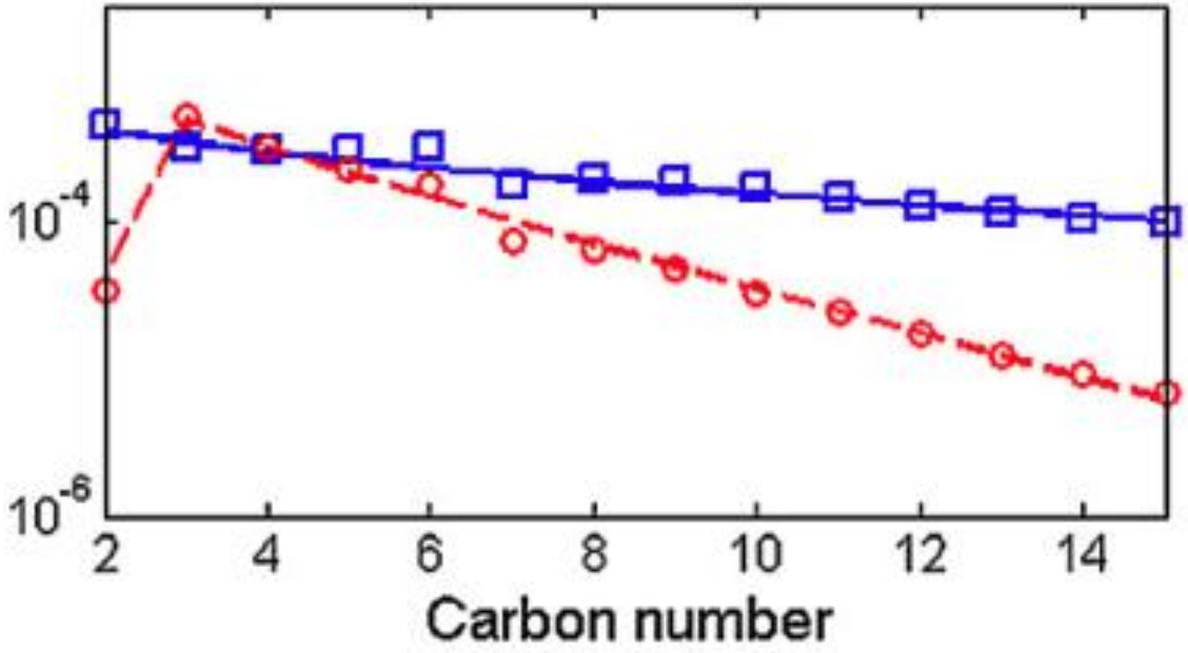
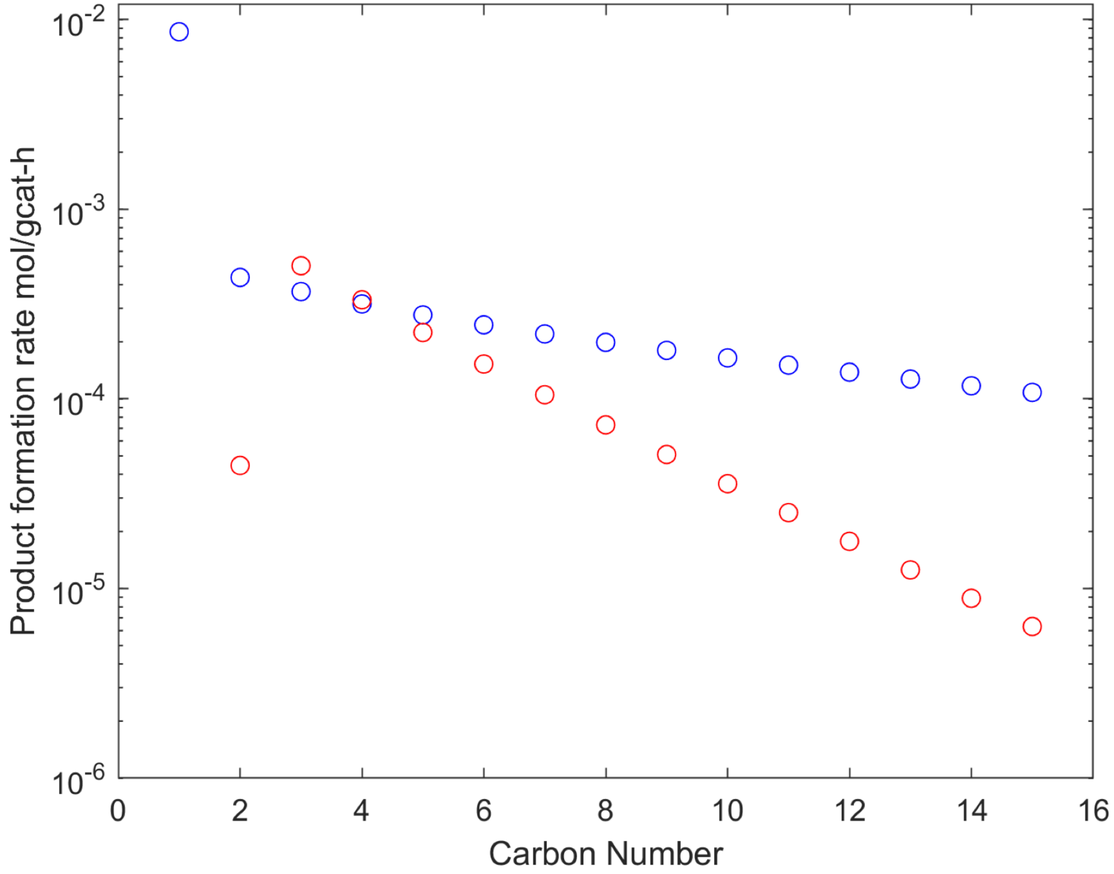
Kinetic modeling—Product formation rate

T = 503 K, P = 1.5 MPa,
H_2/CO = 2.1, WHSV = 11.3 NL/g_{cat}/h.

Calculations from paper



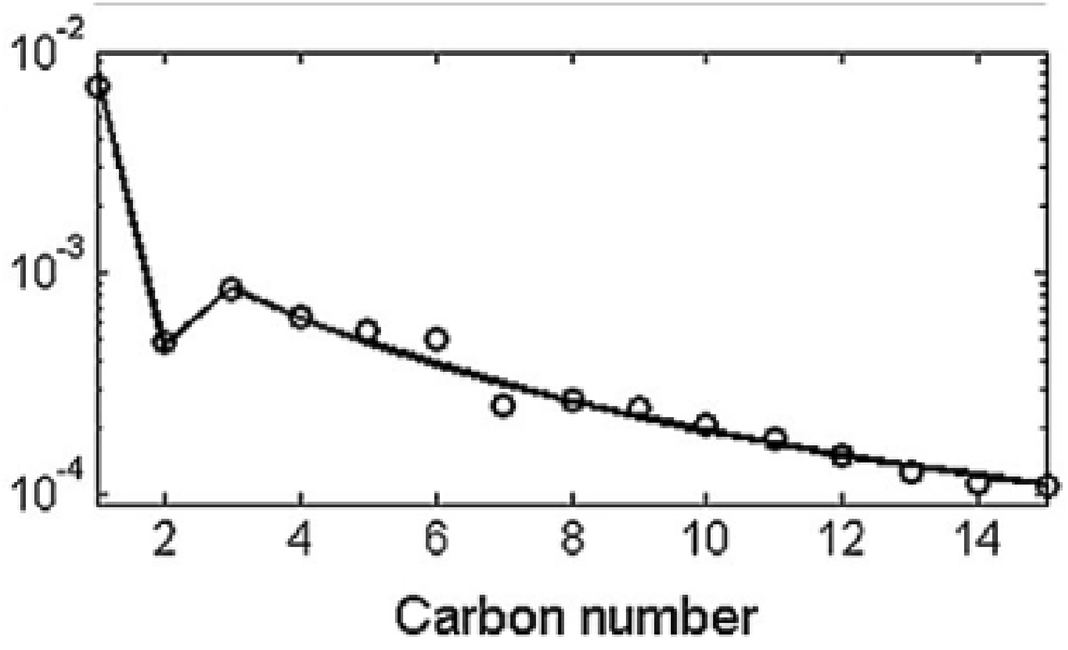
Our calculations based on the paper



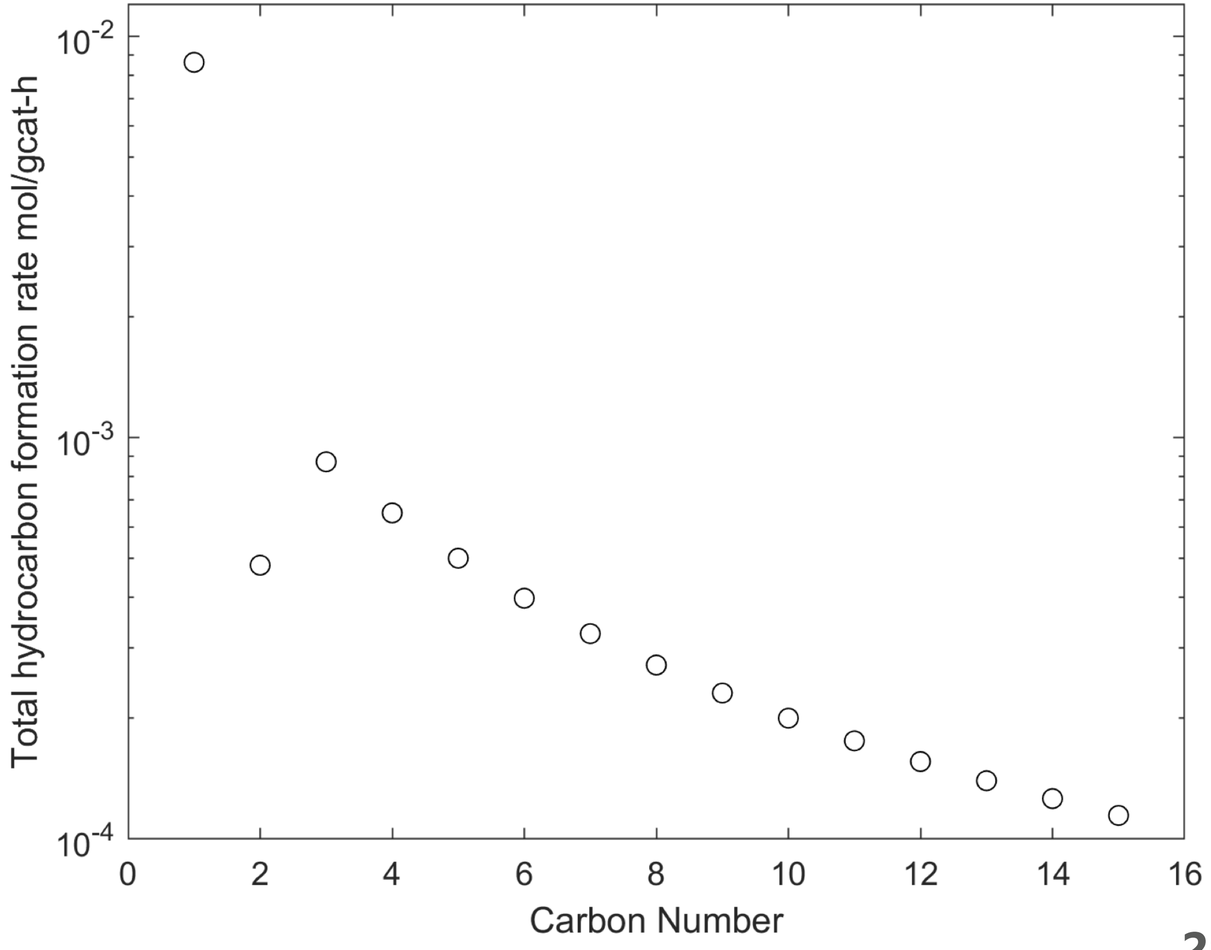
Kinetic modeling—Total hydrocarbon formation rate

T = 503 K, P = 1.5 MPa,
H_2/CO = 2.1, WHSV = 11.3 $NL/g_{cat}/h$.

Calculations from paper



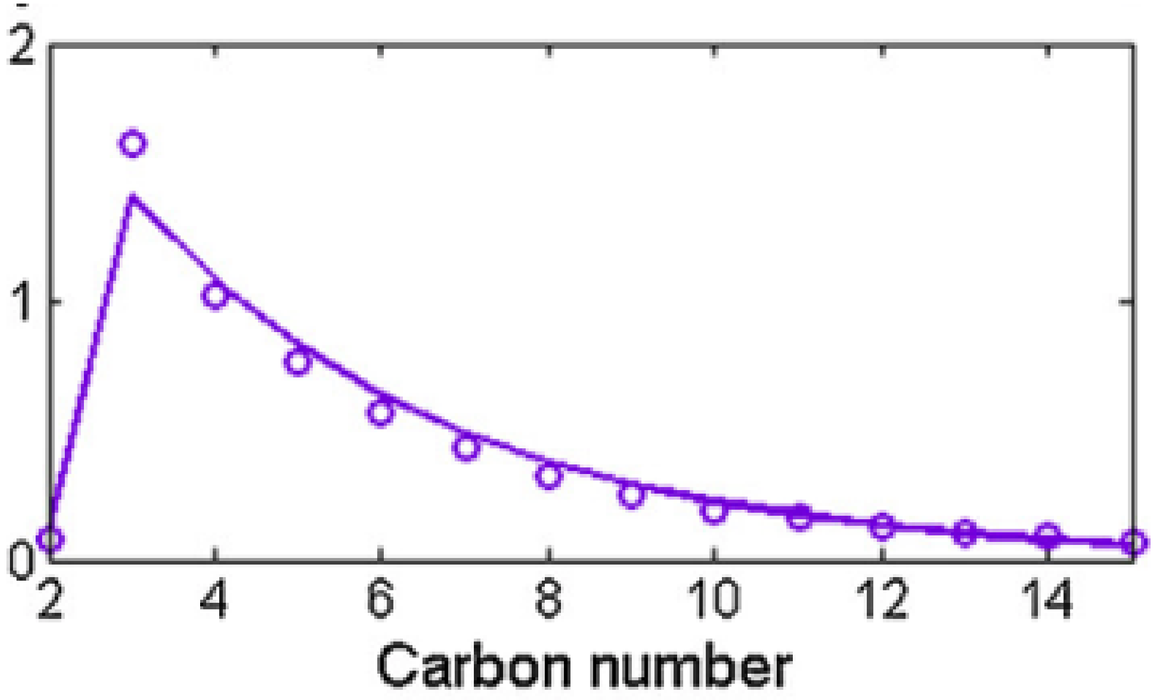
Our calculations based on the paper



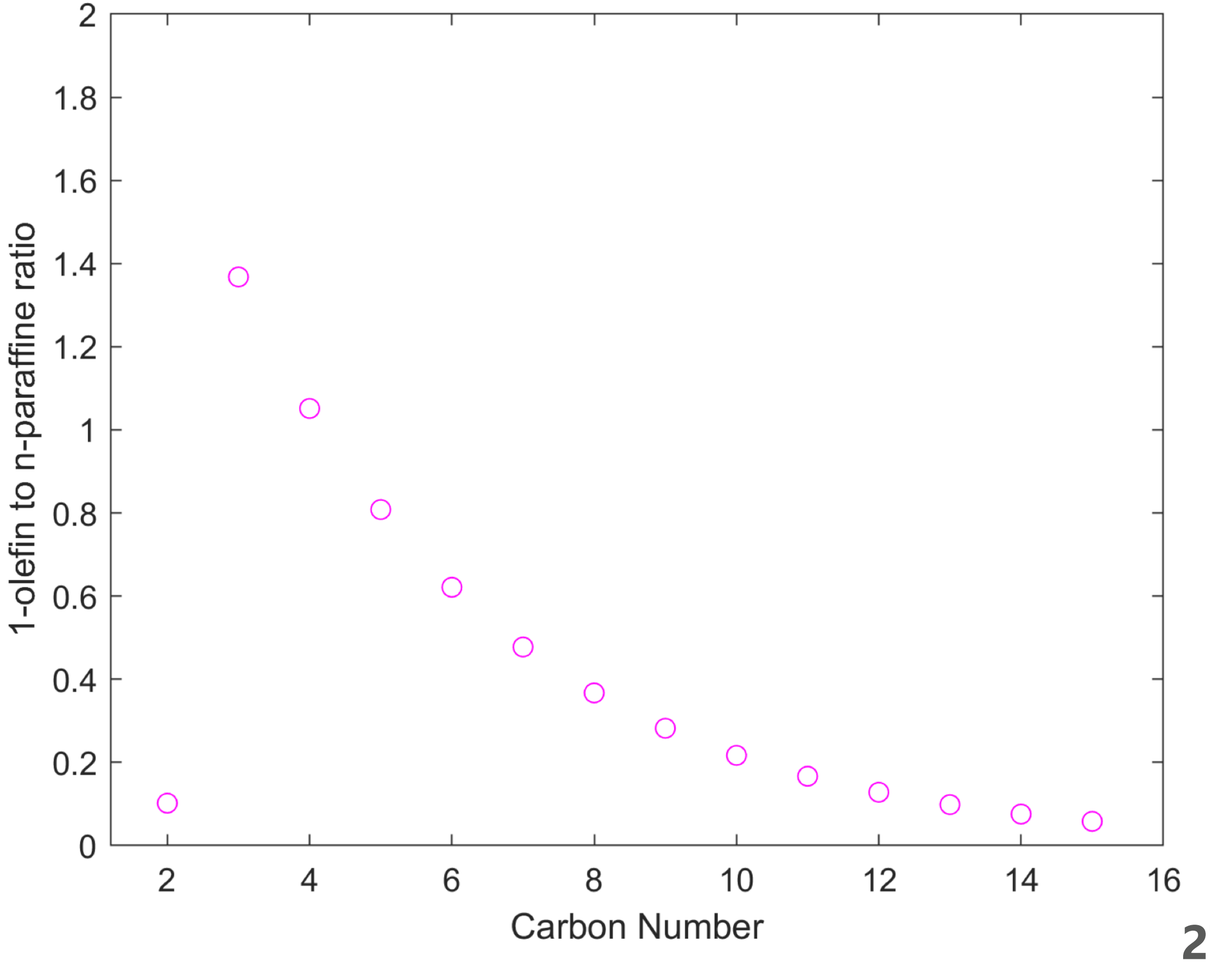
Kinetic modeling—1-olefin to paraffin ratio

T = 503 K, P = 1.5 MPa,
H_2/CO = 2.1, WHSV = 11.3 $NL/g_{cat}/h$.

Calculations from paper

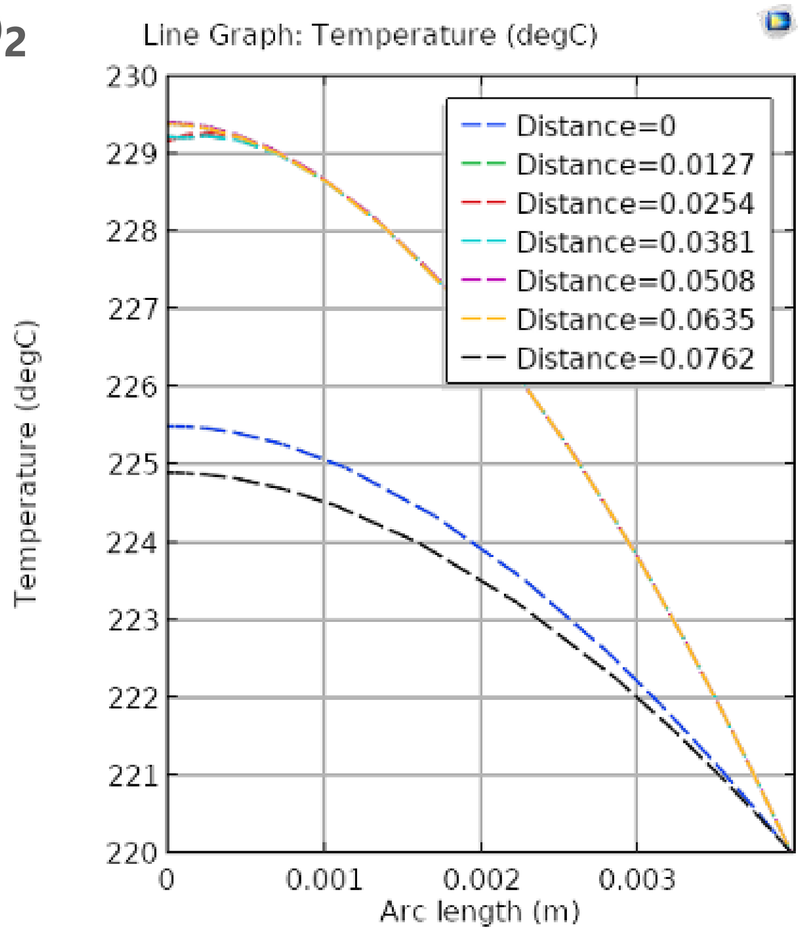


Our calculations based on the paper

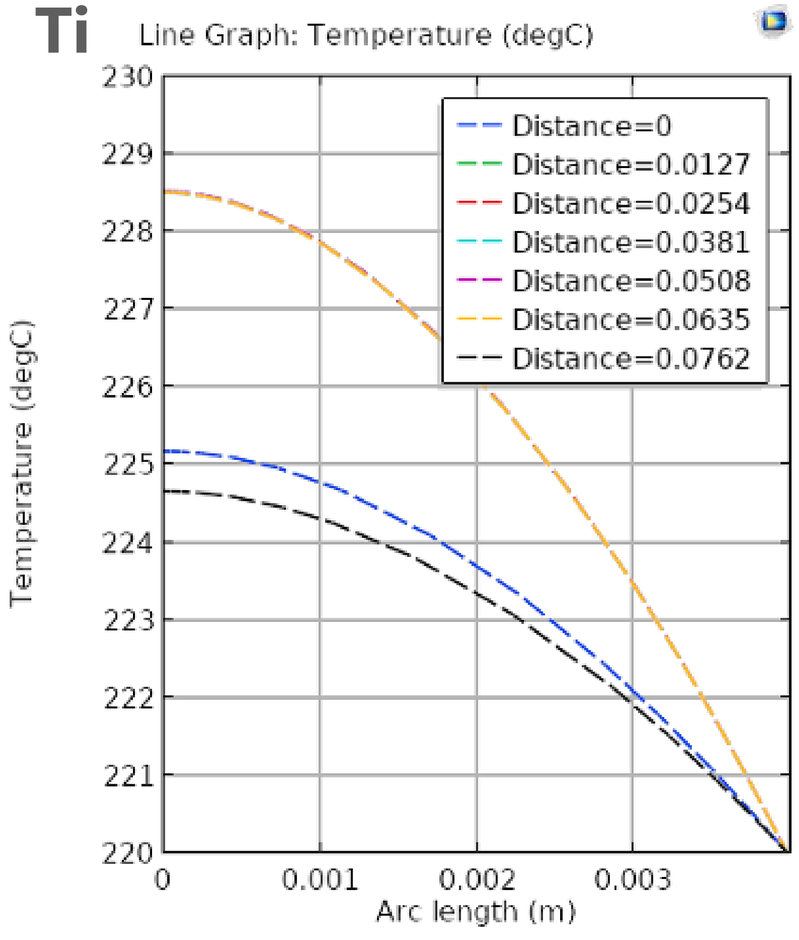


Comsol modeling—Temperature profiles

TiO_2



Ti



Future work

- Add FeCo and Fe nanoparticles to acid-functionalized TiO_2 nanotube structure and TiN support materials.
- Reaction testing of Ti 3D-printed materials.
- 3D-printing of carbon-based structures.
- Additional kinetic and CFD modeling.

Questions?

NETL - Penn State

University Coalition for Fossil Energy Research

- Thank you to DOE/NETL/UCFER for funding this project!
- Group website: https://nanointerfaces.che.utah.edu