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

**Michael Nigra, Bobby Mohanty, Eric Eddings, and Kevin Whitty**

THE UNIVERSITY OF UTAH®

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# University of Utah Team Overview

**Dr. Michael Nigra**
PI

**Dr. Bobby Mohanty**
Co-PI

**Dr. Eric Eddings**
Co-PI

**Dr. Kevin Whitty**
Co-PI

**1 post-doc (part-time) + 2 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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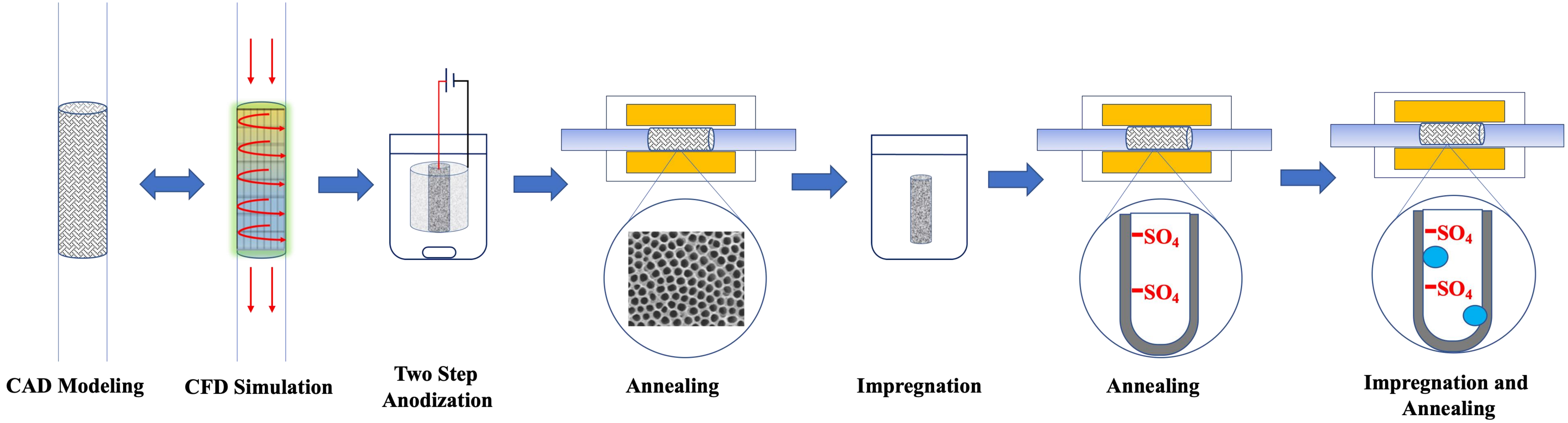
# New conductive bi-functional catalytic materials

- **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

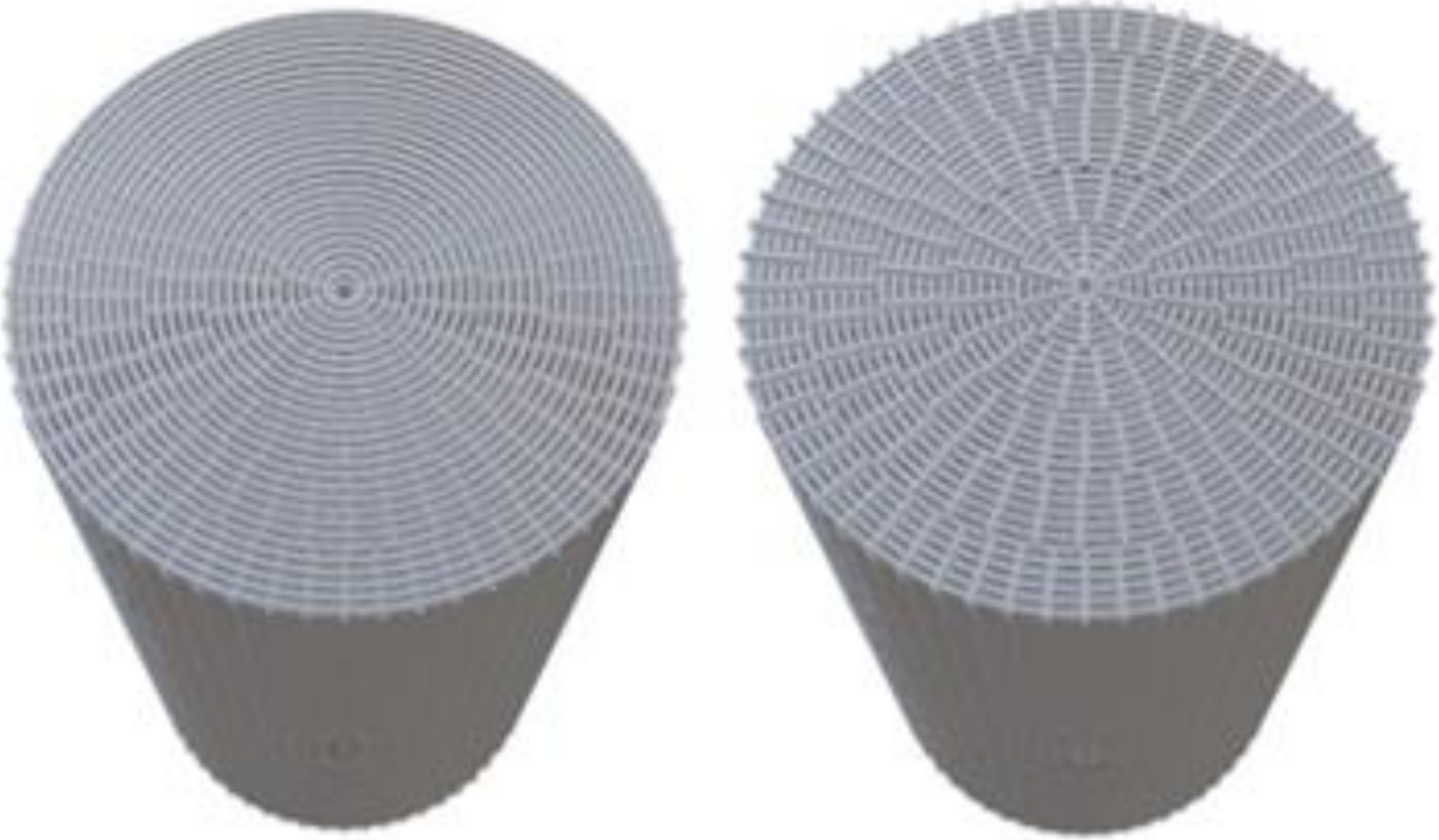
- New materials will consist of structured, bifunctional catalysts for FTS.
- 3-D printing techniques will allow for flexibility in design of catalyst.
- Improved **heat transfer** by:
  - Using a structured catalyst
  - Using a conductive support material.

# Preparation of Ti-based materials



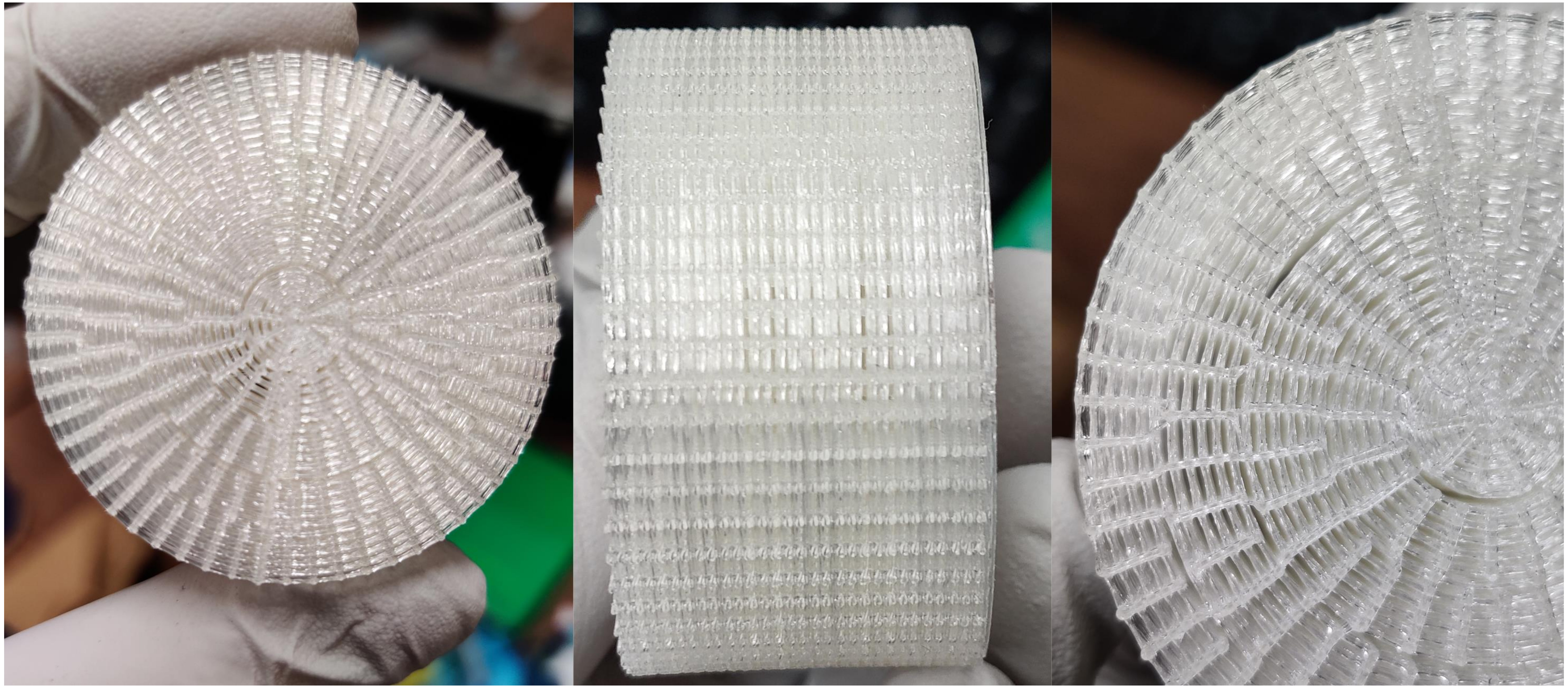
# Proposed structure for Ti-based support materials

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



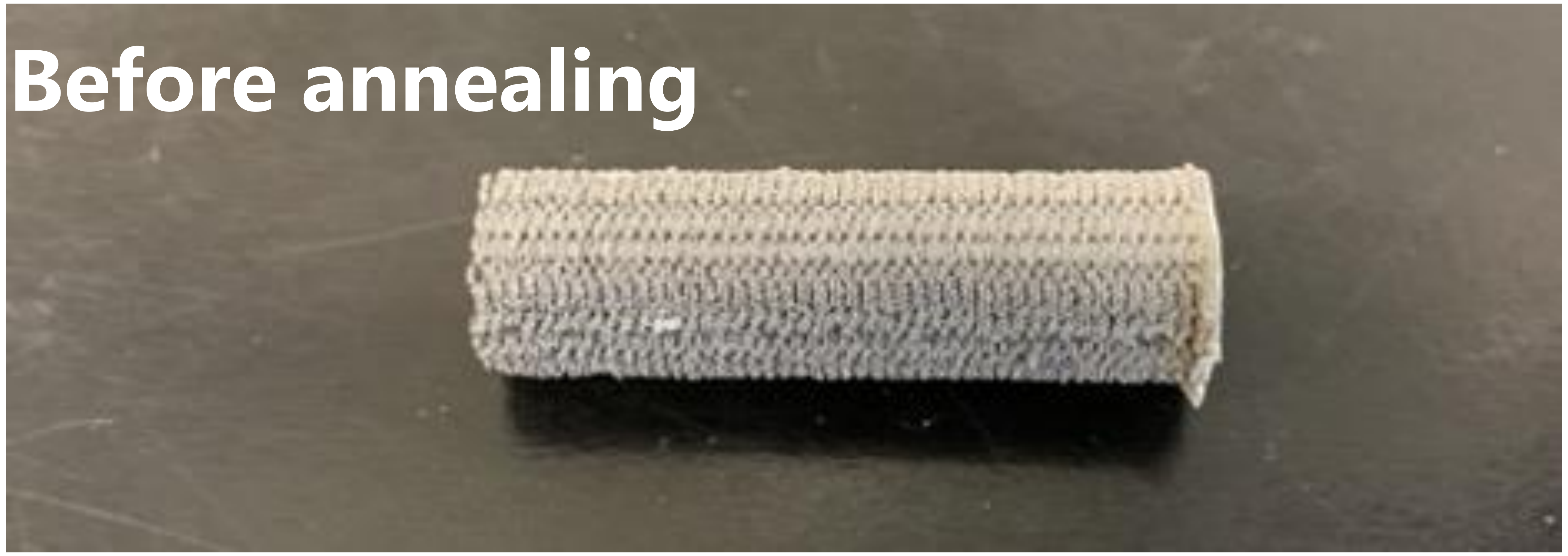
# Materials synthesis—3D printing model structures

- Test printing with PLA polymer before using Ti.



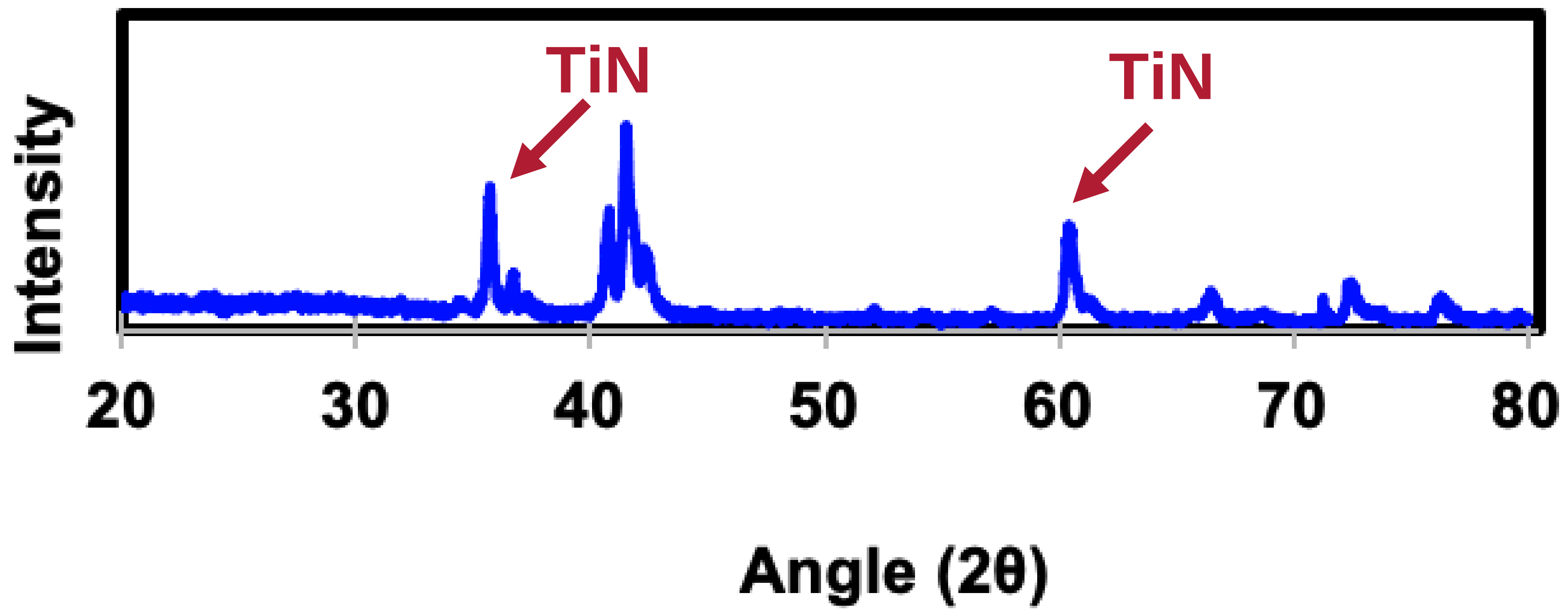
# 3D-printing with optimized printing parameters

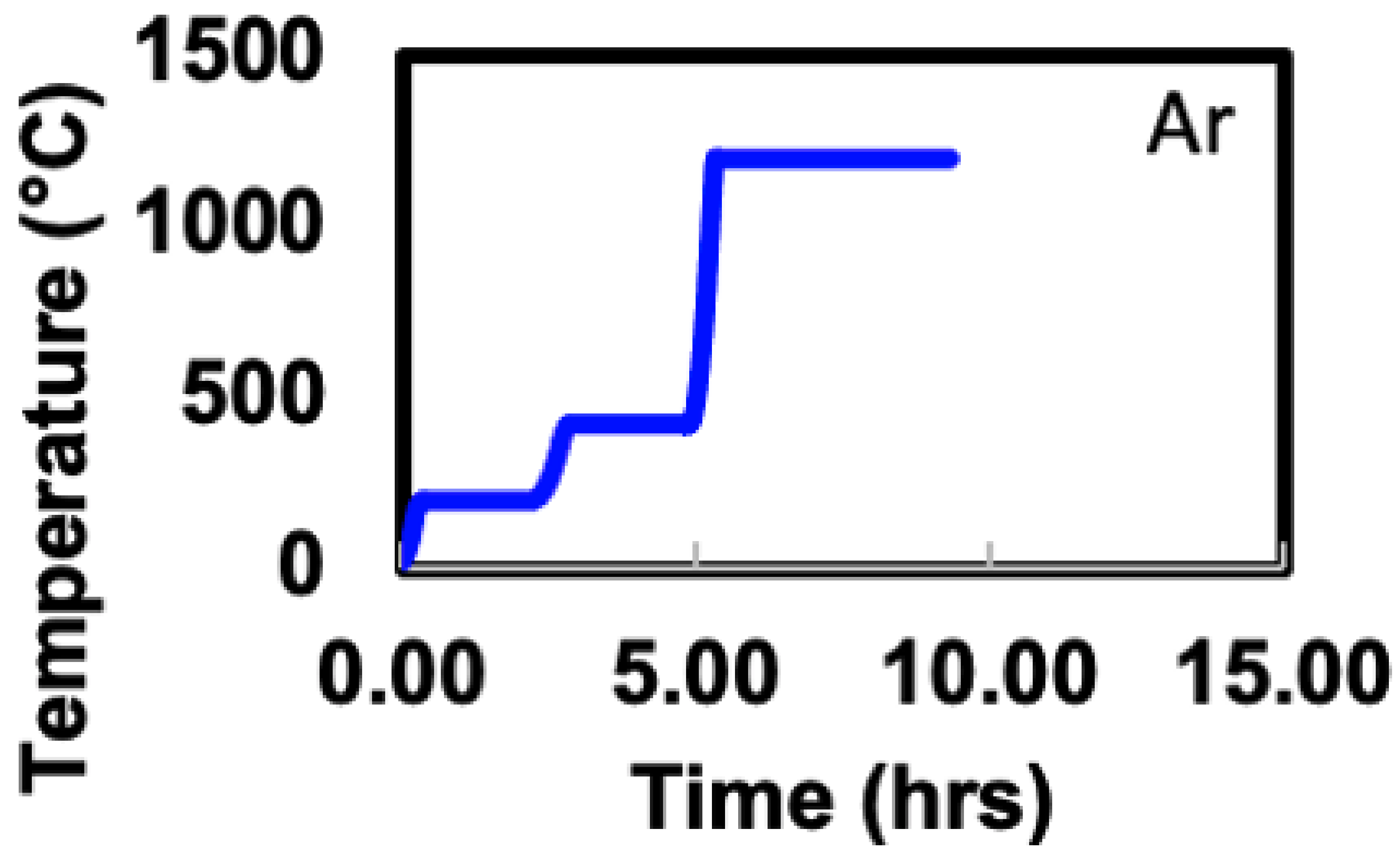
- Example of Ti 3D-printed structured material.




# 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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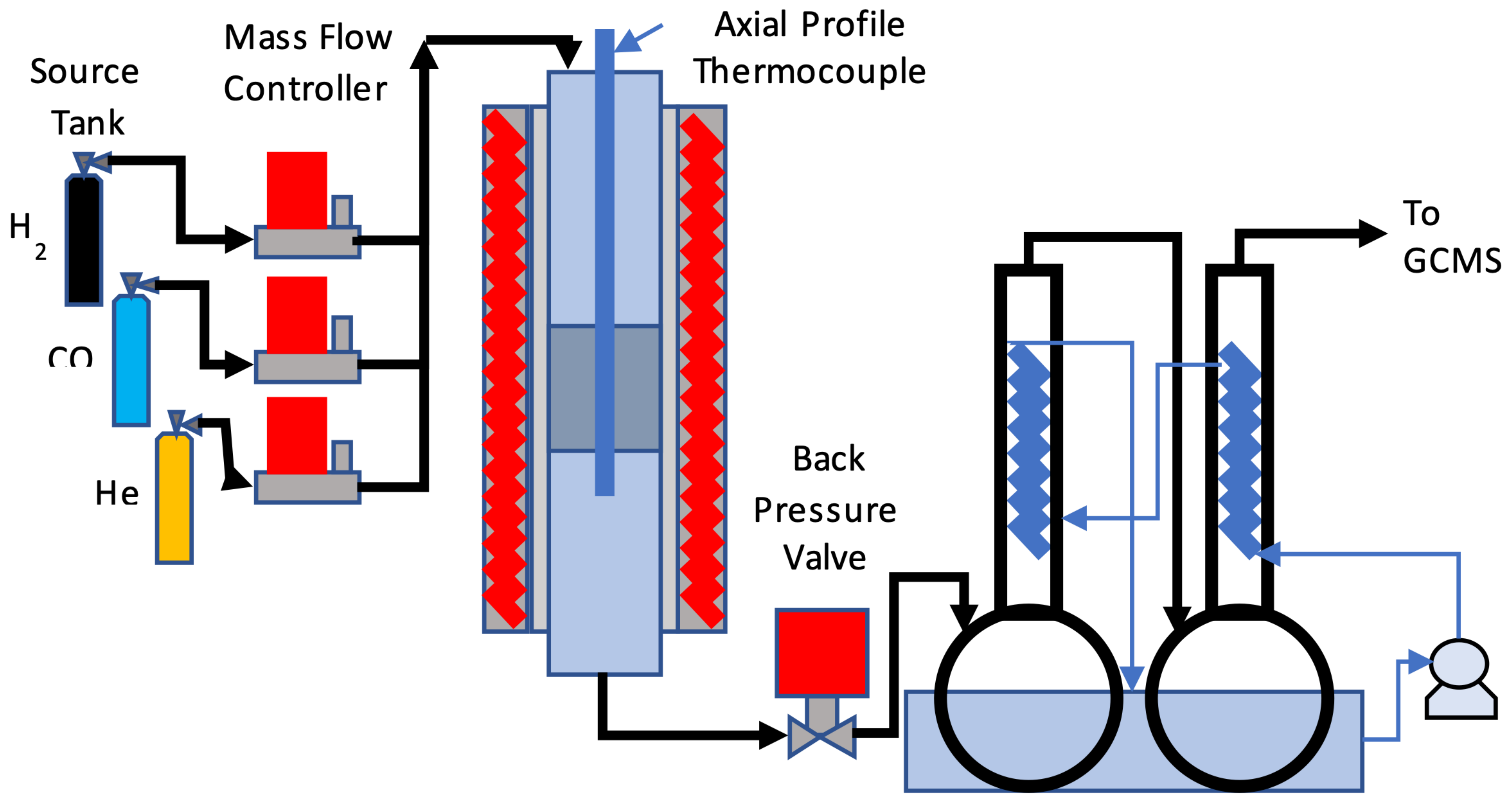
# Reactor set-up

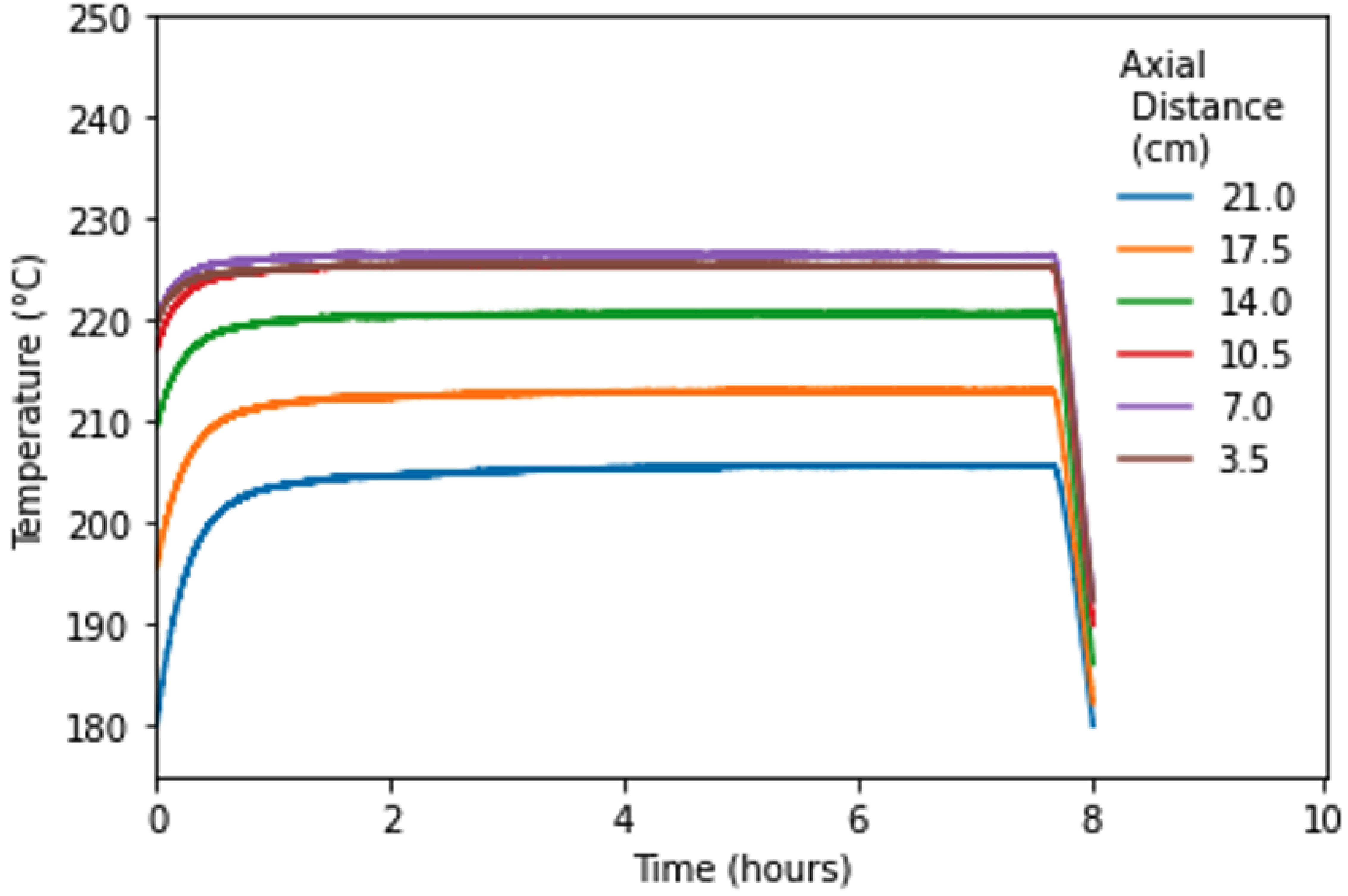


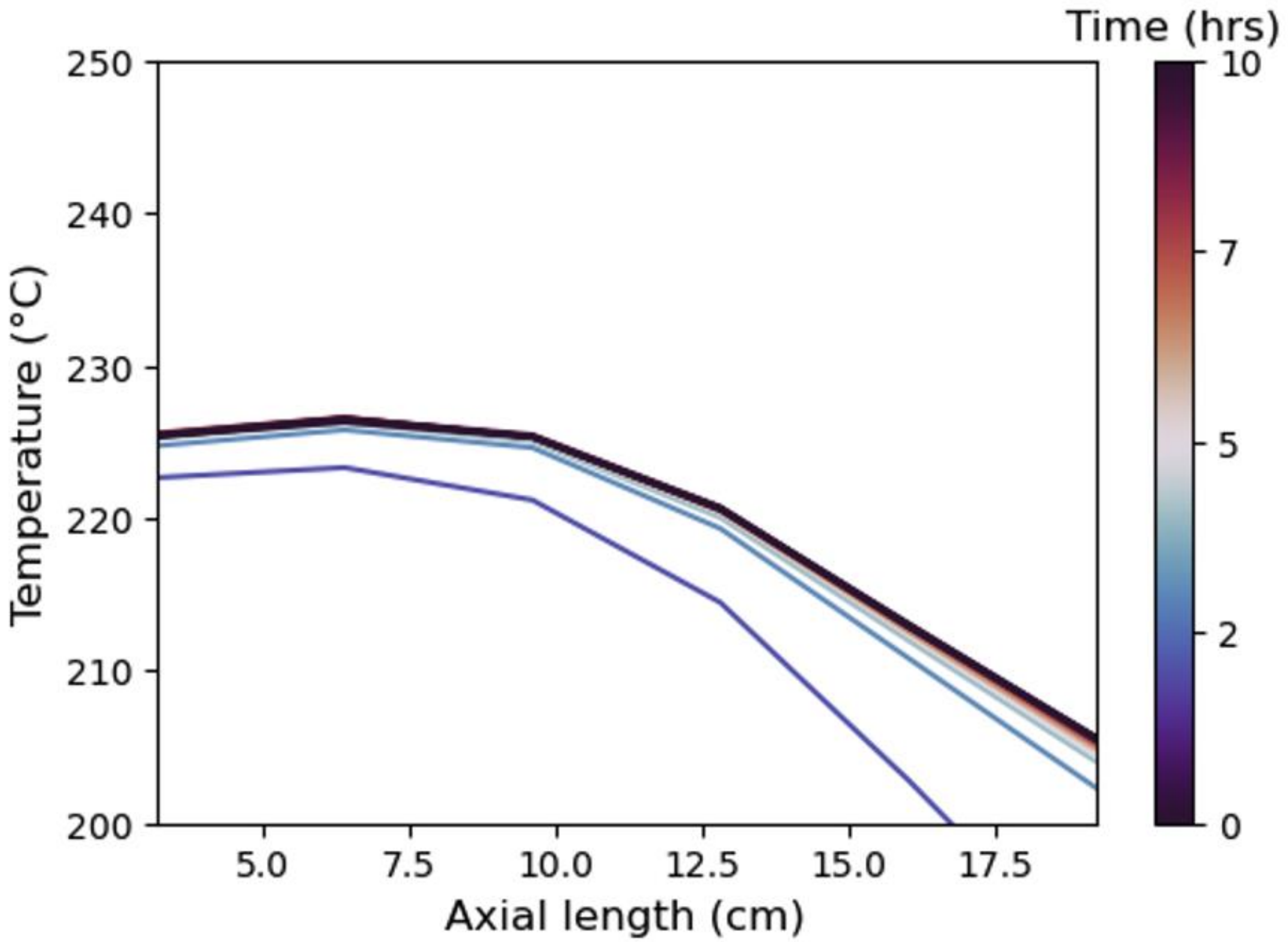

**Reactor diameters:** 1.77 in. and 0.37 in.

# 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.

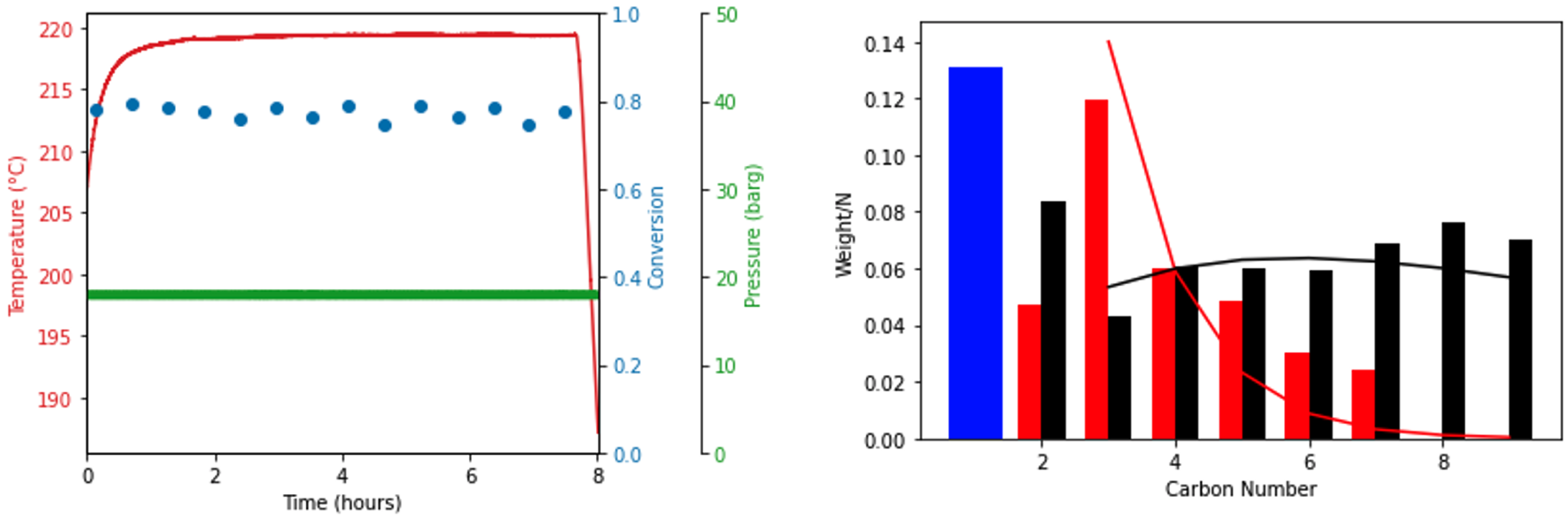
# Baseline catalytic testing—
# Transient temperature profiles




**Reaction conditions:** pressure: 18 barg, gas flow: 175 SCCM (50 SCCM H2, 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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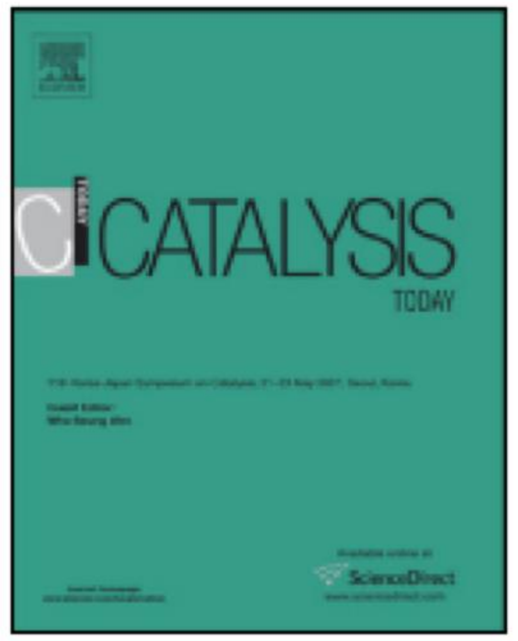


## CO-insertion mechanism based kinetic model of the Fischer–Tropsch synthesis reaction over Re-promoted Co catalyst

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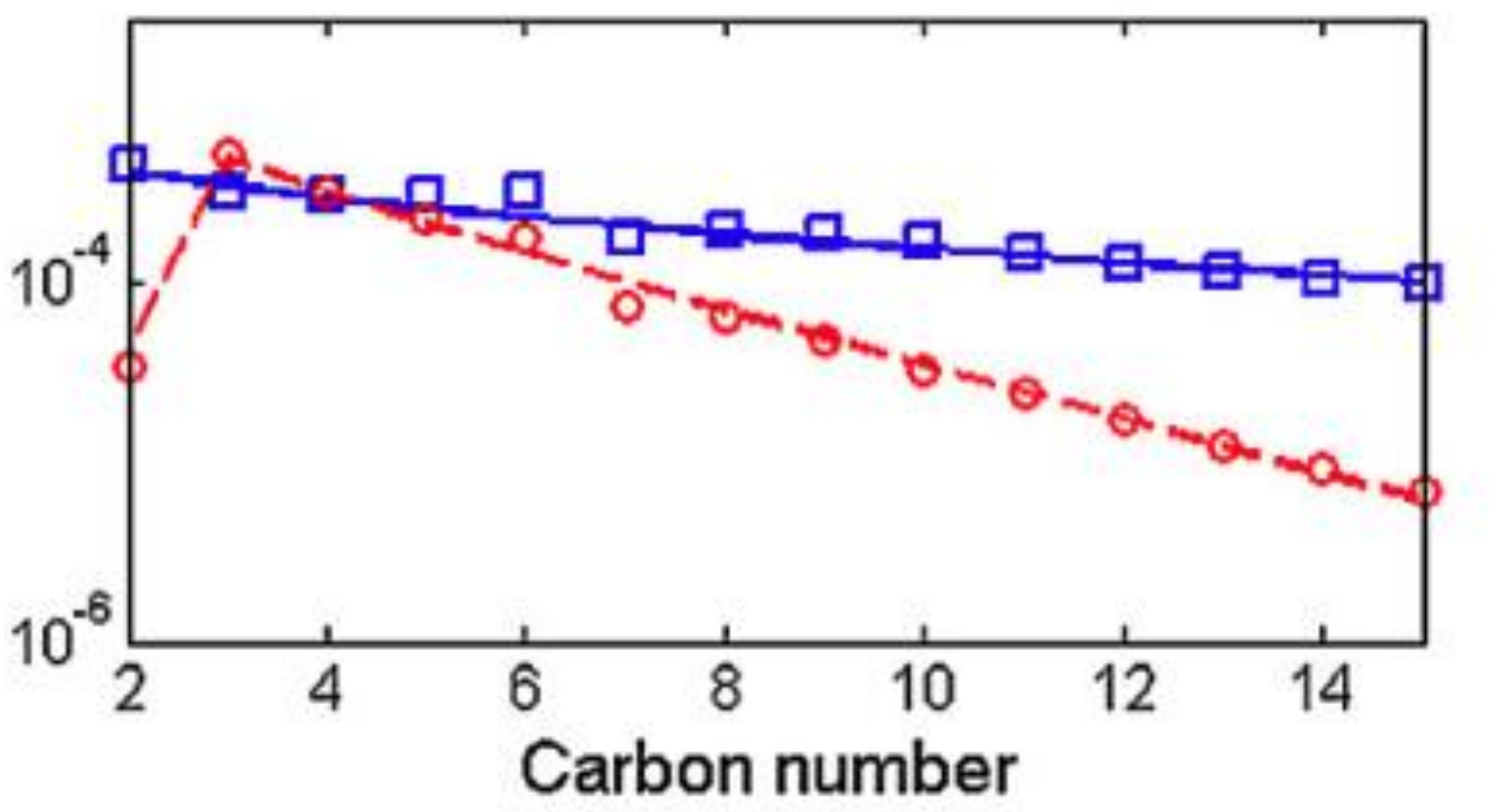
Branislav Todic [a], Wenping Ma [b], Gary Jacobs [b], Burtron H. Davis [b], Dragomir B. Bukur [a,c,*]

[a] *Chemical Engineering Program, Texas A&M University at Qatar, PO Box 23874, Doha, Qatar*
[b] *Center for Applied Energy Research, 2540 Research Park Drive, Lexington, KY 40511, United States*
[c] *Artie McFerrin Department of Chemical Engineering, Texas A&M University, 3122 TAMU, College Station, TX 77843, United States*

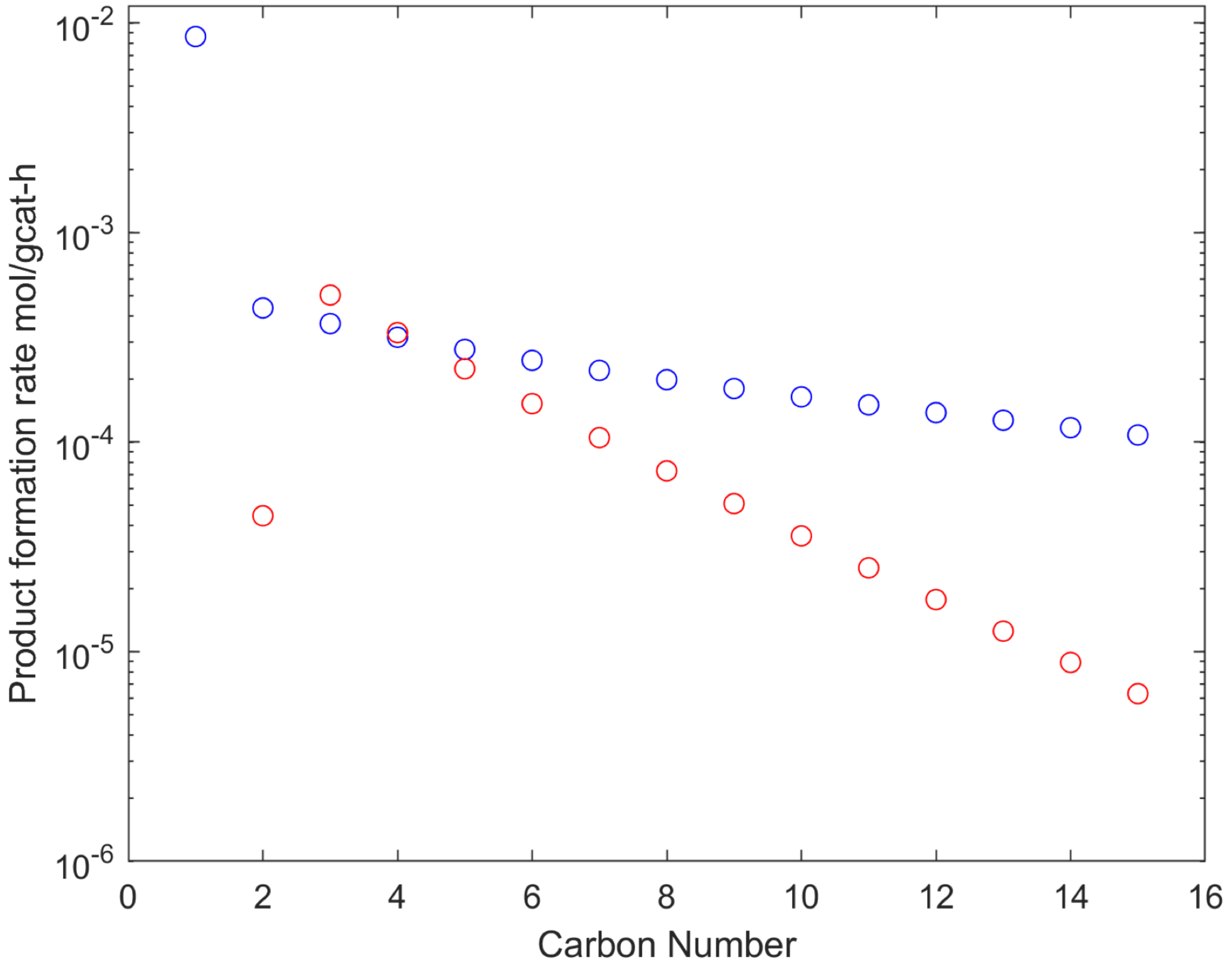
# Kinetic modeling—Product formation rate

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

**Calculations from paper**



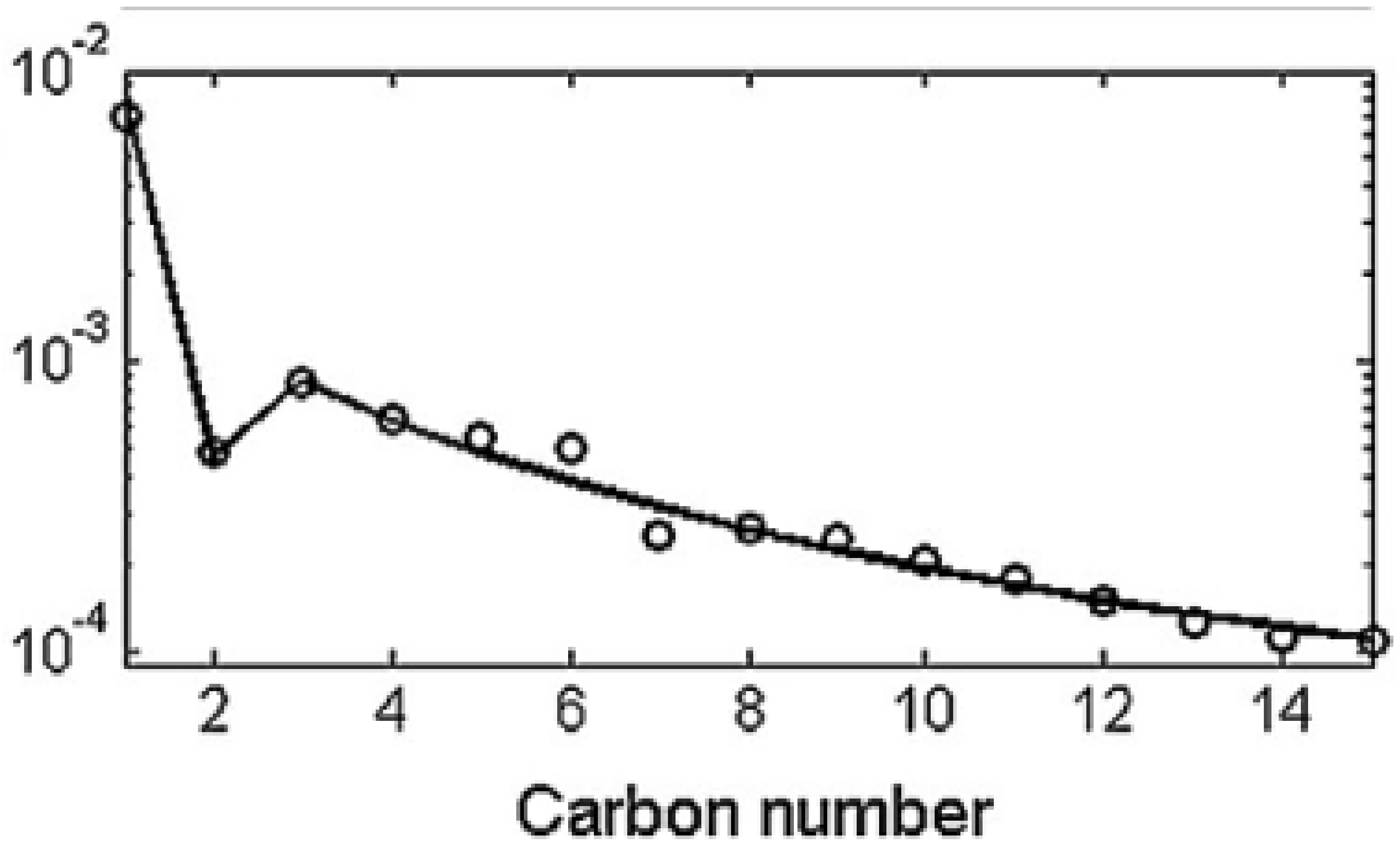

**Our calculations based on the paper**



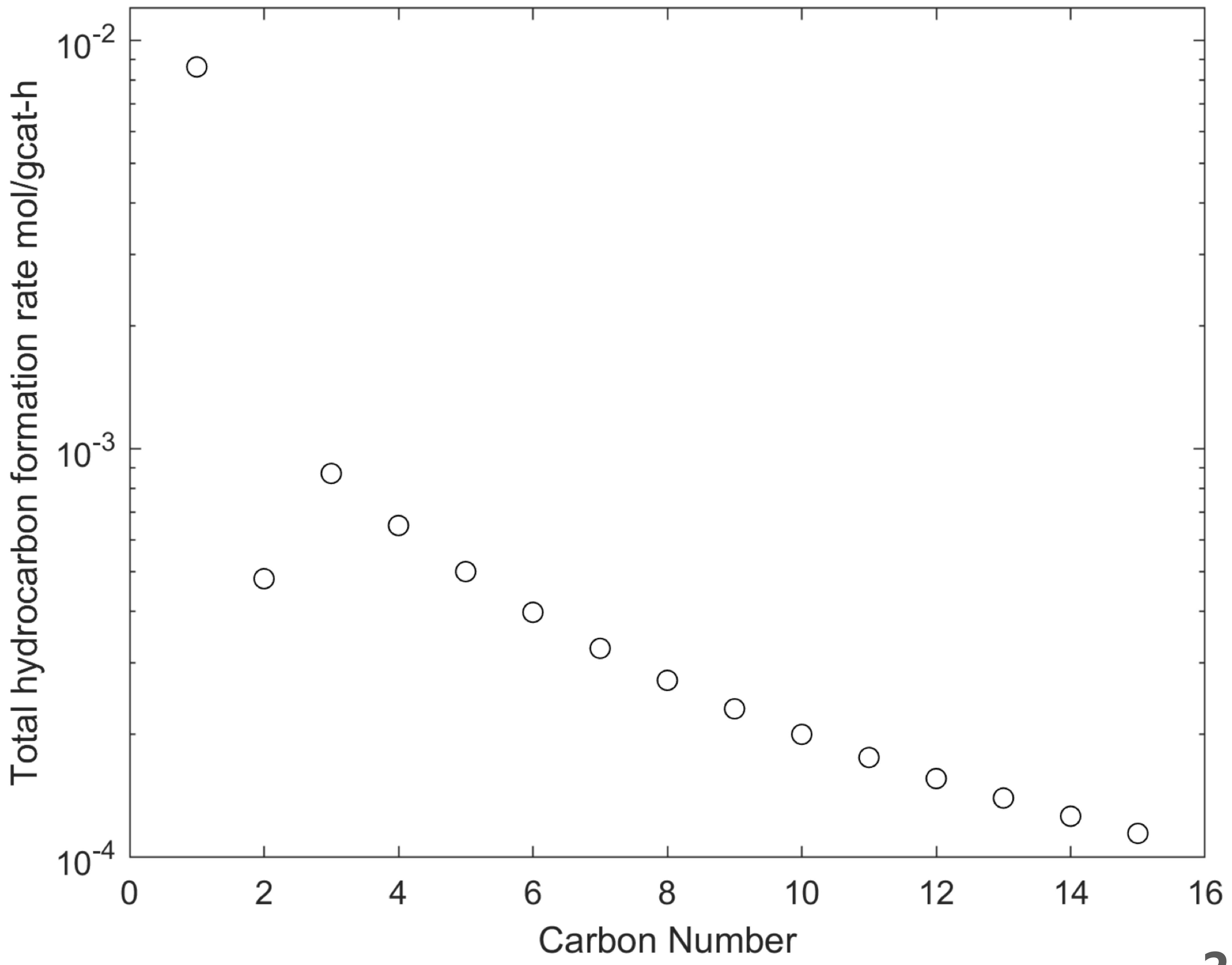
# Kinetic modeling—Total hydrocarbon formation rate

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

**Calculations from paper**



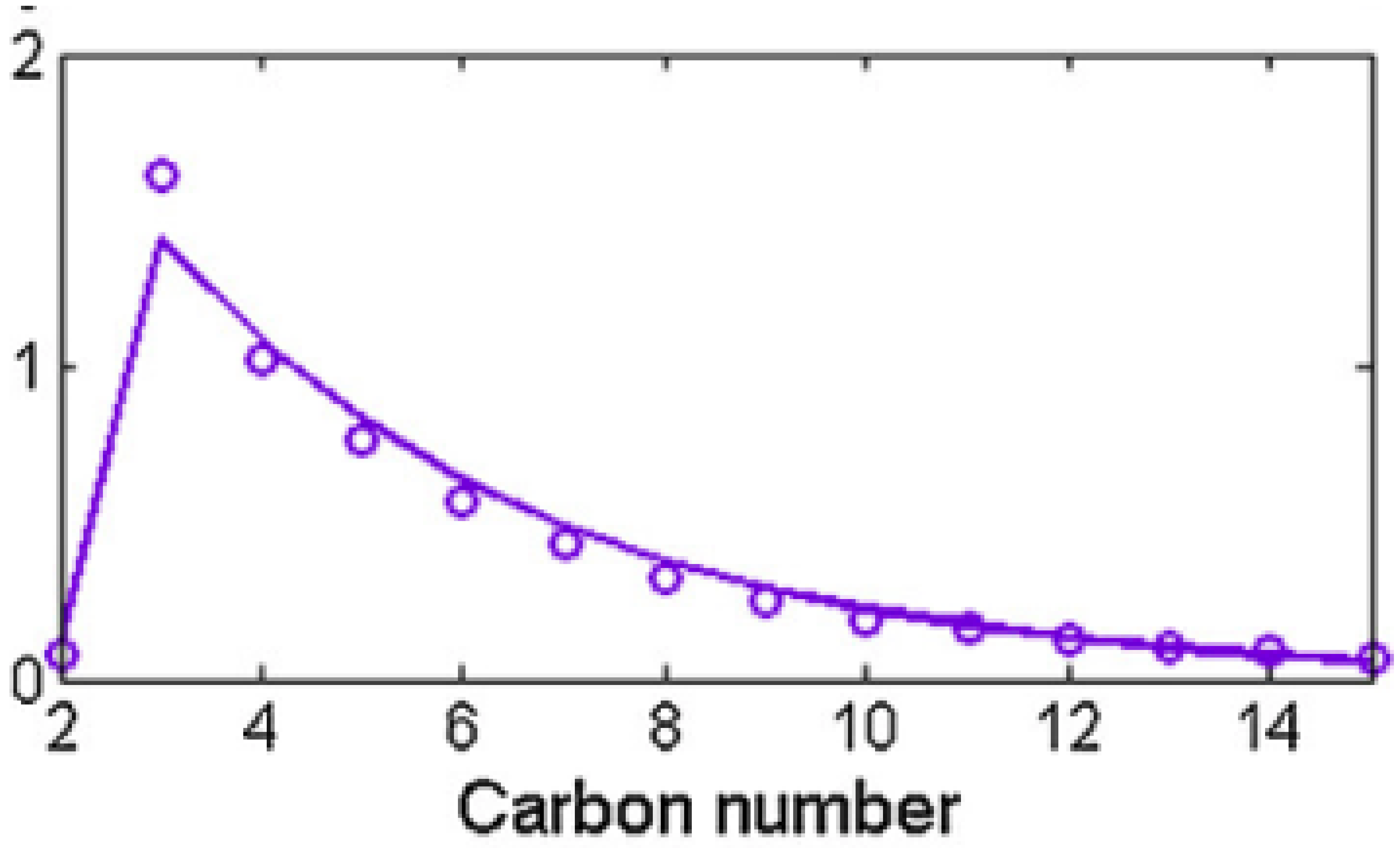

**Our calculations based on the paper**



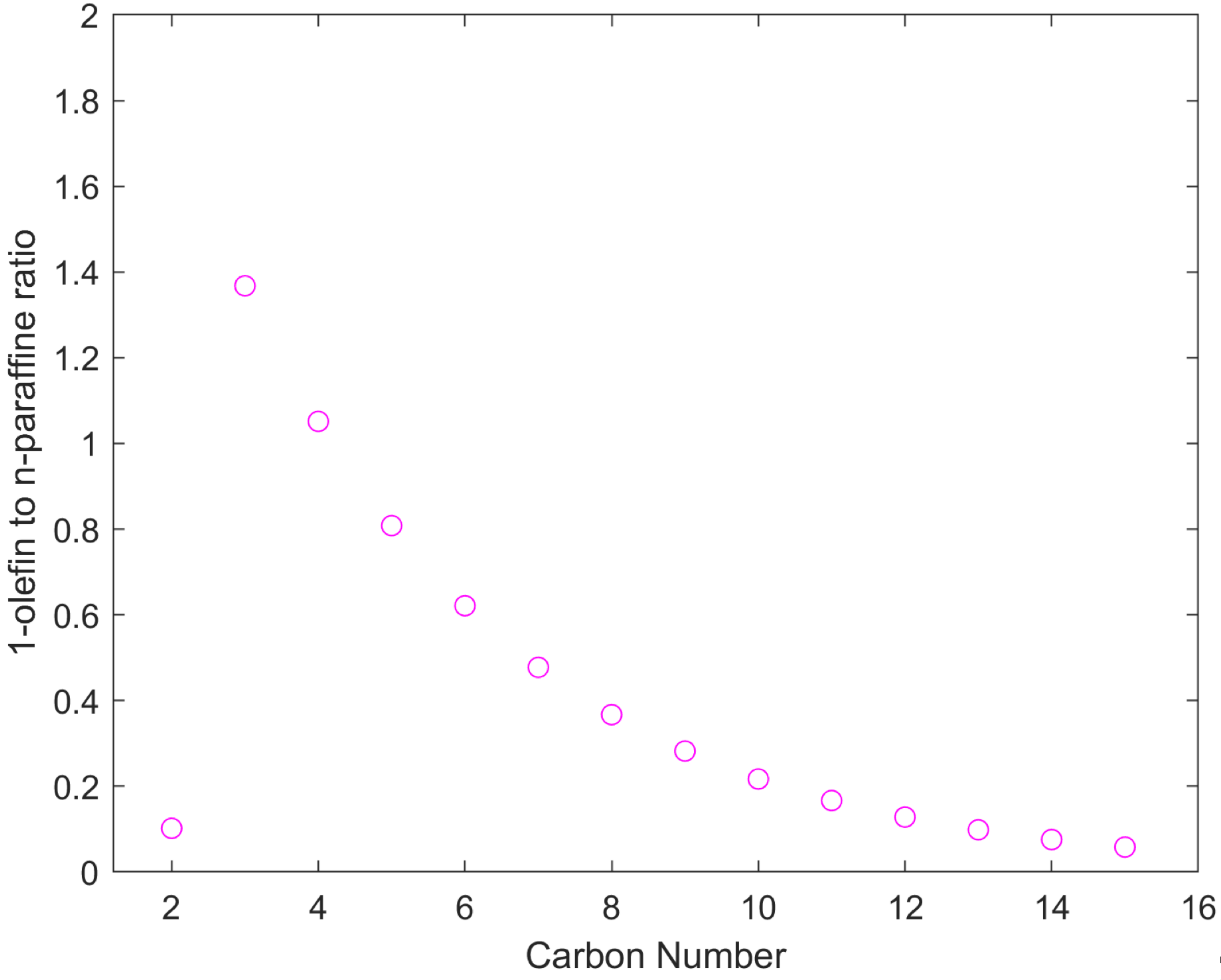
# Kinetic modeling—1-olefin to paraffin ratio

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

**Calculations from paper**

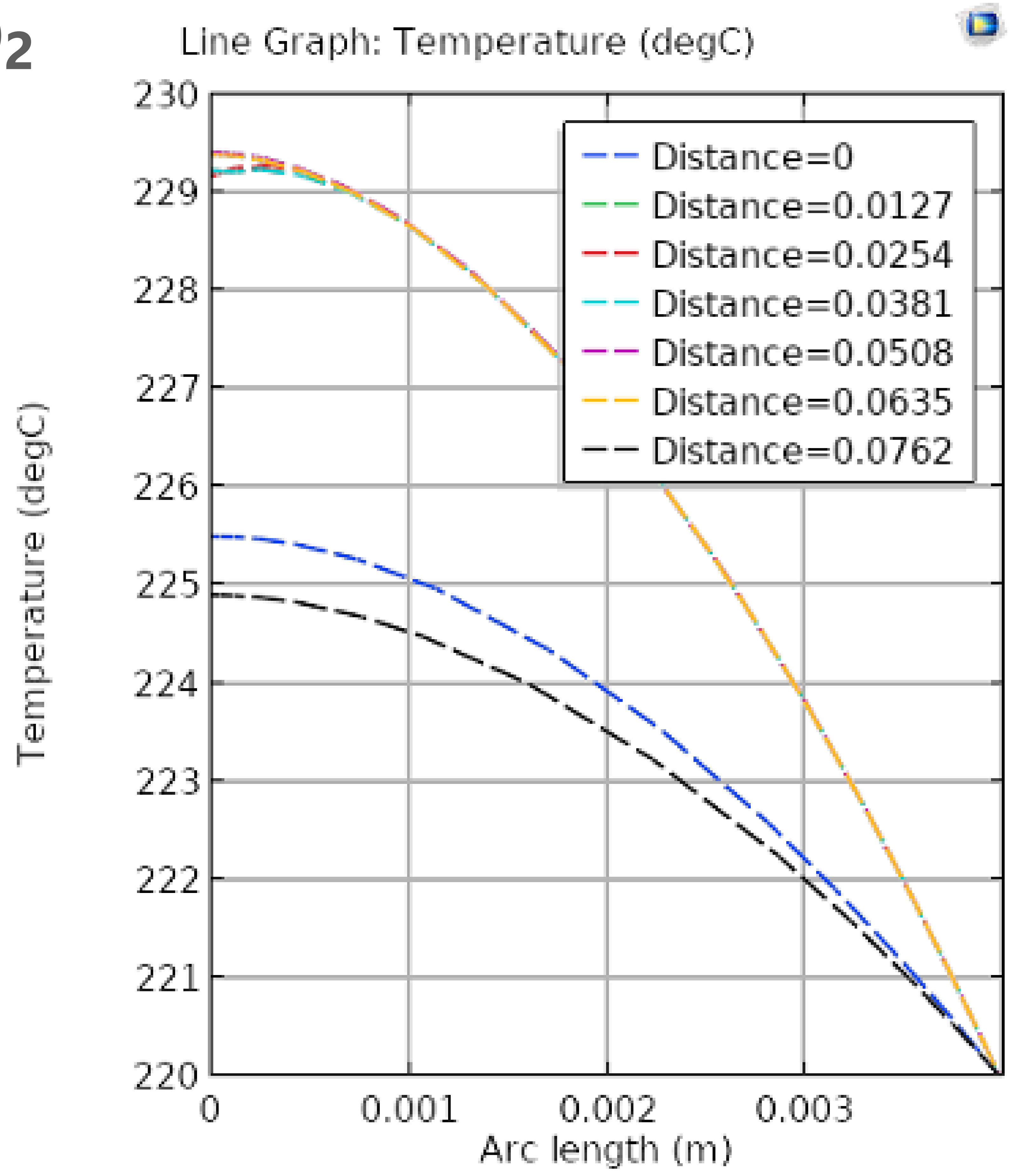



**Our calculations based on the paper**

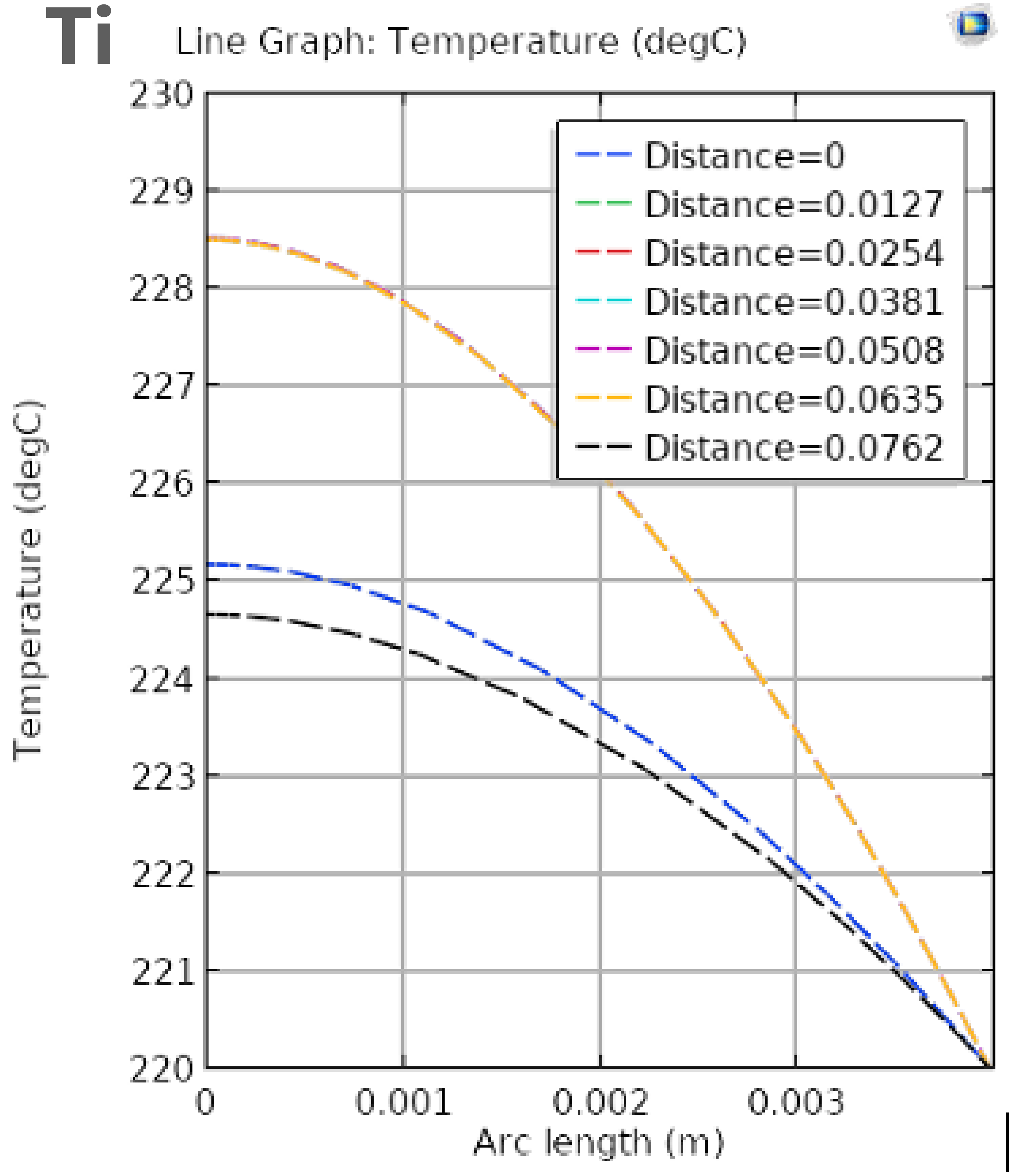


# Comsol modeling—Temperature profiles

TiO2




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