

# Pressurized Oxidative Pyrolysis (POP)

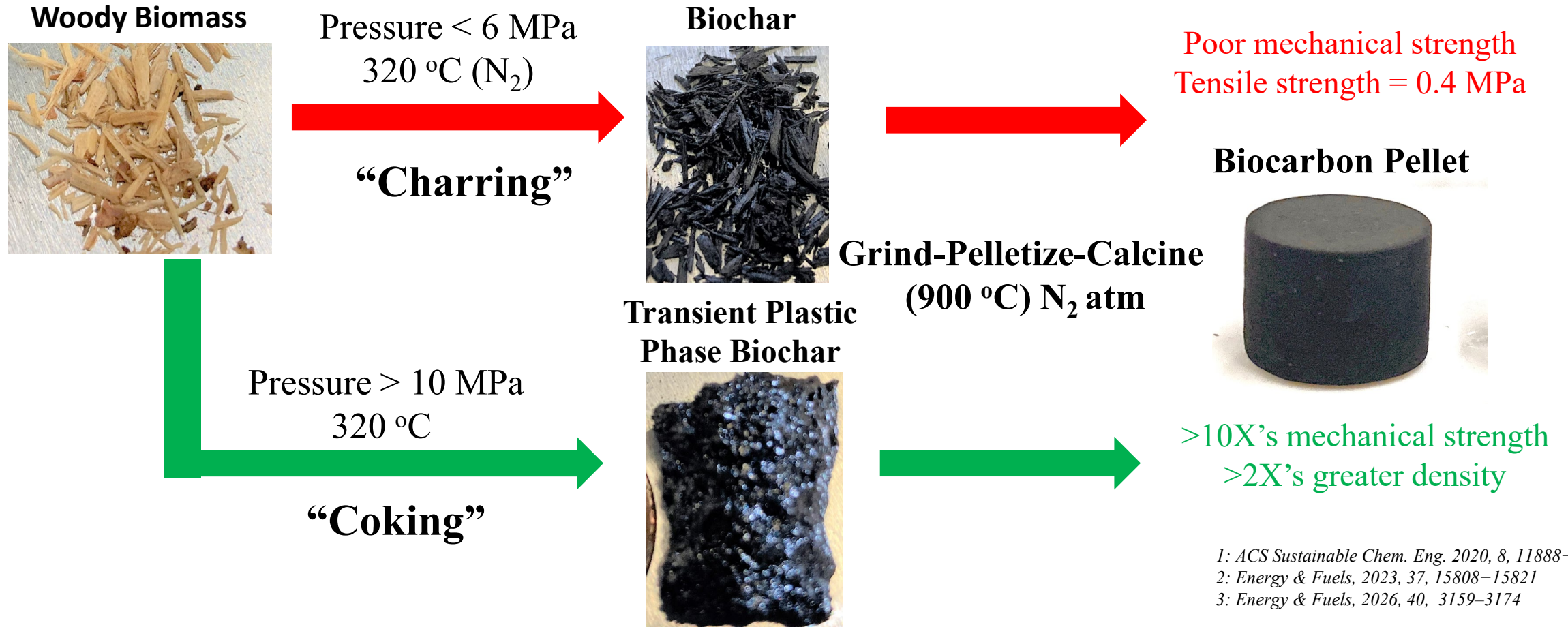
## A Low-Temperature, Autothermal Regime for Intensified Biomass Conversion

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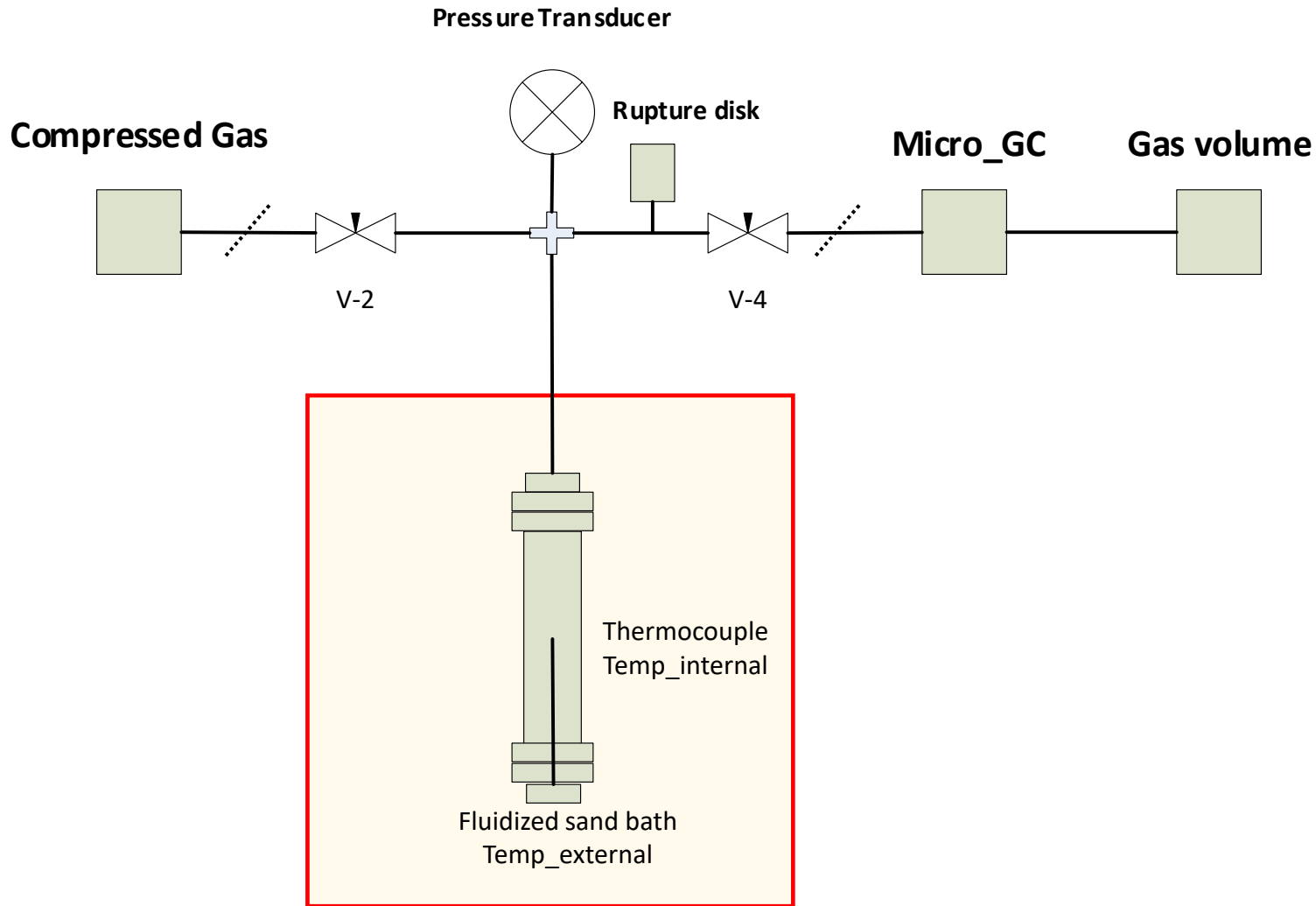
# Background: Biocarbon Engineering Via Pressurized Pyrolysis



- Can O<sub>2</sub> addition produce TPPB auto-thermally and retain favorable properties?

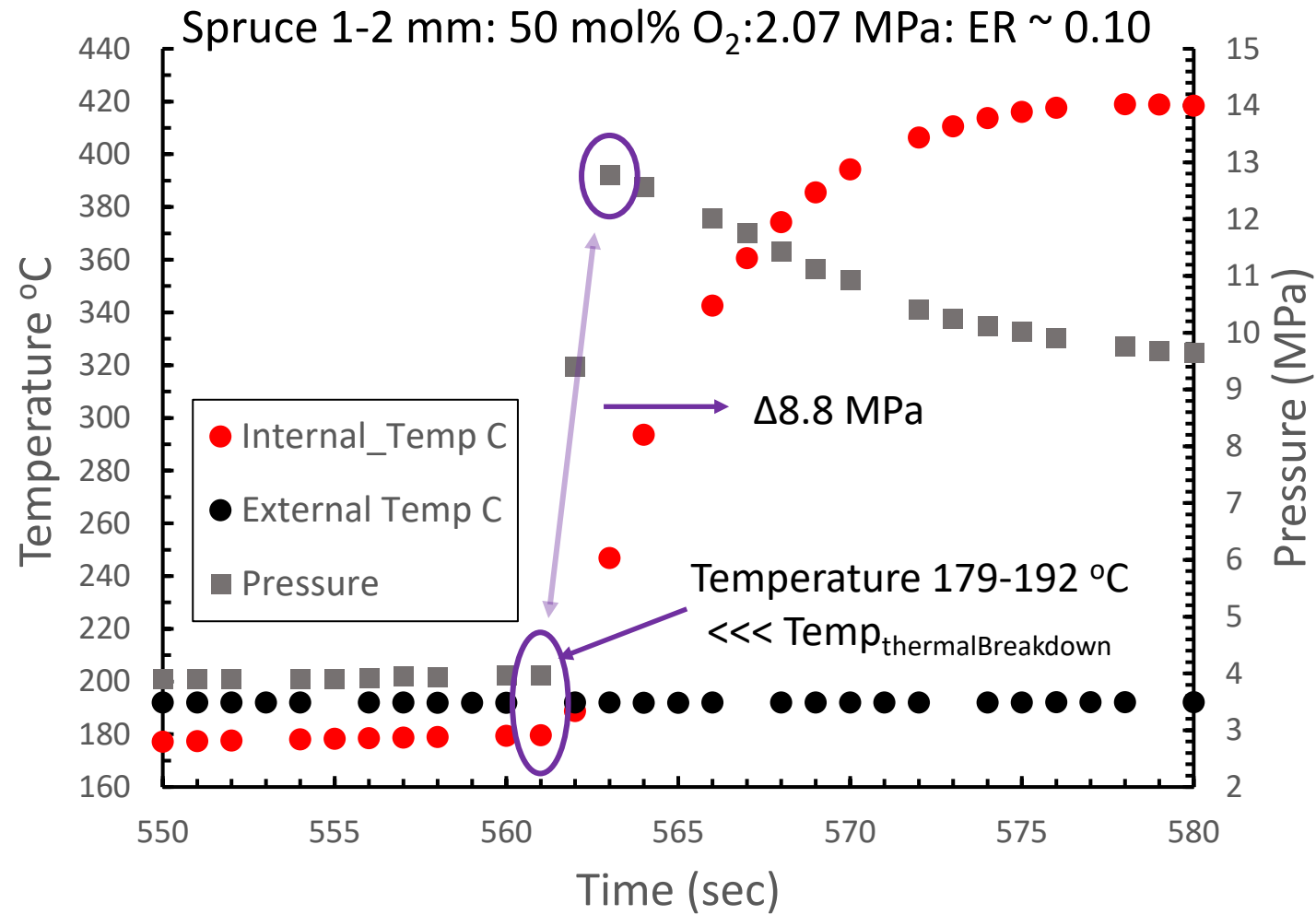
1: ACS Sustainable Chem. Eng. 2020, 8, 11888–11905  
2: Energy & Fuels, 2023, 37, 15808–15821  
3: Energy & Fuels, 2026, 40, 3159–3174

# Reactor System Wall Heated Tube Bomb (WHTB)



- Batch reactor: Swagelok parts SS tubing
  - 1 inch OD, 6 inch length
  - Closed system
  - Heated with fluidized sand bath
- $\text{SandBath}_{\text{mass}} \gg \text{Reactor}_{\text{mass}}$
- Submerge reactor in sand-bath
  - Single thermocouple (bulk temp)
  - Monitor temperature and pressure ( $\text{s}^{-1}$ )
  - Remove from Sandbath cool to RT
  - Release pressure measure gas volume and composition ( $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ )

# Introduction: Pressurized Oxidative Pyrolysis



- Observed with: wood, straw, algae, polyolefins, rubber, biocarbon.
- No reaction with PET and polystyrene.
- Metals reduce onset temperature (~ 30 °C)
- Tolerates high moisture content (~ 40 wt% H<sub>2</sub>O)
- Occurs without O<sub>2</sub> enrichment (~ 3.1 MPa)
- Good biocarbon precursor (TS > 10 MPa)
- Verified O<sub>2</sub>:CO<sub>2</sub> gas systems

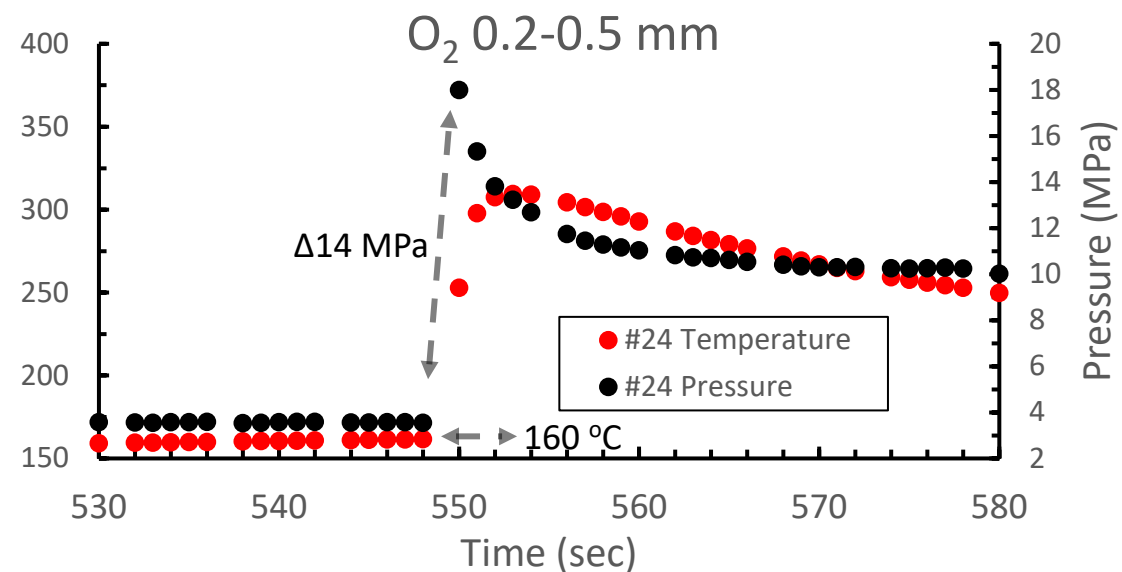
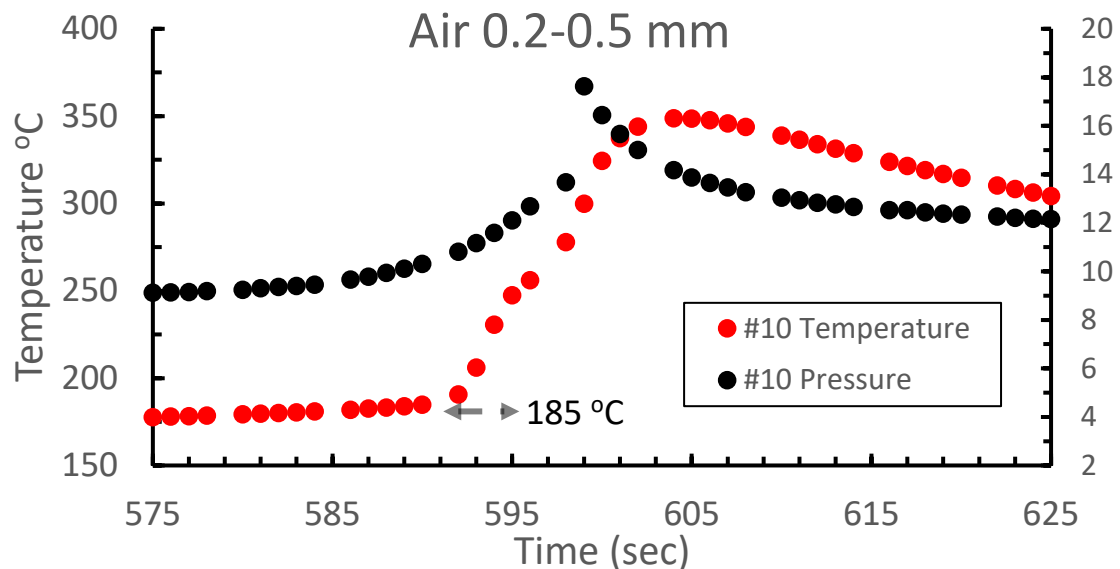
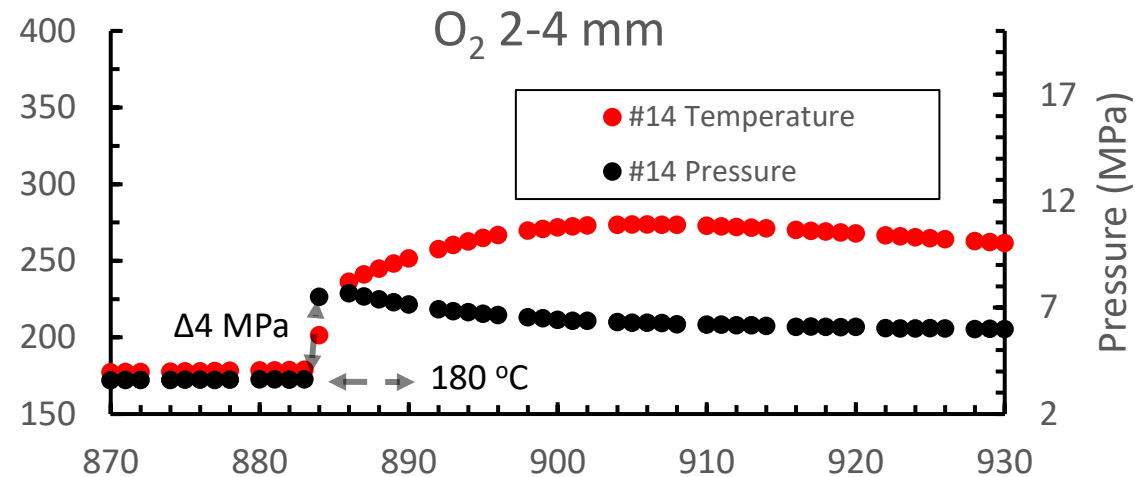
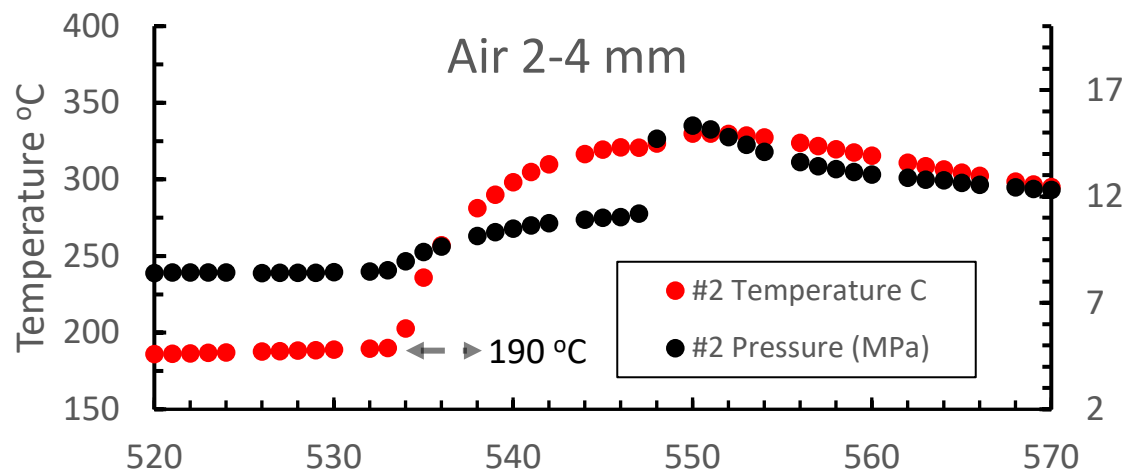
# Purpose of This Study: How Does Particle Size Impact POP

**Feedstock:** Spruce wood ~ 11 g/test

- Low ash content (reduce impact of inorganics)
- ER constant for all particle sizes (within a gas condition)
- All conditions run in triplicate (24 tests total)

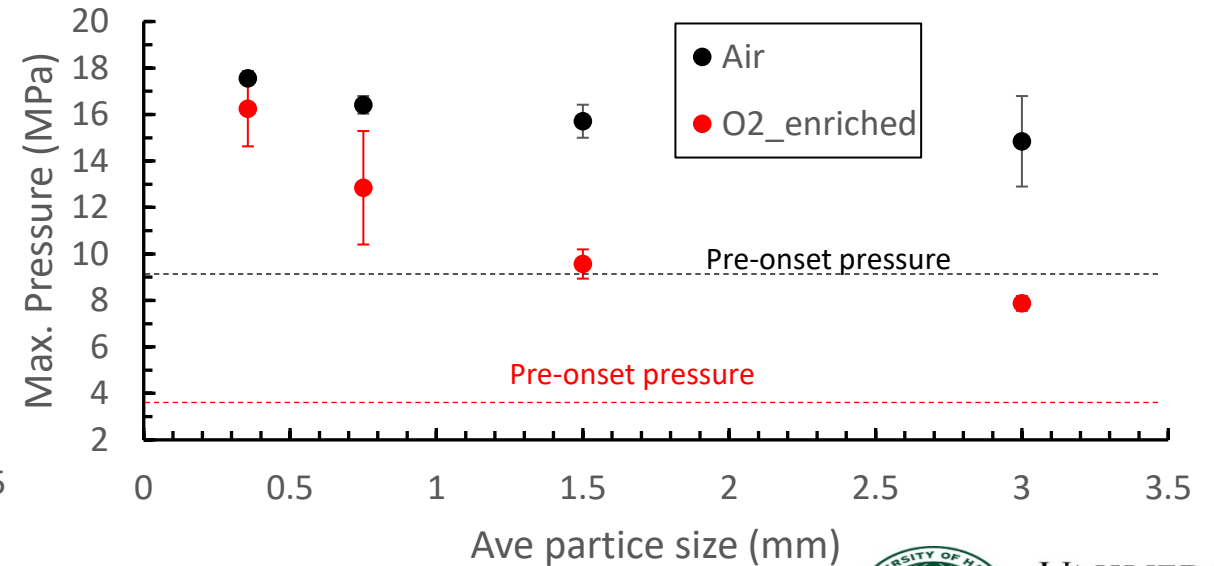
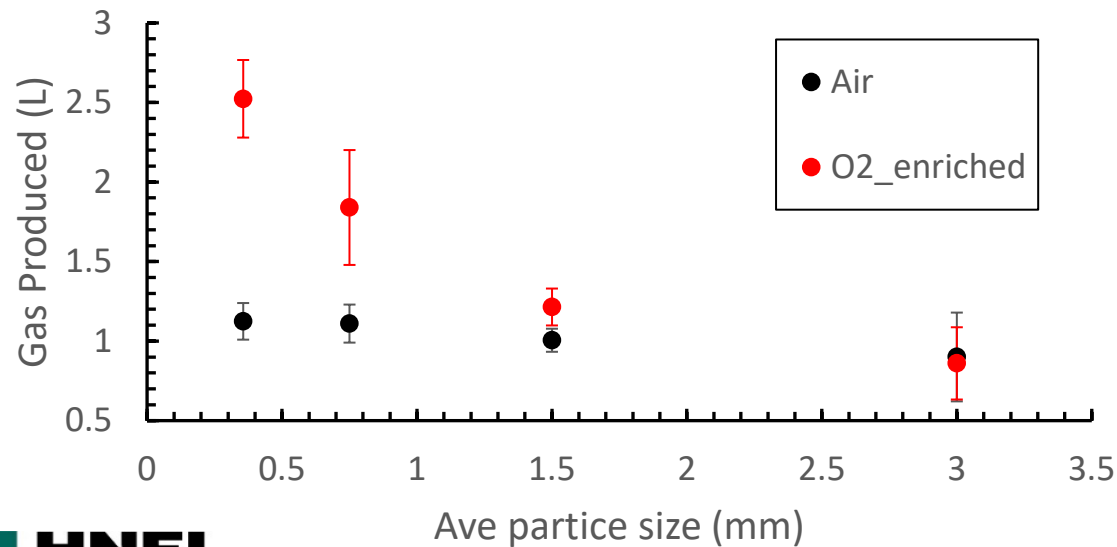
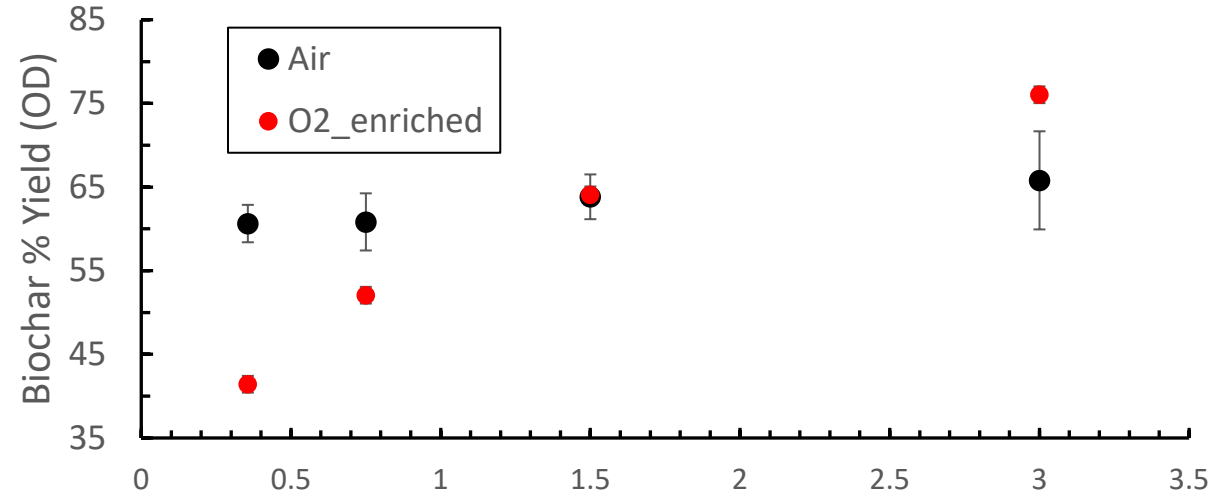
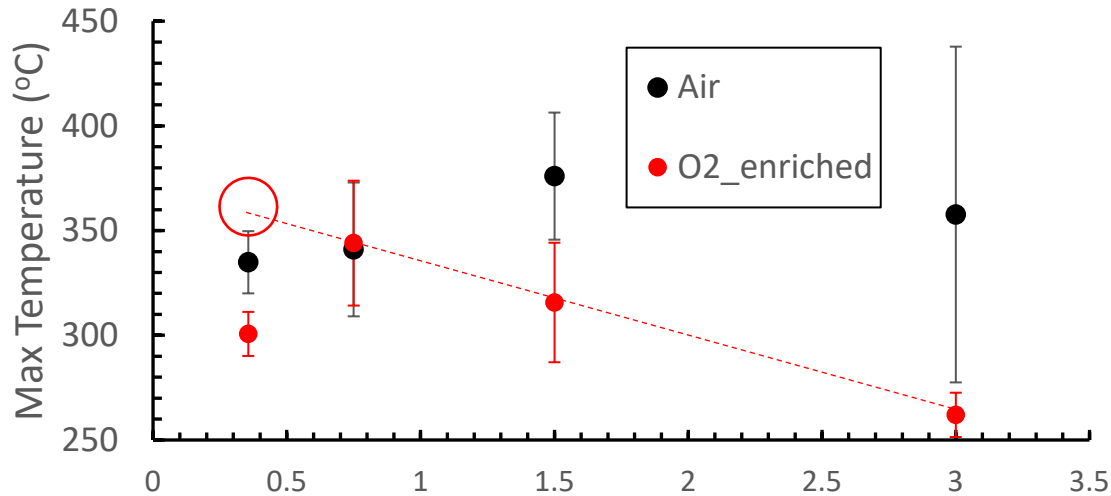
| Particle Size | Relative External Surface area | Gas Parameters                                            | 5.17 MPa Air<br>ER ~0.090 | 85% O <sub>2</sub> 2.1 MPa<br>ER ~ 0.150 |
|---------------|--------------------------------|-----------------------------------------------------------|---------------------------|------------------------------------------|
| 2-4 mm        | 1×                             | pO <sub>2</sub> (MPa)                                     | 1.09                      | 1.79                                     |
| 1-2 mm        | 2×                             | O <sub>2</sub> inventory (mmol O <sub>2</sub> /g biomass) | 3.4                       | 5.3                                      |
| 0.5-1.0 mm    | 4×                             | Oxidation heat inventory (kJ/g biomass)                   | 0.7–1.3                   | 1.2–2.1                                  |
| 0.2-0.5 mm    | 9×                             | Gas ballast (mol total gas/mol O <sub>2</sub> )           | 4.8                       | 1.2                                      |

# Selected Temperature-Pressure Traces

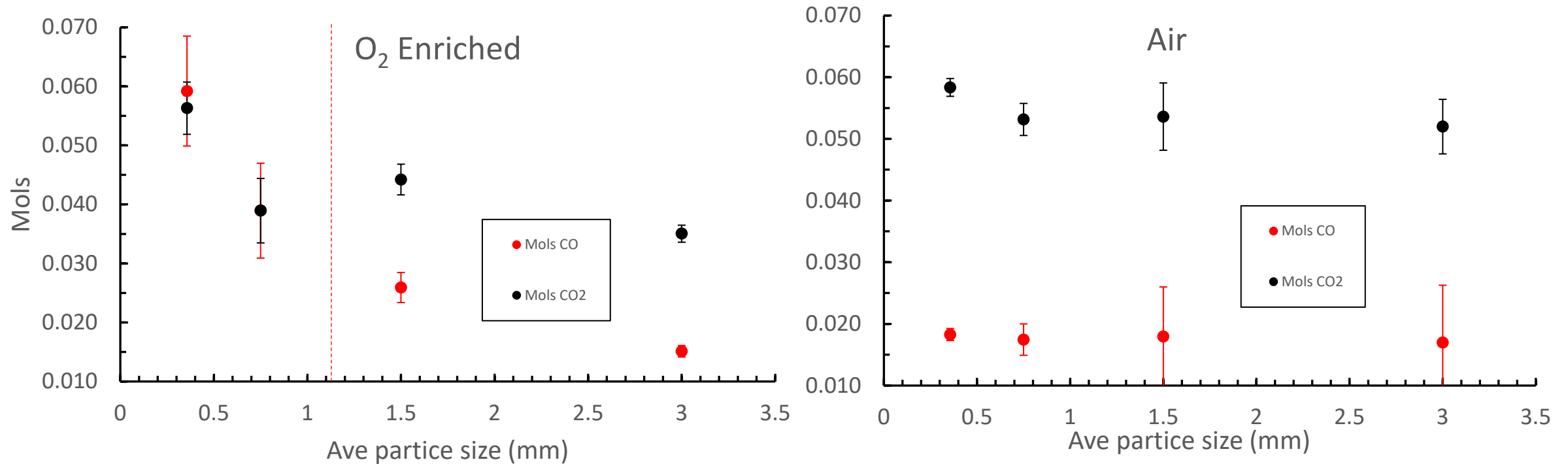


- Pressure rise detected before bulk temperature (O<sub>2</sub> enrichment)
- Temperature and Pressure move together (Air)

# Max Temp, Biochar Yield, Gas Production, and Max Pressure



# CO:CO<sub>2</sub> Product Gas Ratio



- Higher CO:CO<sub>2</sub> ratio => O<sub>2</sub> starved
- O<sub>2</sub> enrichment and small particles leads to significant changes in CO:CO<sub>2</sub> ratio
- Additional evidence of reaction regime change

# Appearance of POP Biochar Products

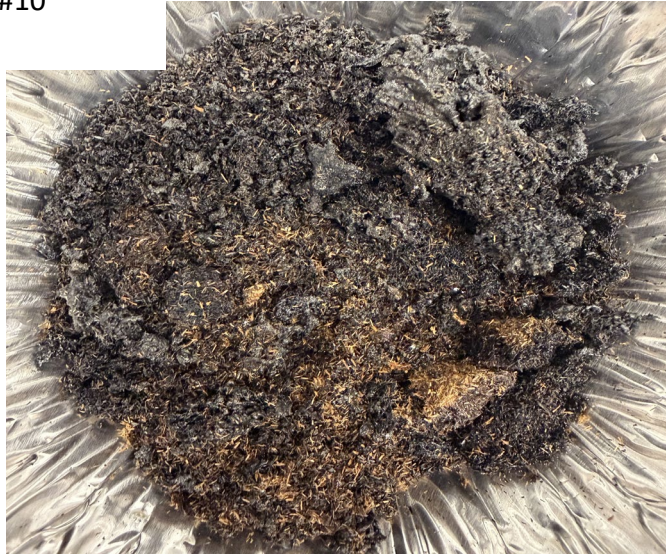
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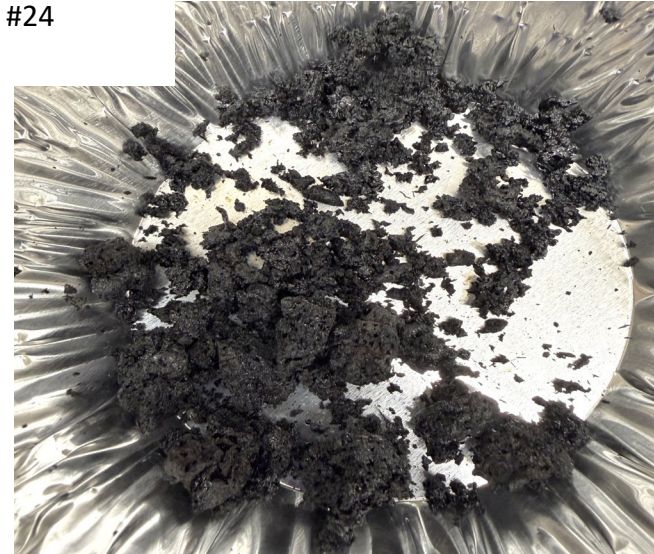
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#10



#24



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# Intense POP (0.2-0.5 mm O<sub>2</sub>) Calcination-Vitrification



900 °C (N<sub>2</sub>)  
5 °C/min



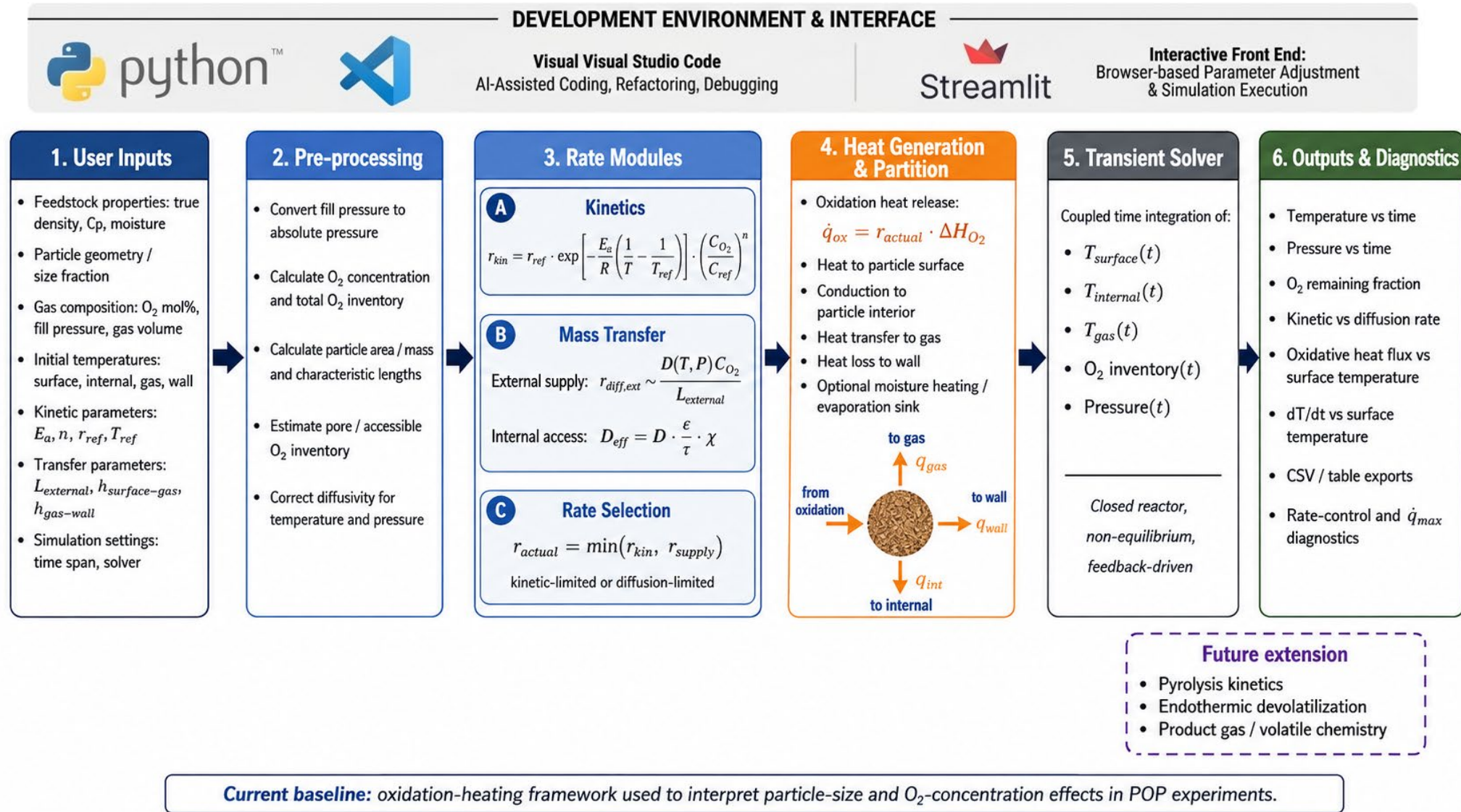
- Dense, shiny, ceramic feel (clinking sound)
- Clearly different thermal transformation than standard biochar

# Gas Physisorption Comparison

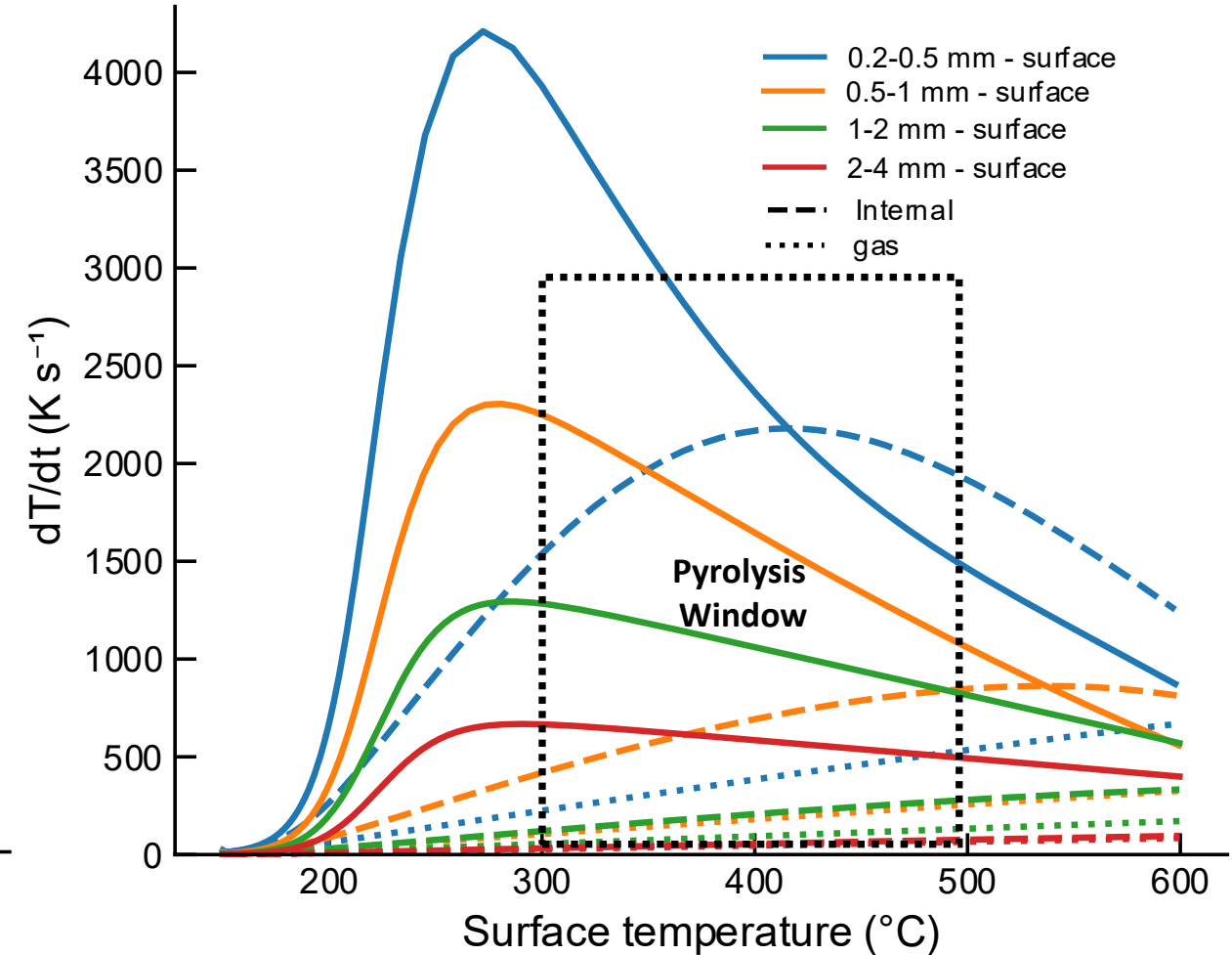
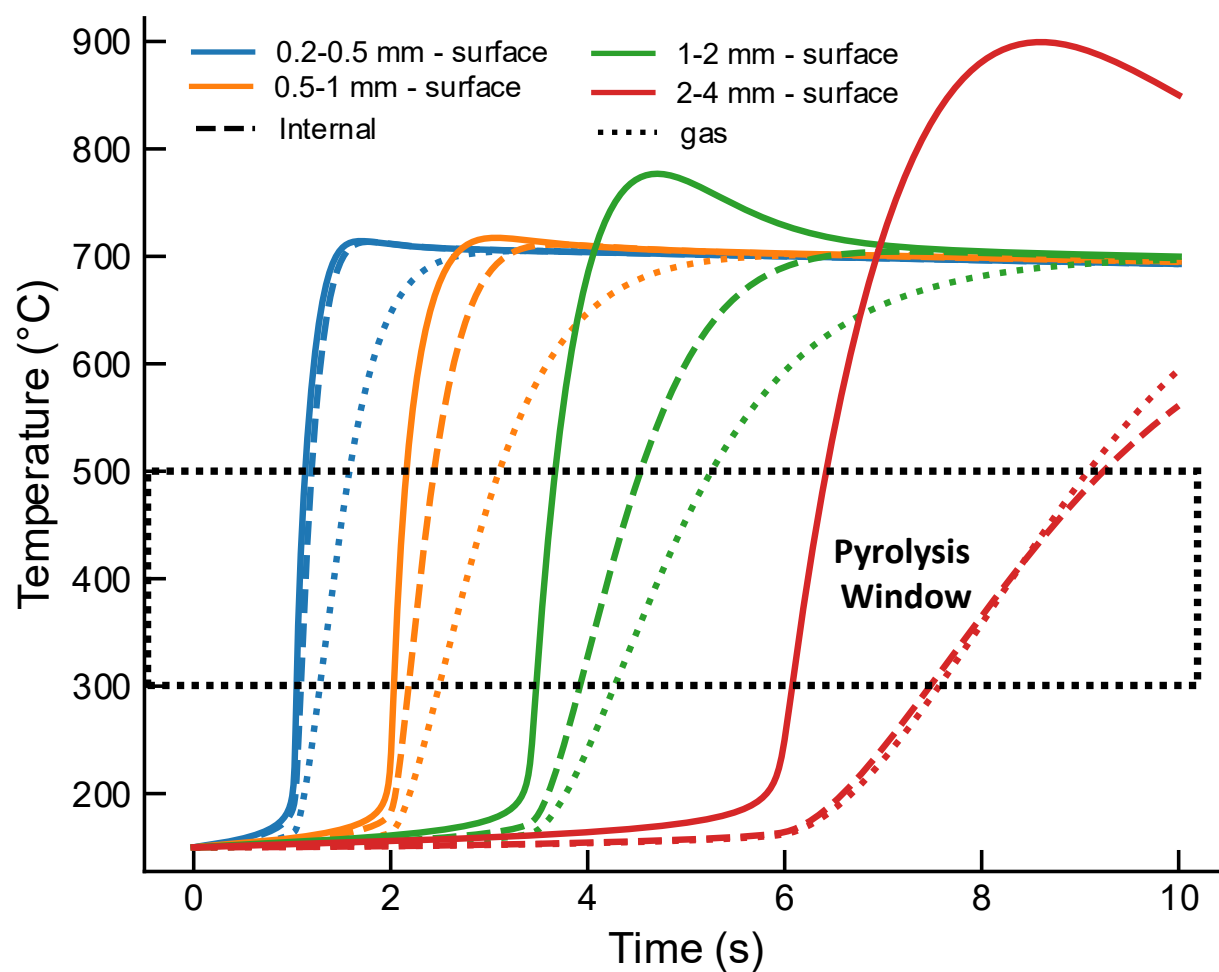
| Sample                               | N <sub>2</sub> surface area (m <sup>2</sup> /g) | CO <sub>2</sub> surface area (m <sup>2</sup> /g) | N <sub>2</sub> :CO <sub>2</sub> | Structural interpretation     |
|--------------------------------------|-------------------------------------------------|--------------------------------------------------|---------------------------------|-------------------------------|
| Spruce-direct                        | 377                                             | 231                                              | 1.6                             | Conventional biocarbon        |
| (2-4 mm O <sub>2</sub> enriched)     | 125.55                                          | 405.8                                            | 0.31                            | Microporous biocarbon         |
| (0.5-1 mm O <sub>2</sub> enriched)   | 69.64                                           | 349.6                                            | 0.2                             | Partially Vitrified biocarbon |
| (0.2-0.5 mm O <sub>2</sub> enriched) | 13.1                                            | 315.5                                            | 0.04                            | Vitrified biocarbon           |

- CO<sub>2</sub> physisorption: sensitive to pore < 7 Å diameter
- N<sub>2</sub> physisorption: underrepresents pores < 7 Å
- Intense POP results in **ultra-microporous** biocarbon

# Computational Simulation of POP Thermal Feedback

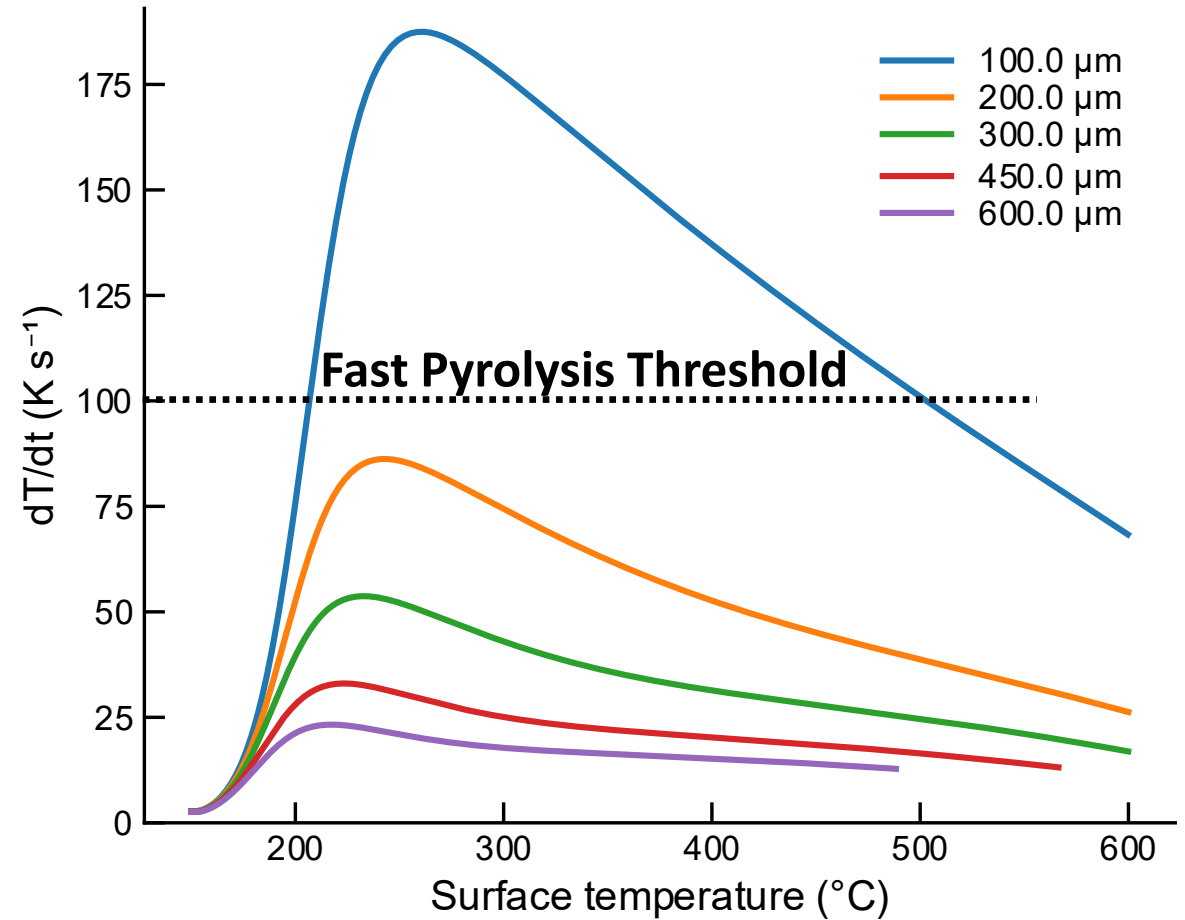
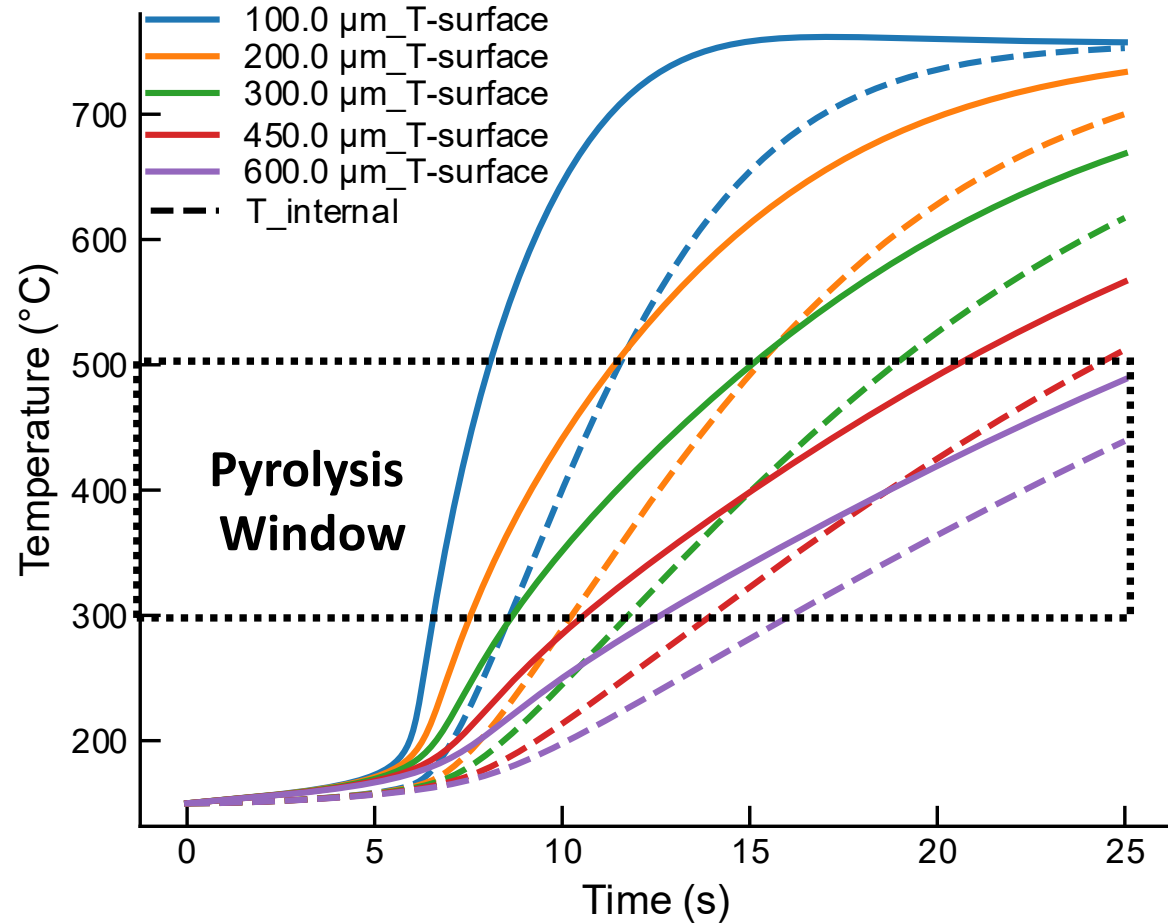


# Simulations of O<sub>2</sub>-Enriched Oxidative Heating



- Simulations with constant and aggressive external mass transfer effective layer = 30  $\mu\text{M}$
- Smallest particles likely closer to 20  $\mu\text{M}$
- Extremely high transient surface heating rates  $\gg 1000$   $^{\circ}\text{C/s}$

# Pressure Spike Requires Enhanced O<sub>2</sub> Transport (2-4 mm O<sub>2</sub>-Enriched)



- 600 μm approximates stagnant diffusion for 2–4 mm splinters
- Observed pressure spike requires faster surface heating
- Best-fit  $L_{ext} \approx 100\text{--}200\text{ }\mu\text{m}$ , implying  $Sh_{eff} \approx 3\text{--}6$
- Gas generation and pressure rise create reaction-driven pseudo-mixing
- This correction can guide  $L_{ext}$  estimates for smaller particles

# Conclusions:

- POP creates a rapid, low-temperature, autothermal thermochemical conversion regime.
- Rapid pressure excursions indicate coupled oxidative heating resulting in rapid volatile formation.
- Particle size shifts the reaction from distributed heating to intense whole particle conversion.
- O<sub>2</sub>-enrichment result in more uniform, highly converted precursors.
- Extreme POP simulations suggest heating rates in excess of 1000 °C/s
- Smoldering combustion reactions provide a new handle for engineering biomass-derived carbon.

# Acknowledgements

- Kyle & Christian Castillo



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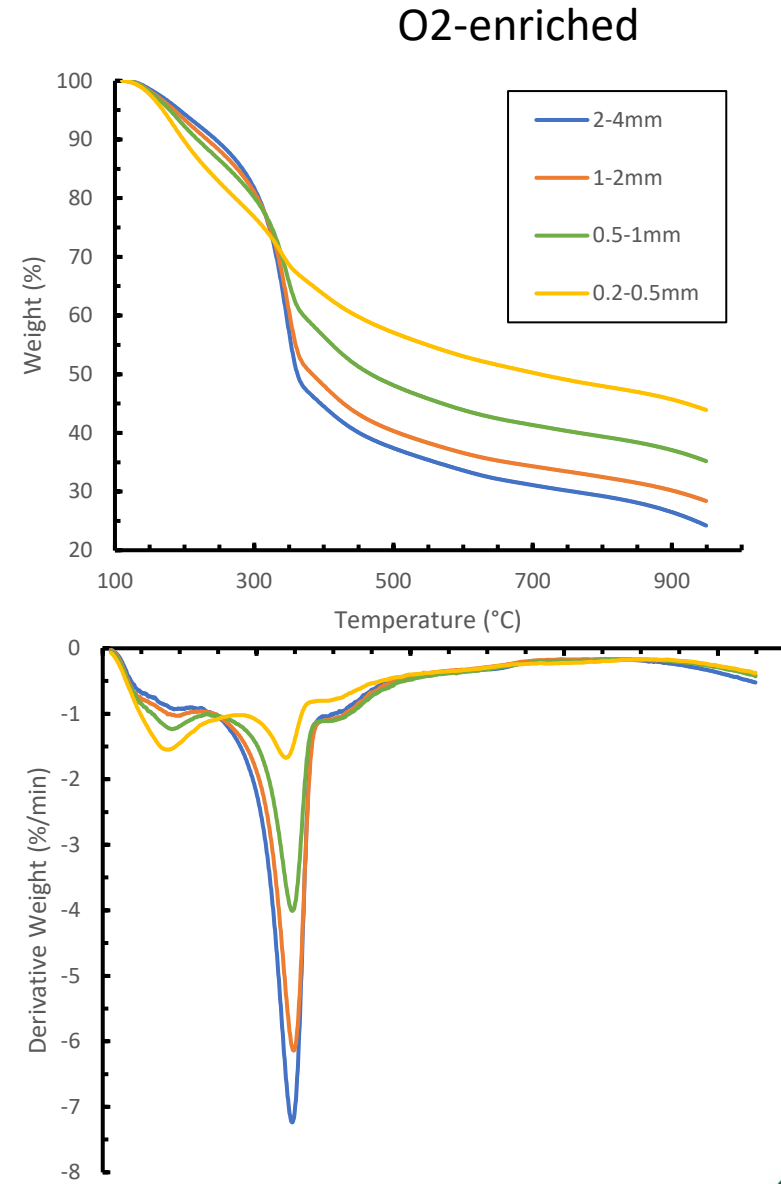
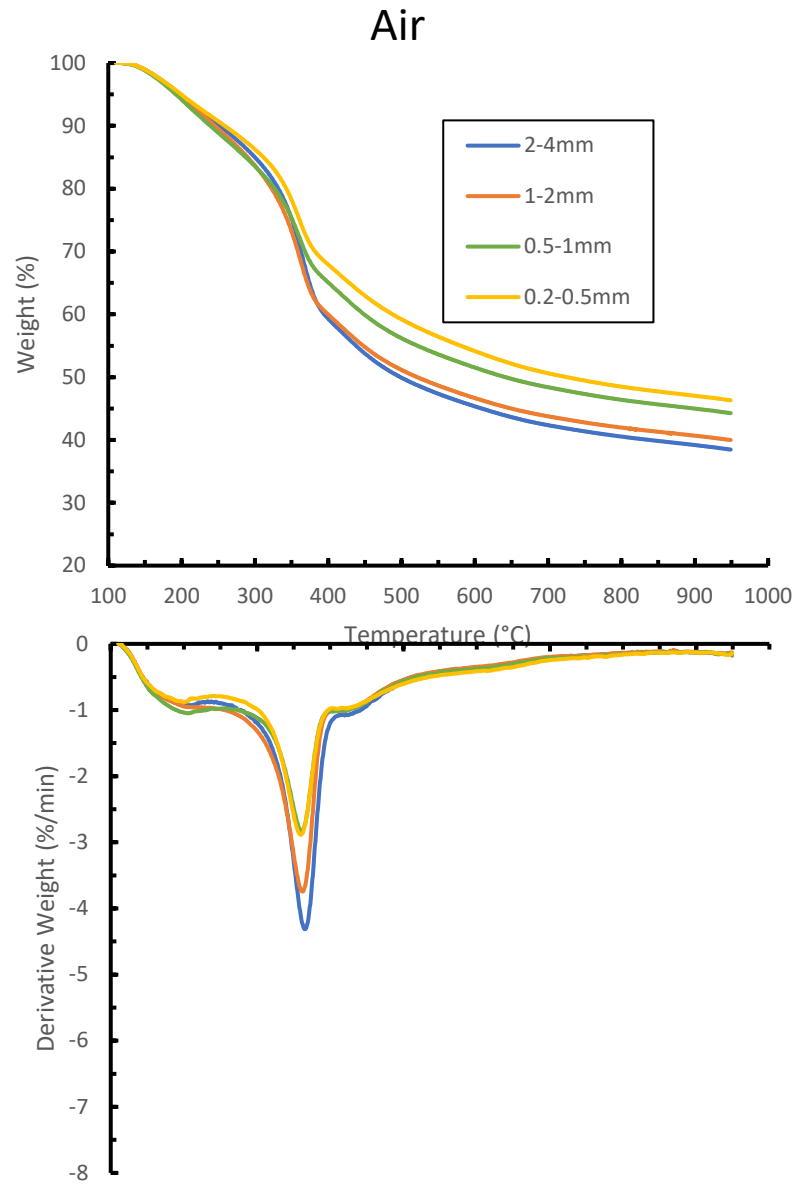
PREM

PARTNERSHIPS FOR RESEARCH  
AND EDUCATION IN MATERIALS

# Mahalo!

## Questions?

# TGA Analysis of Biochars



# Hypothesis to Explain POP

