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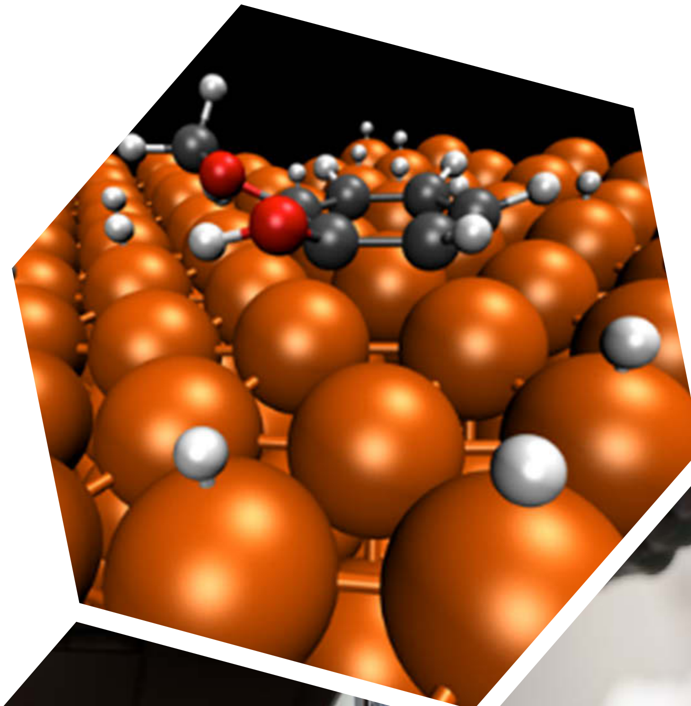
Chemical Catalysis for Bioenergy

Challenges for Scaling-up Biomass Catalytic Fast Pyrolysis Process Technology: A Case Study for Ex situ CFP in Fixed-bed Configuration

Calvin Mukarakate



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U.S. DEPARTMENT OF ENERGY | Office of ENERGY EFFICIENCY & RENEWABLE ENERGY
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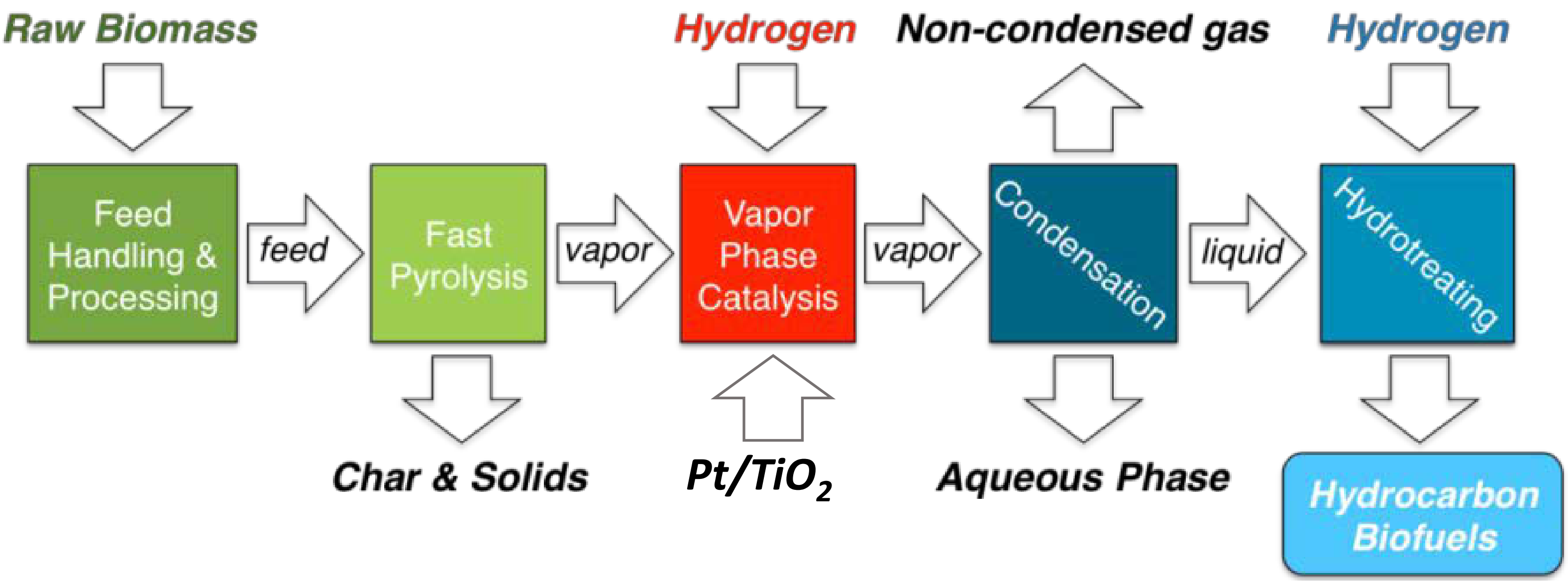
Catalytic Fast Pyrolysis Process: Background

CFP catalysts need to achieve extensive deoxygenation and high carbon yields

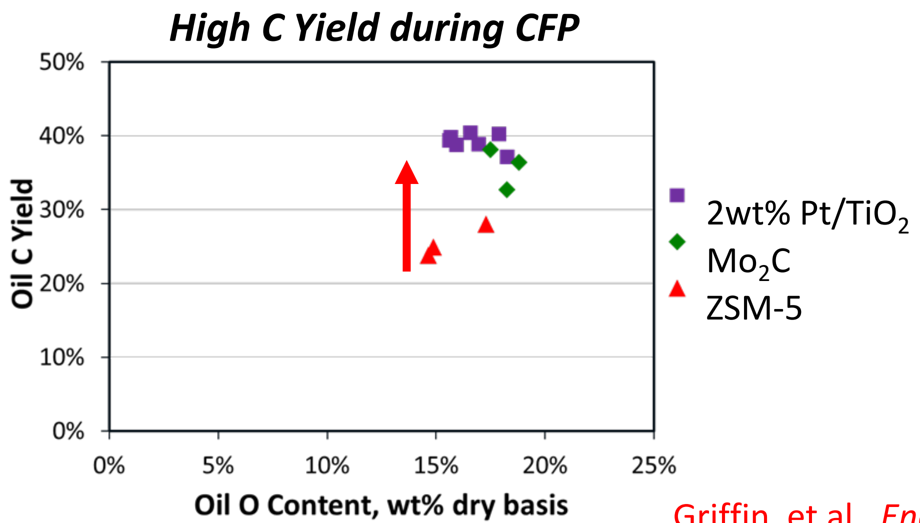


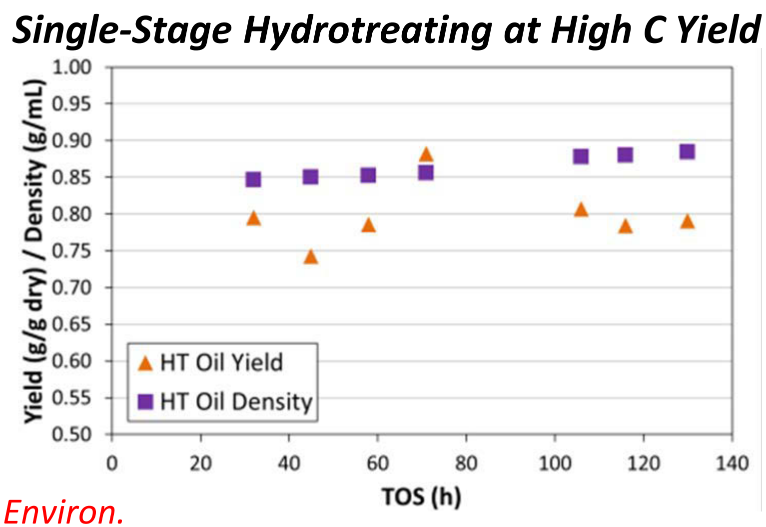
D. Ruddy. *Green Chemistry* **2014**, *16*, 454.

Carbon yield is a major economic driver for the integrated CFP-HT process

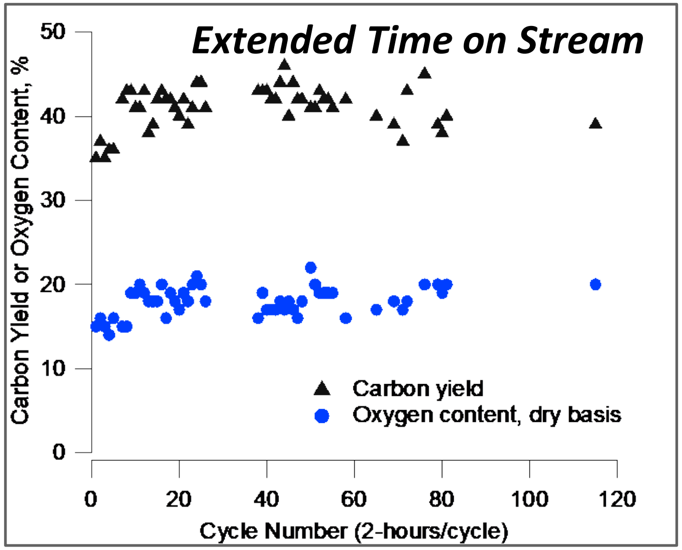
Ex situ Fixed-bed CFP: Summary

Demonstrated high carbon yield and catalyst regenerability, yielding a CFP oil that can be hydrotreated in a single-stage unit to <1wt% O





Griffin, et al., *Energy Environ. Sci.*, 2018, 11, 2904-2918

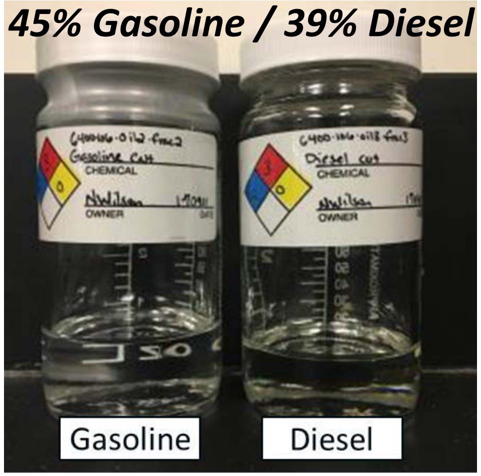


Pt/TiO$_2$

TOS: 2 hours (B:C 3)
Feed: Clean pine
Pyrolysis 500 °C,
Upgrading 400 °C

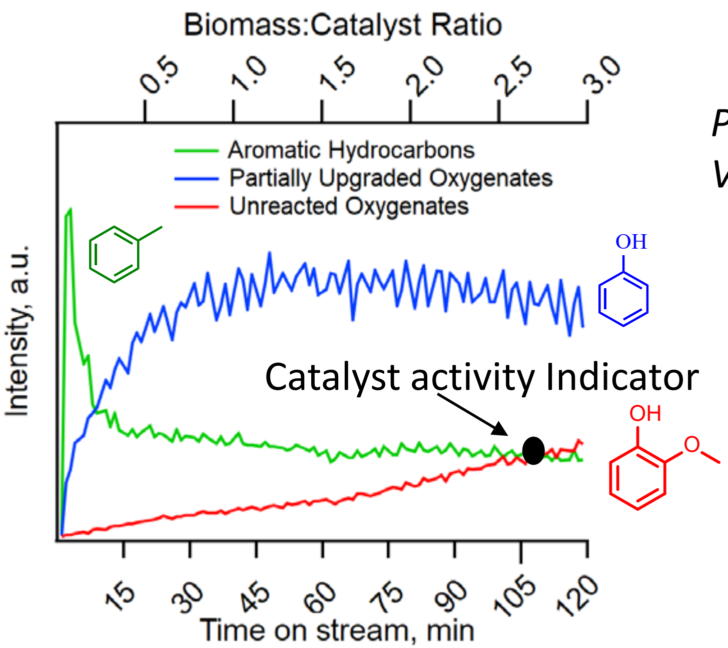
Blendstocks Production:

45% Gasoline / 39% Diesel



Ex-situ Fixed-Bed CFP Reactor Configuration

The CFP technology was optimized to an online-to-regeneration ratio of 0.4, which is equivalent to seven fixed-bed reactors

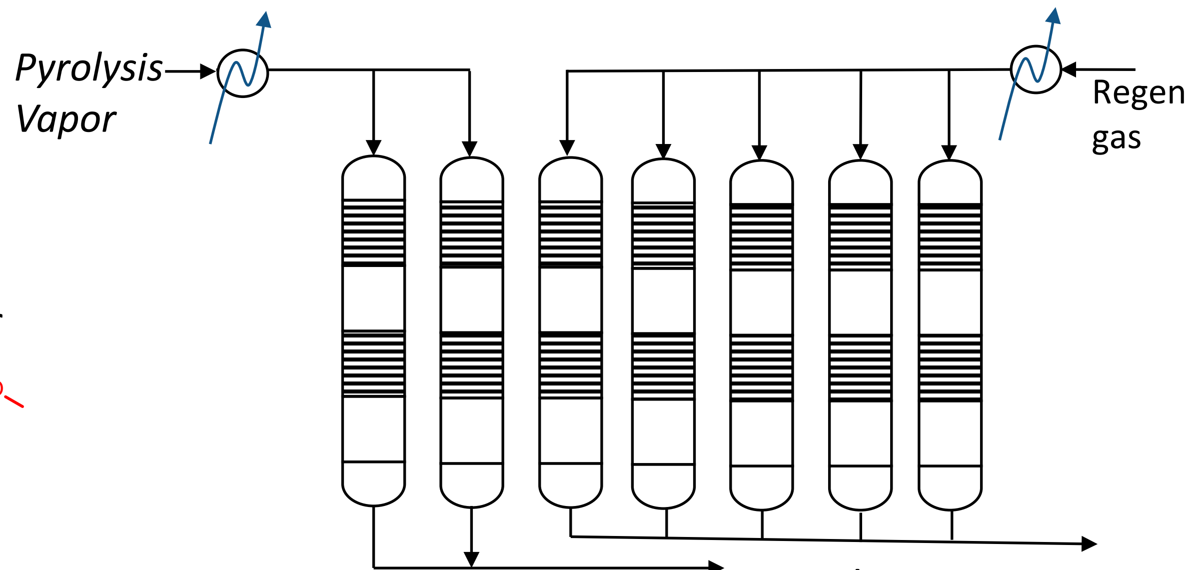


Time on stream: 2h

Regeneration: 5h

- Oxidation 3h and Reduction 2h

CFP Fixed-Bed Reactor Configuration



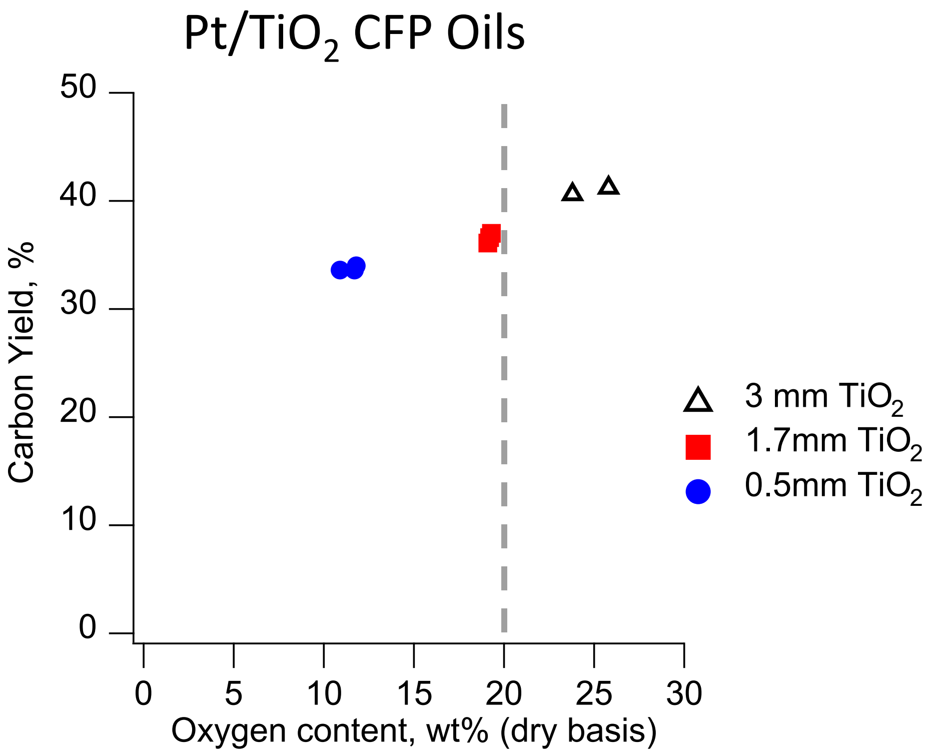
Online reactors/Regeneration reactors = 2/5

Approaches for cost reduction

- Reduce number of reactors (TOS↑ & Regen. Time↓)
- Low-cost feedstocks (e.g. forest residues)

Effect of TiO_2 Support on CFP Performance

Biomass vapor deoxygenation performance of Pt/TiO_2 improves with type and size of support



TOS: 2 hours (B:C 3)
Feed: Clean pine
Pyrolysis 500 °C, Upgrading 400 °C

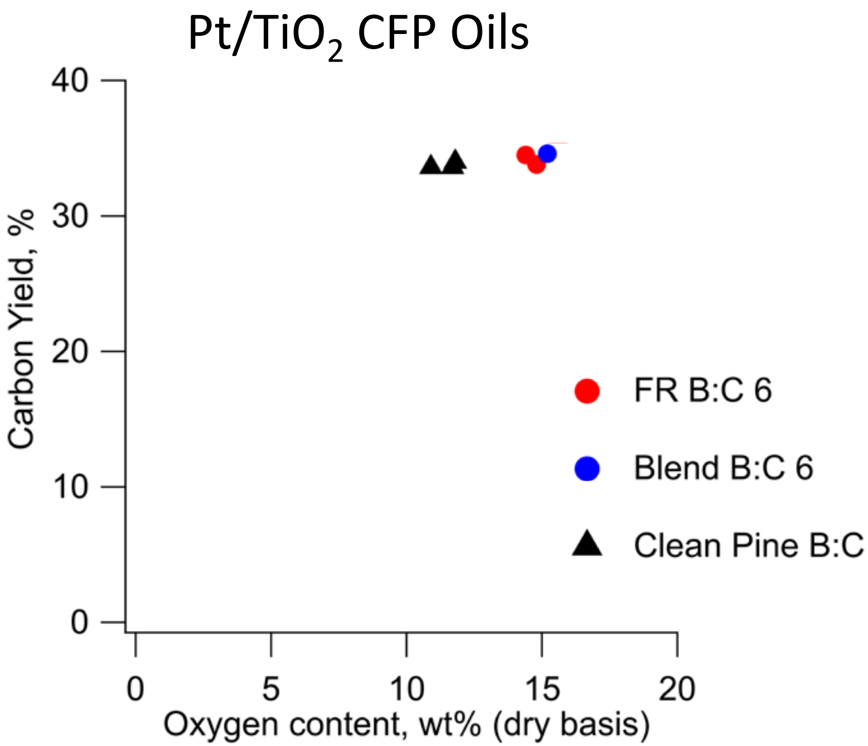
Carbon yield increase with oxygen content

- Challenges with single-stage hydrotreating
- Target O contents < 20 wt%

The 0.5mm TiO_2 support offers an opportunity to increase TOS

Feedstocks Screening Using 0.5mm TiO_2 Support

The 0.5mm TiO_2 support increased the CFP TOS by 600% and still produced oil with oxygen content < 20%



TOS: B:C 3 (2h) B:C 6 (4 h) B:C 12 (8h)

Feed: FR: Forest residue

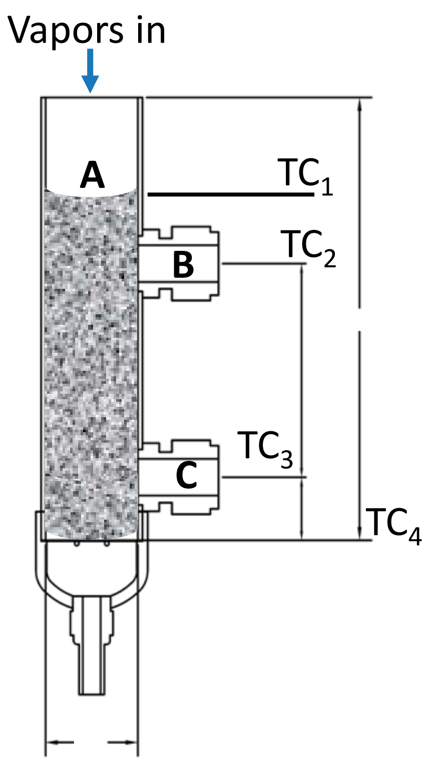
Blend: 50%CP and 50%FR

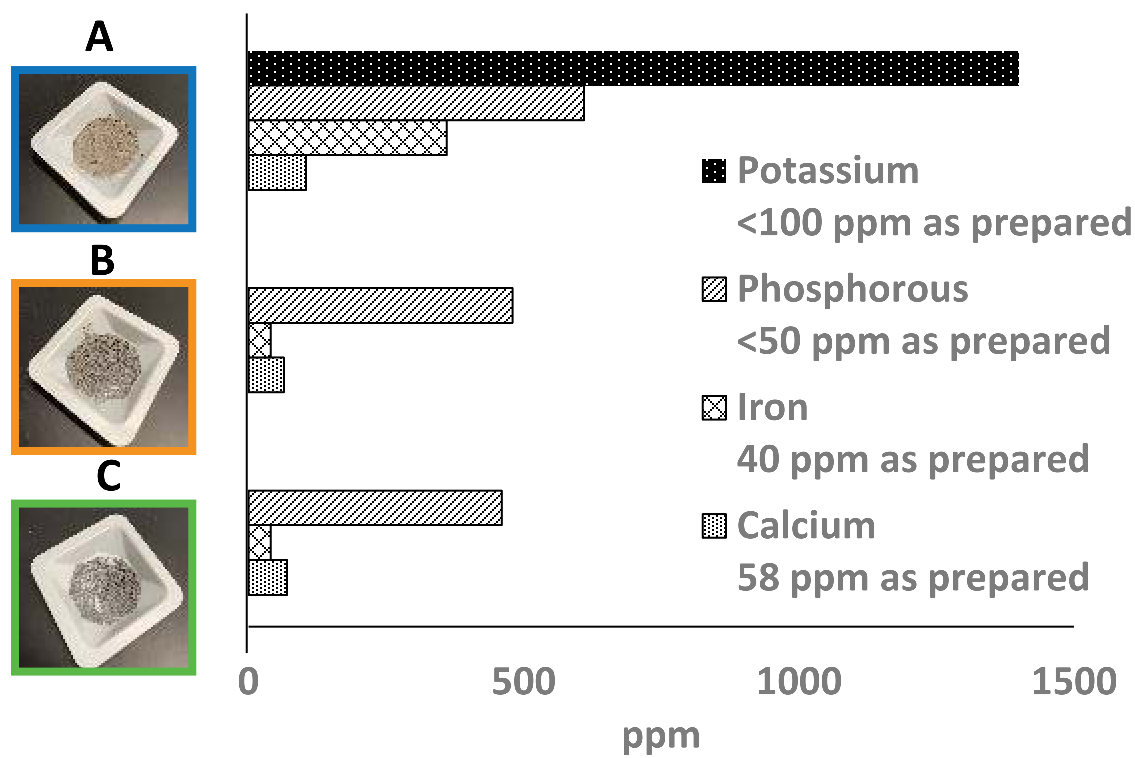
Pyrolysis 500 °C, Upgrading 400 °C

Process Challenges for Fixed-bed reactor: Pt/TiO_2

Irreversible deactivation of Pt/TiO_2 can occur if the catalyst is exposed to high temperatures: Pt sinters and TiO_2 changes phases

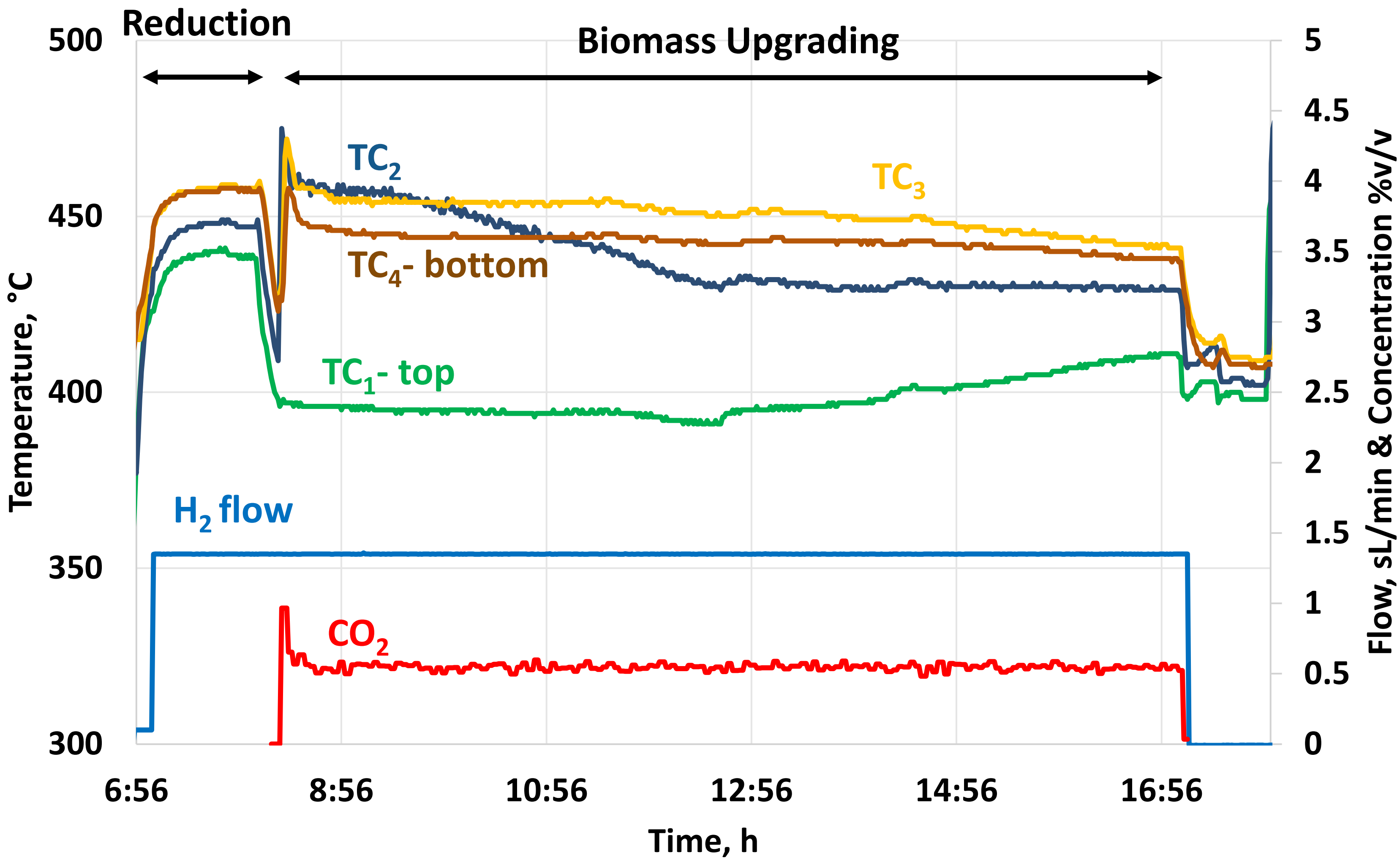
- The reactions for upgrading biomass vapors are exothermic
- Catalyst regeneration with oxygen is also exothermic
  - Irreversible deactivation
  - Fragmentation of the catalyst





Catalyst Bed Reduction and Biomass Upgrading Temps.

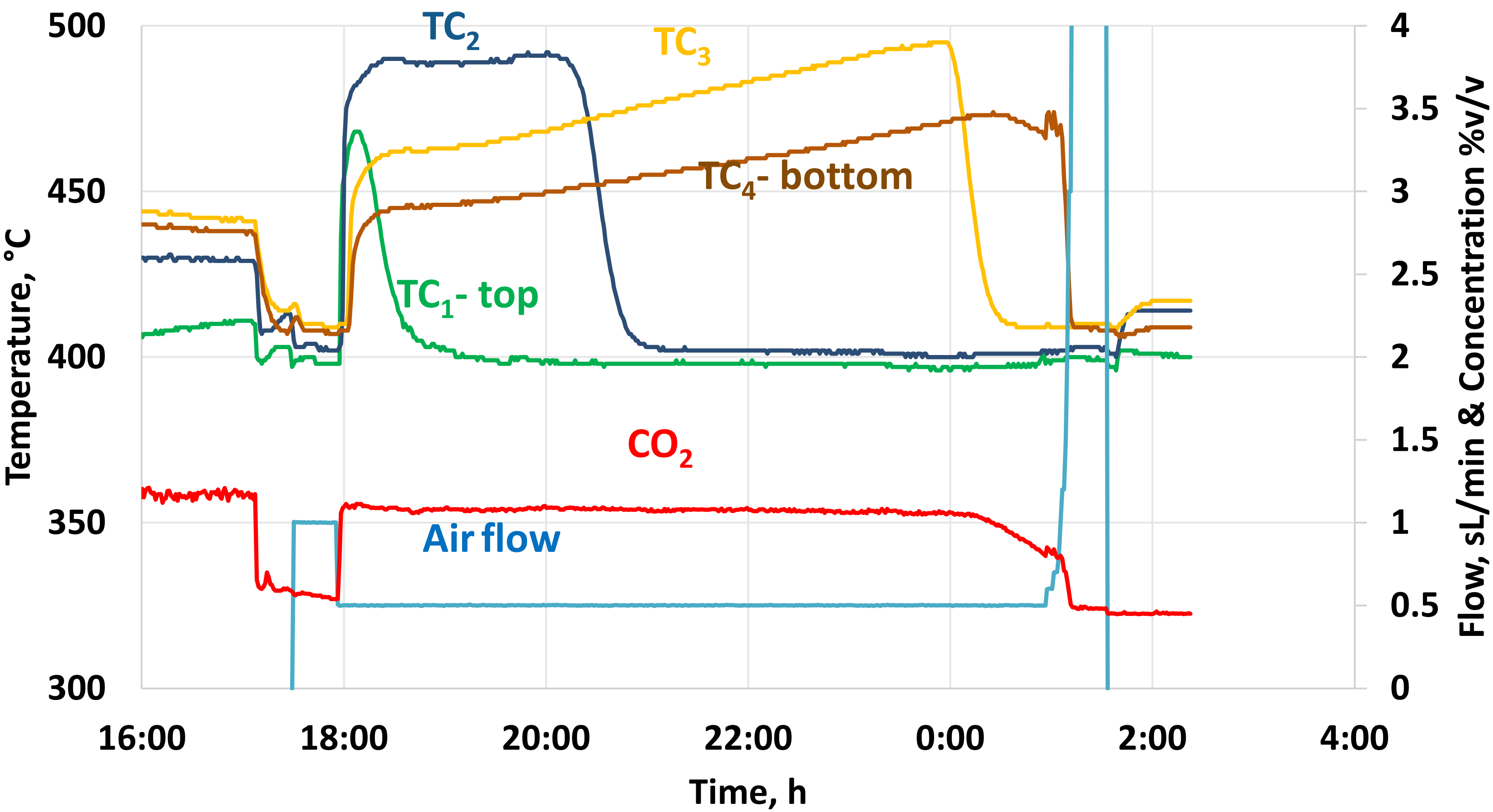
Furnace temperature is set to 450 °C during reduction and 400 °C during biomass upgrading



Catalyst pretreatment time = 1 h CFP run time/cycle ≈ 8-9

Catalyst Regeneration: Catalyst bed Temperatures

Coke burn-off begins at the bed top and continues down the catalyst bed

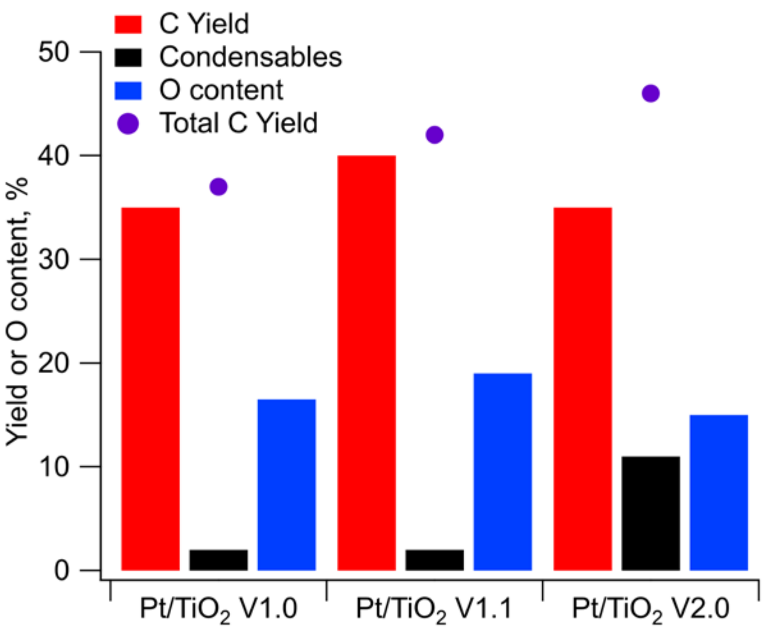


Furnace set to 400 °C

Total oxidation time ≈ 9

Pt/TiO_2 CFP Summary

The cost for CFP using a fixed-bed approach has been reduced by 19% in the last two years using TEA guided research



Pt/TiO_2	V1.0	V1.1	V2.0
CFP C balance (%)	87	88	100
HT eff.	91	89	95
Fuel Blendstocks C Yield (%)	33	36	33
Co-product credit, $/GGE*	-	-	0.52
MFSP, $/GGE	4.09	3.80	3.33
Cost reduction (vs. 2017), %	-	7%	19%

Abhijit Dutta, et al. 2019. *Ex Situ CFP 2019 State of Technology and Future Research*. NREL/TP-5100-76269.

What does this mean for scaling up the CFP fixed-bed Technology with the 0.5 mm TiO_2 support?

*Tune in to the next presentation by **Bruce Adkins**, for more information.*

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