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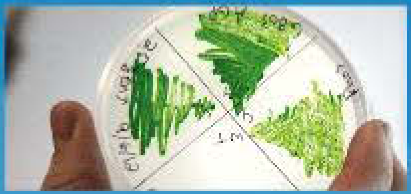



Catalytic Upgrading of Biomass Pyrolysis Vapors at Bench Scale with Platinum on Titania

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Scott Palmer, Matt Fowler, and Calvin Mukarakate

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NREL/PR-5100-74670

Overview

- Status of and motivations for upgrading biomass pyrolysis vapors to fuel intermediates with Pt/TiO_2 and H_2
- Progress in reducing process cost
  - Reducing catalyst cost
  - Reducing regeneration time
  - Varying upgrading parameters
  - Catalyst lifetime
  - Changing pyrolysis temperature
- Constraints
  - Not increase oxygen in oil
  - Not increase hydrotreating requirements
  - Not decrease yield

Why Pt/TiO2 catalytic fast pyrolysis and hydrotreating?

- Monday talk (C. Mukarakate, “Performance Comparison of three Biomass Catalytic Fast Pyrolysis Pathways…”) and Griffin et al. paper (below)
  - **Hydrotreating** (HT) of **Catalytic fast pyrolysis oils** (CFP) is **lower cost and more reliable** than hydrotreating of raw pyrolysis oil
  - **CFP with Pt/TiO_2 and hydrogen gives higher yield** (and carbon yield) than ZSM-5 upgrading
    - Some HDO of oxygenates means less carbon lost as CO_x
    - Hydrogenation of coke precursors reduces carbon lost to coke

	Carbon Yield	Oxygen content
[1]Pt/TiO_2	38%	16%
[2]HZSM5	24%	22%

1. Griffin et al. E&ES, 2018, DOI: 10.1039/c8ee01872c
2. Paasikallio et al. Grn. Chem. 2014, 16, 3549

CFP process

- **OIL PRODUCTION**

BIOMASS → **PYROLYSIS** → **CATALYTIC UPGRADING** → **AQUEOUS** / **OIL**

- Pine

- 500°C
- 0.8 bar H_2
- 1.0 bar total

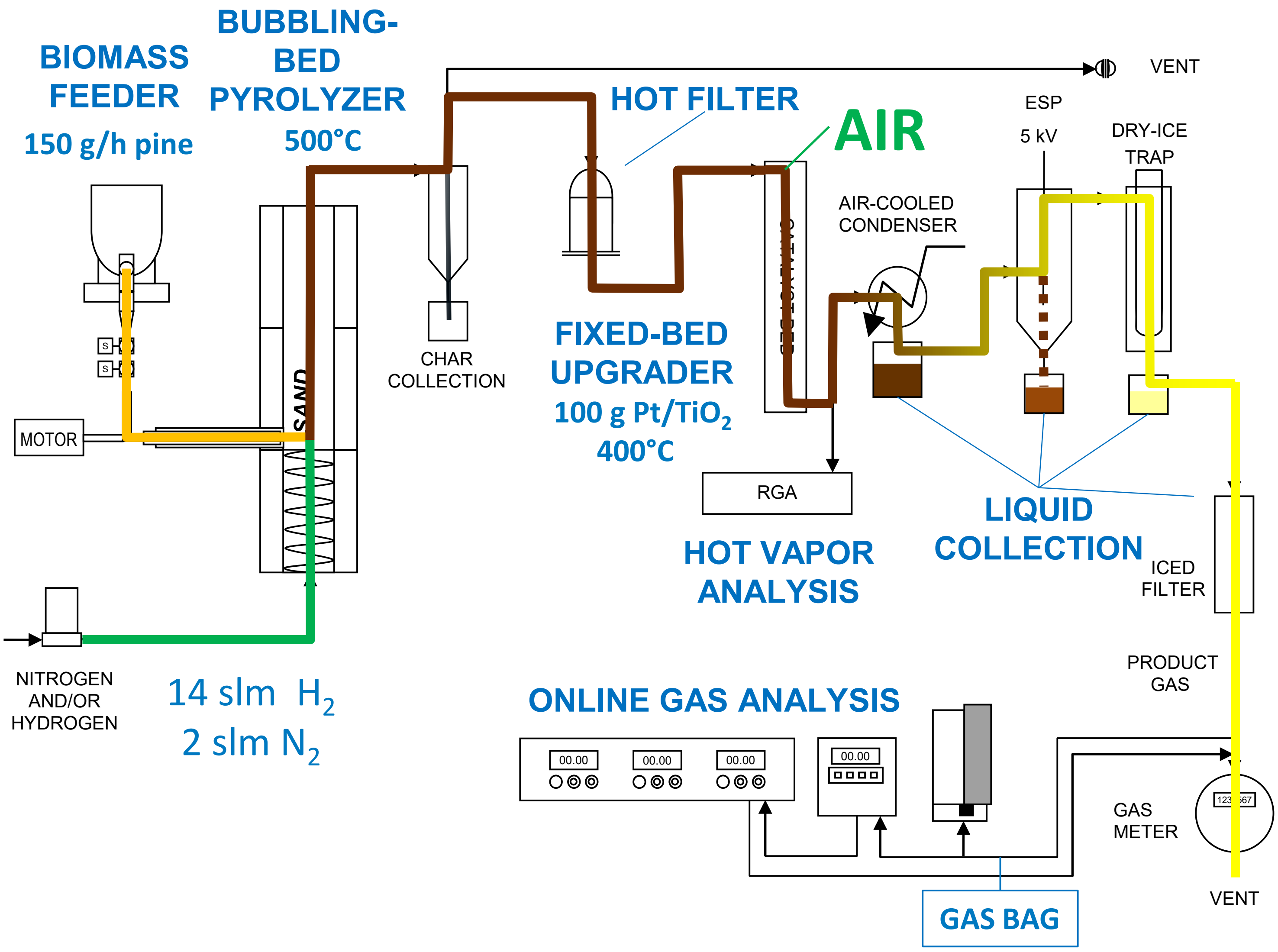
- Pt/TiO_2
- Fixed bed
- 400°C

OIL ↓ HYDROTREAT (HT) AND BLEND TO FUEL

- **REGENERATION OF FIXED-BED CATALYST**

USED Pt/TiO_2 → **OXIDIZE O_2 /N_2 3 h** → **REDUCE IN H_2 2 h**

Experimental System



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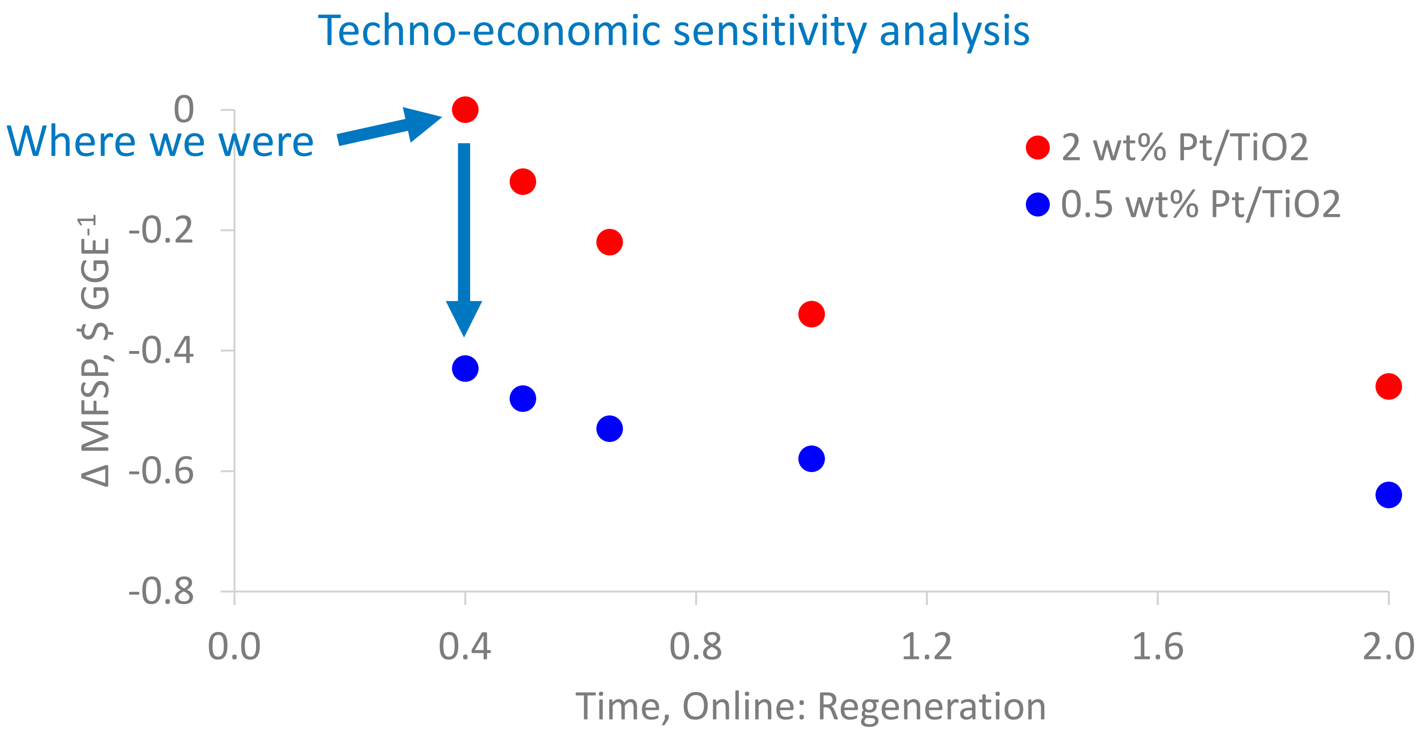
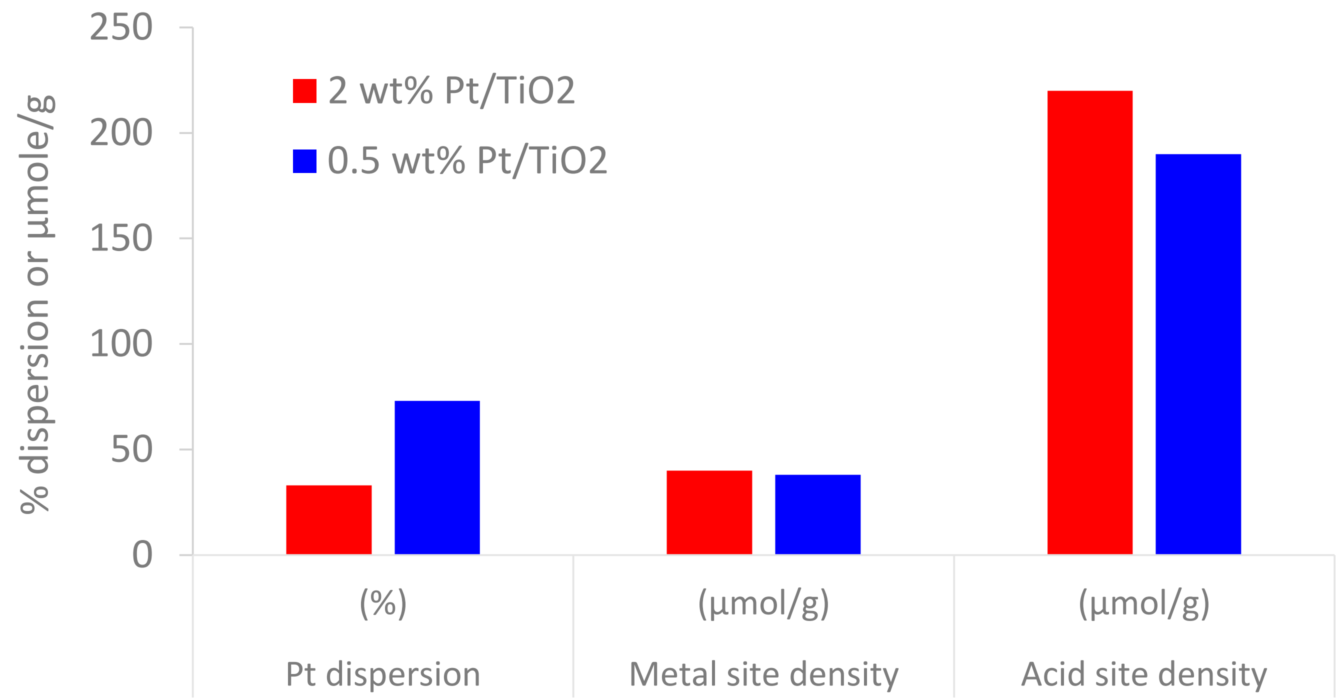
Process cost is sensitive to catalyst cost



- Need to decrease platinum while maintaining performance

Adapted from Griffin et al. E&ES, 2018, DOI: 10.1039/c8ee01872c

Can a lower Pt (cost) catalyst work? Catalyst properties



- 2% Pt made by incipient wetness
- 0.5% Pt by strong electrostatic adsorption (SEA)
- Higher dispersion of Pt on 0.5% makes properties of two catalysts very similar

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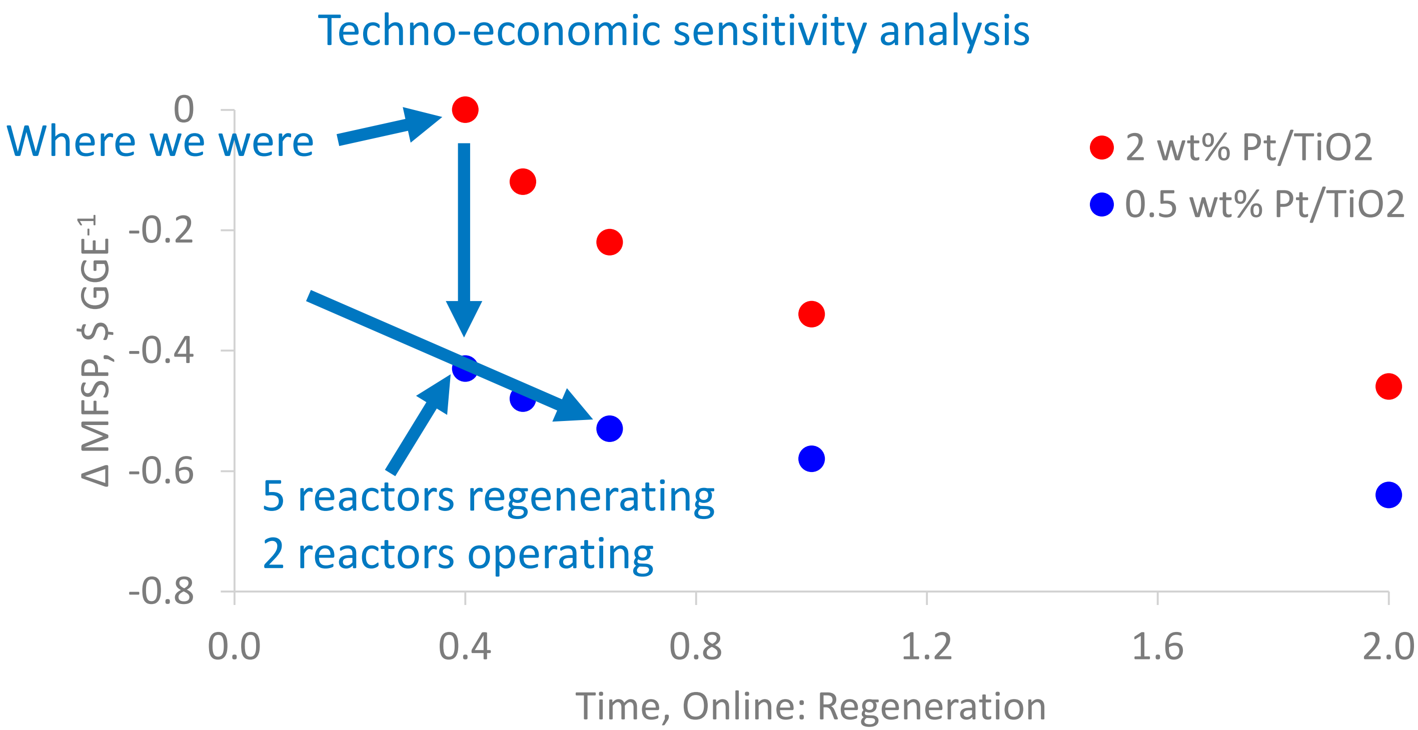
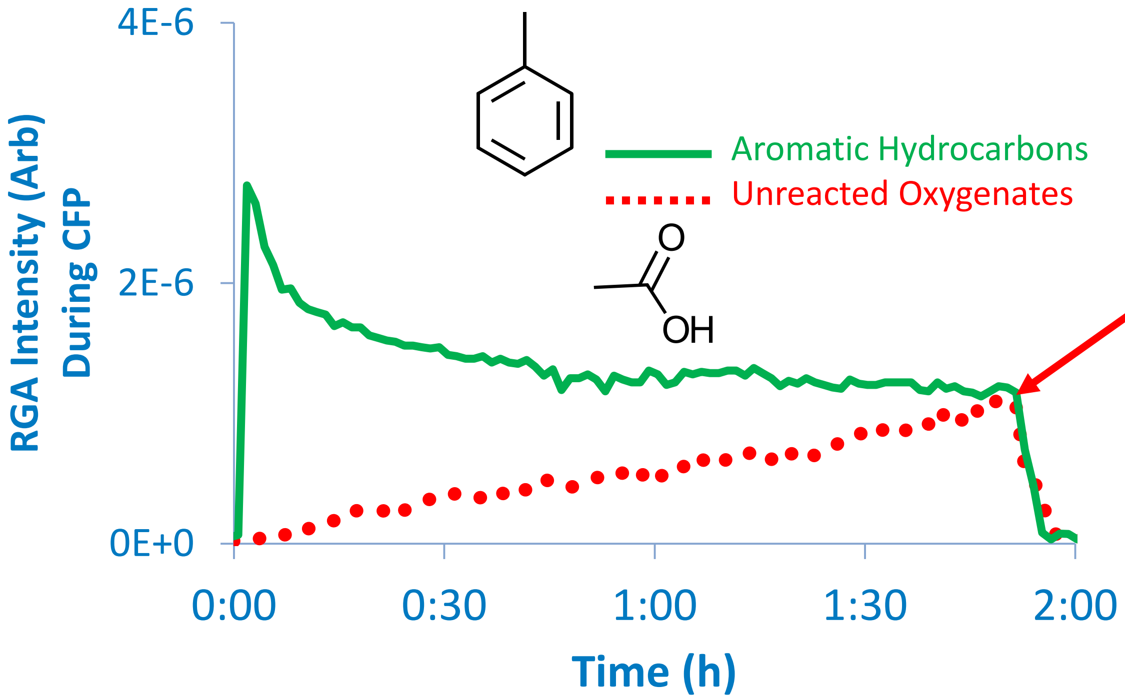


- Increasing online : regeneration time reduces number of reactors and catalyst inventory

Adapted from Griffin et al. E&ES, 2018, DOI: 10.1039/c8ee01872c

When is regeneration necessary?

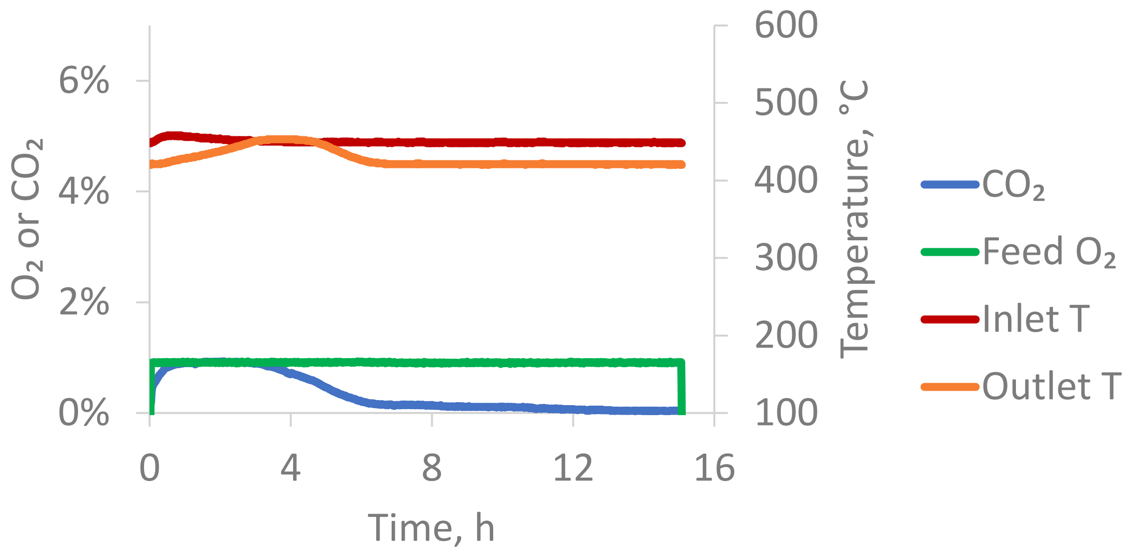


Biomass-to-catalyst (B:C) = 3

Gives 16-20% O, max. for good HT

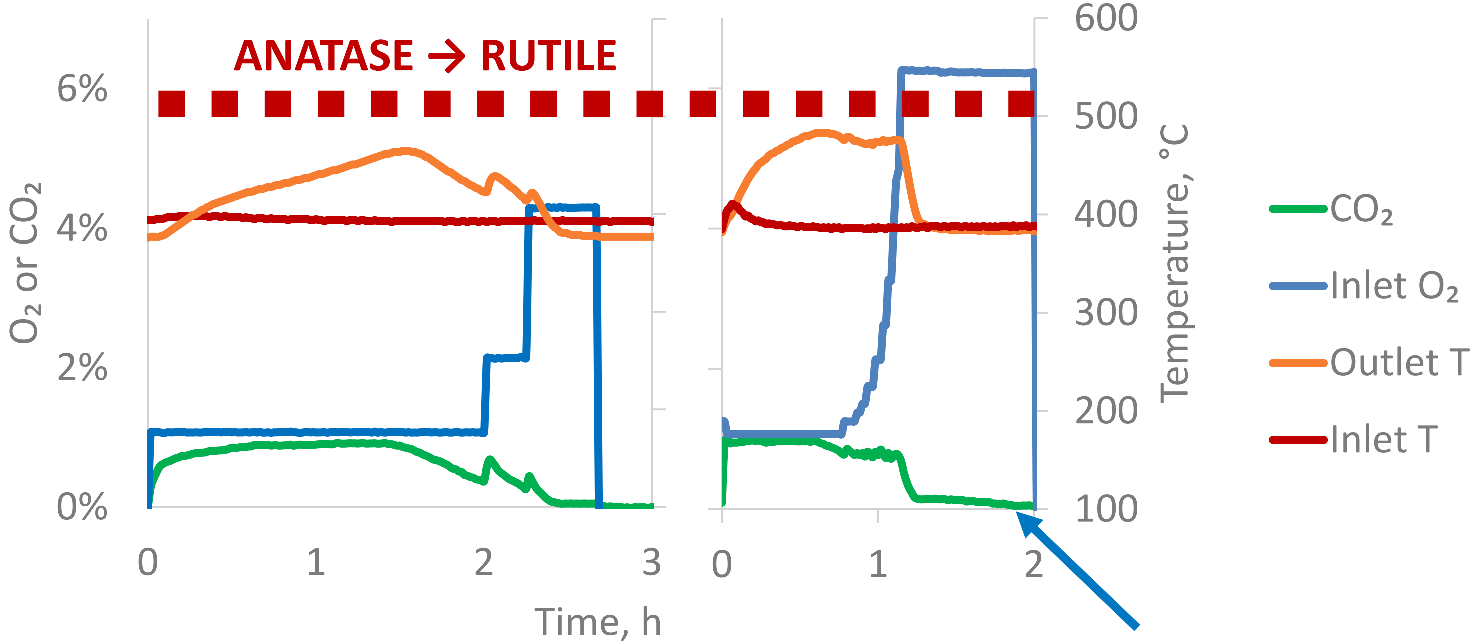
Regeneration Protocols

- Remove coke → oxidize in O_2/N_2 mixture
  - overnight in 1% O_2/99% N_2 at 450°C



- Reactivate catalyst → treat in H_2
  - 2+ h with 85% H_2/15% N_2
- Overall 17 h

Shorter regenerations achieved



- Catalyst oxidation shown above
- Also, Reduction time reduced to ~1h in 85% H_2
- Online: regeneration 2:3 (0.66)

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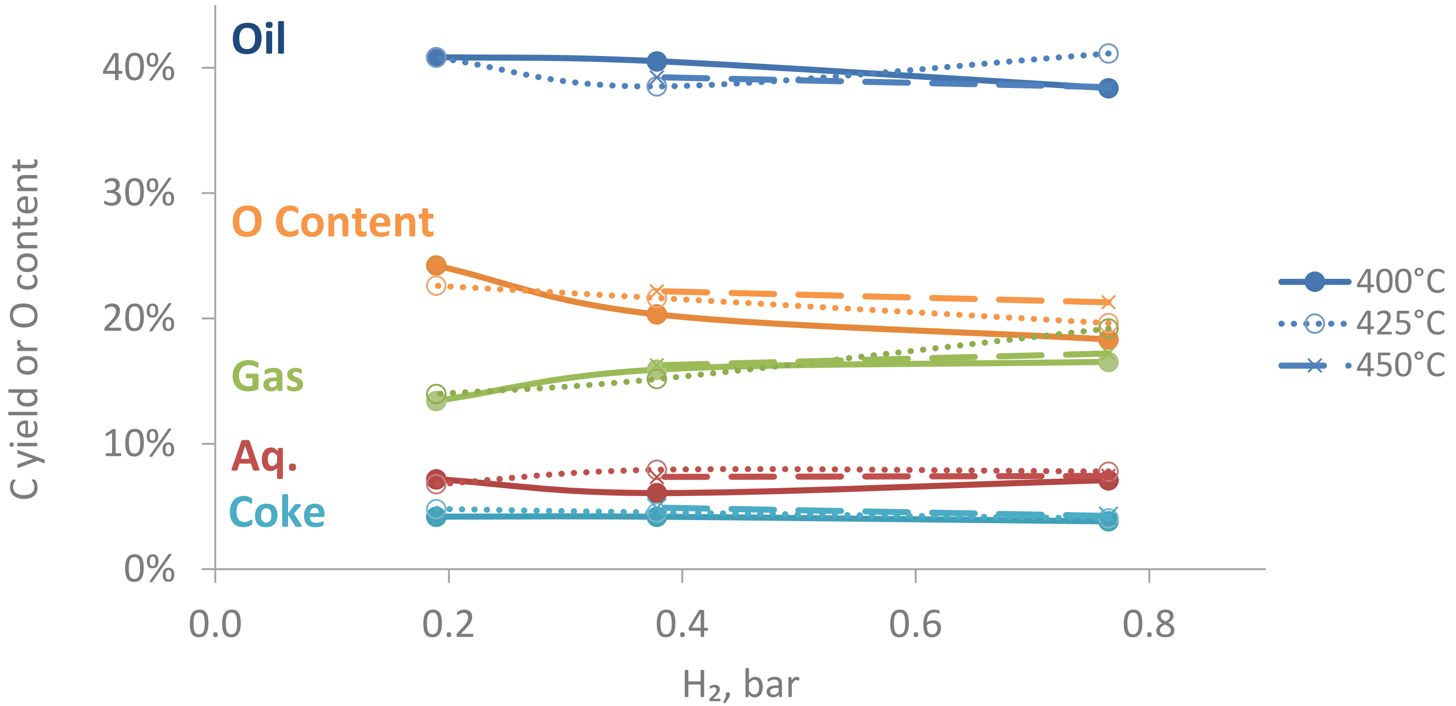
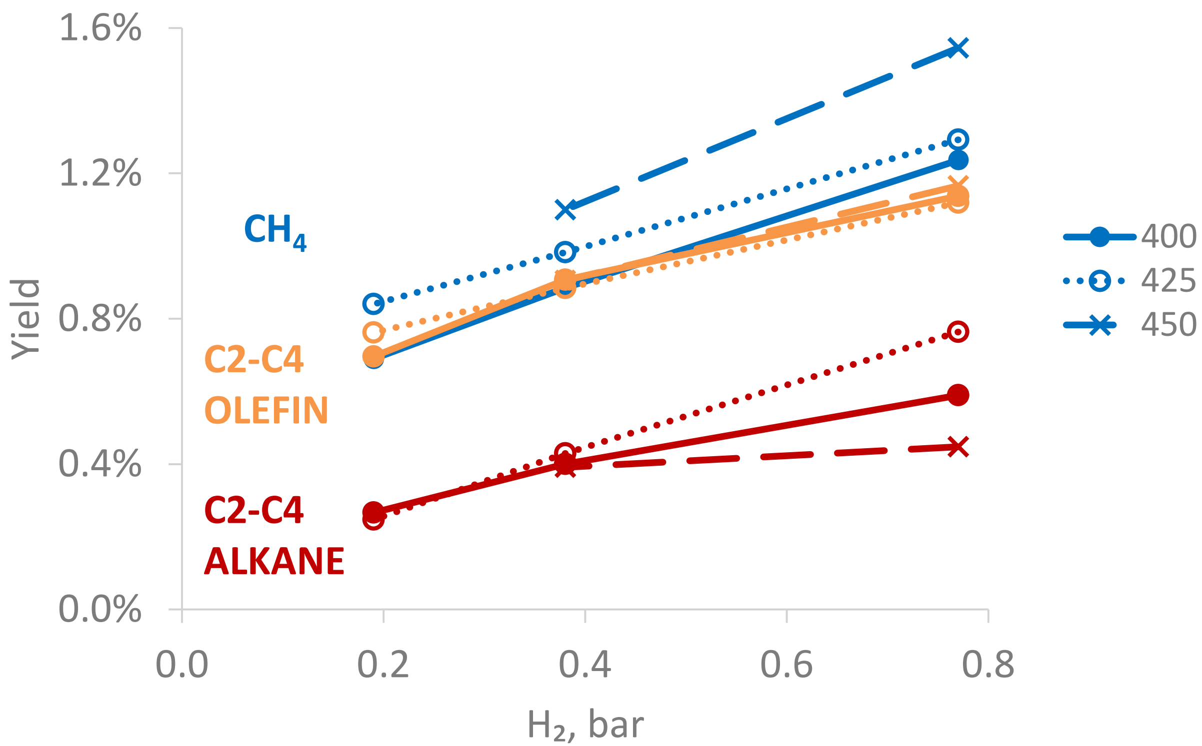
Varying hydrogen partial pressure and catalyst temp.



- Temperature effects are not significant
- Increasing hydrogen partial pressure
  - Decreases oil oxygen content
  - Increases gas yield
  - Enhances hydrodeoxygenation

Impact of H_2 Partial Pressure on Gas Yields

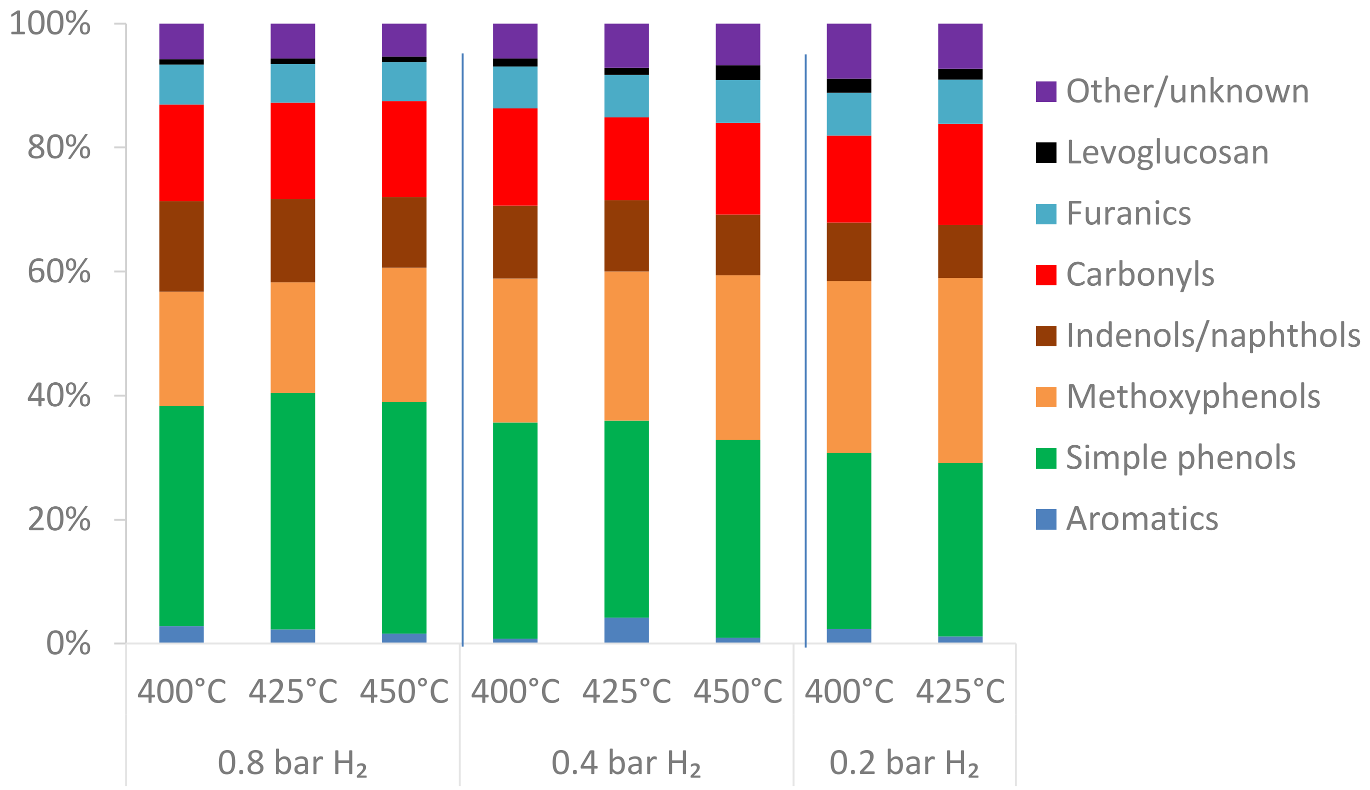


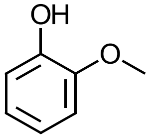
Increasing H_2 partial pressure

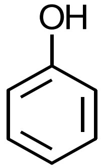
- Increases CH_4 and light alkane and alkene formation (increased cracking)
- Increases aqueous mass yield

Consistent with increased hydrodeoxygenation (HDO)

GC/MS composition changes with H_2 partial pressure & T_{cat}







- As H_2 decreases, more methoxyphenols, less alkylphenol/phenol

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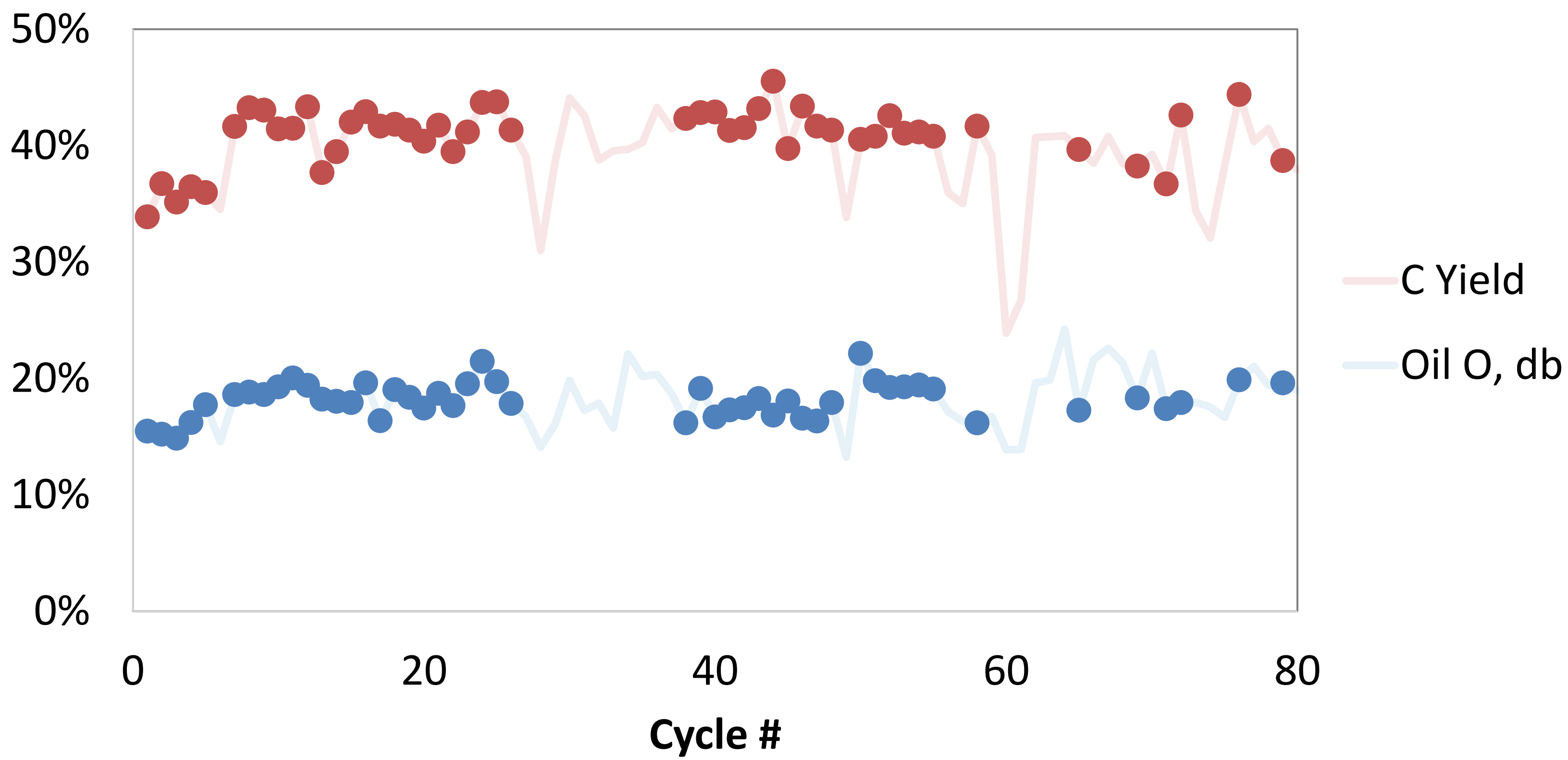
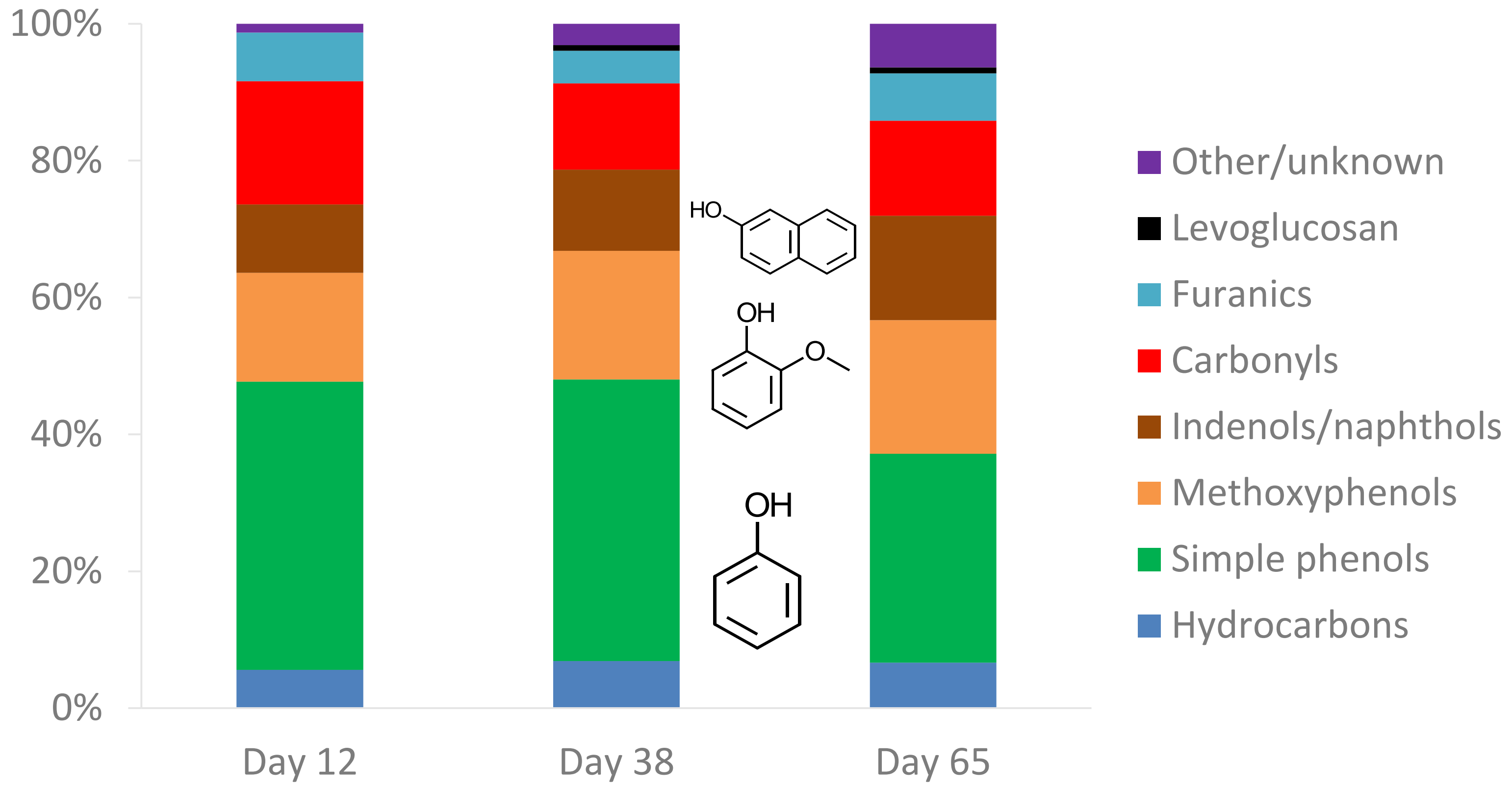
Catalyst stable past 150 hours



- Highlighted points are Pine/500C/400C/0.8 bar H_2/ B:C = 3
- Each cycle is 2 h
- Stable after initial break-in

Only slight variations in composition with catalyst aging



- Slight decrease in phenols, increase in methoxyphenols and naphthols

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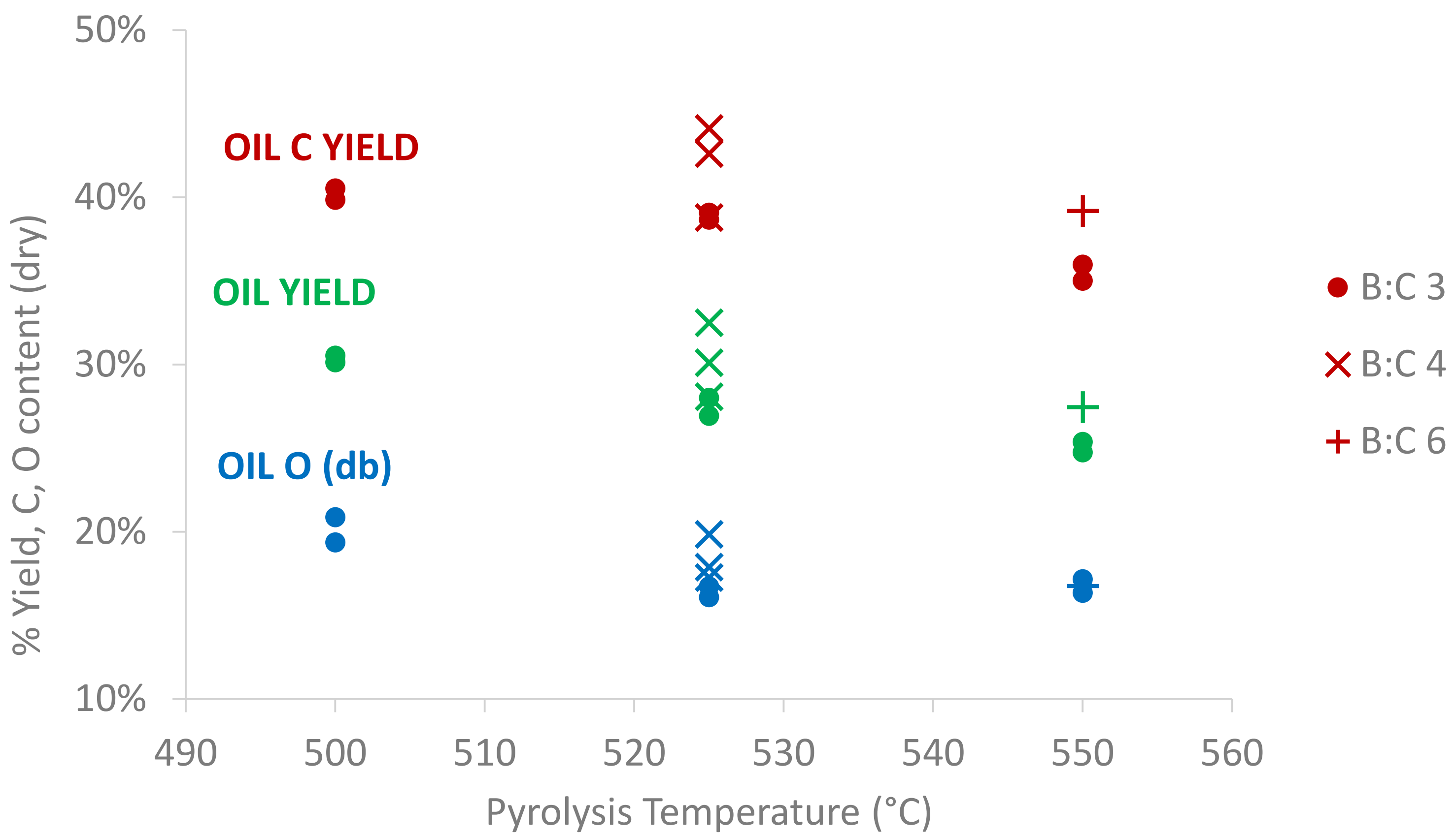
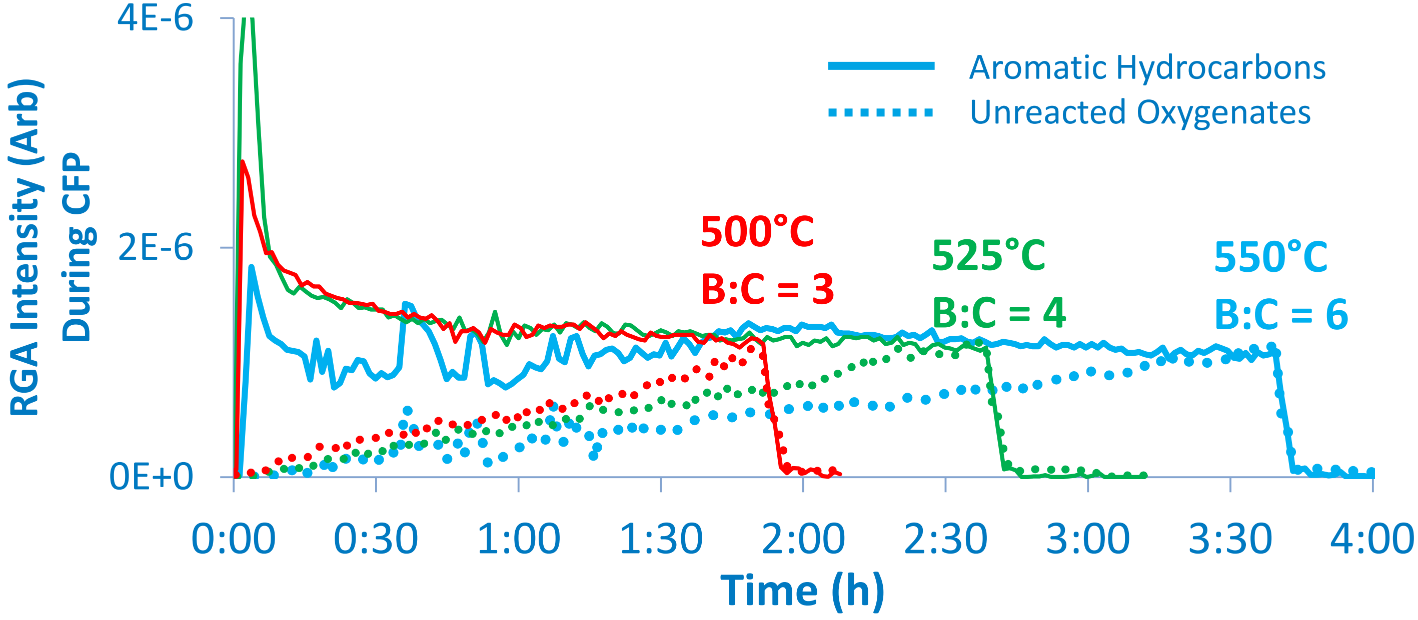
Higher pyrolysis temperature gives higher B:C at low O



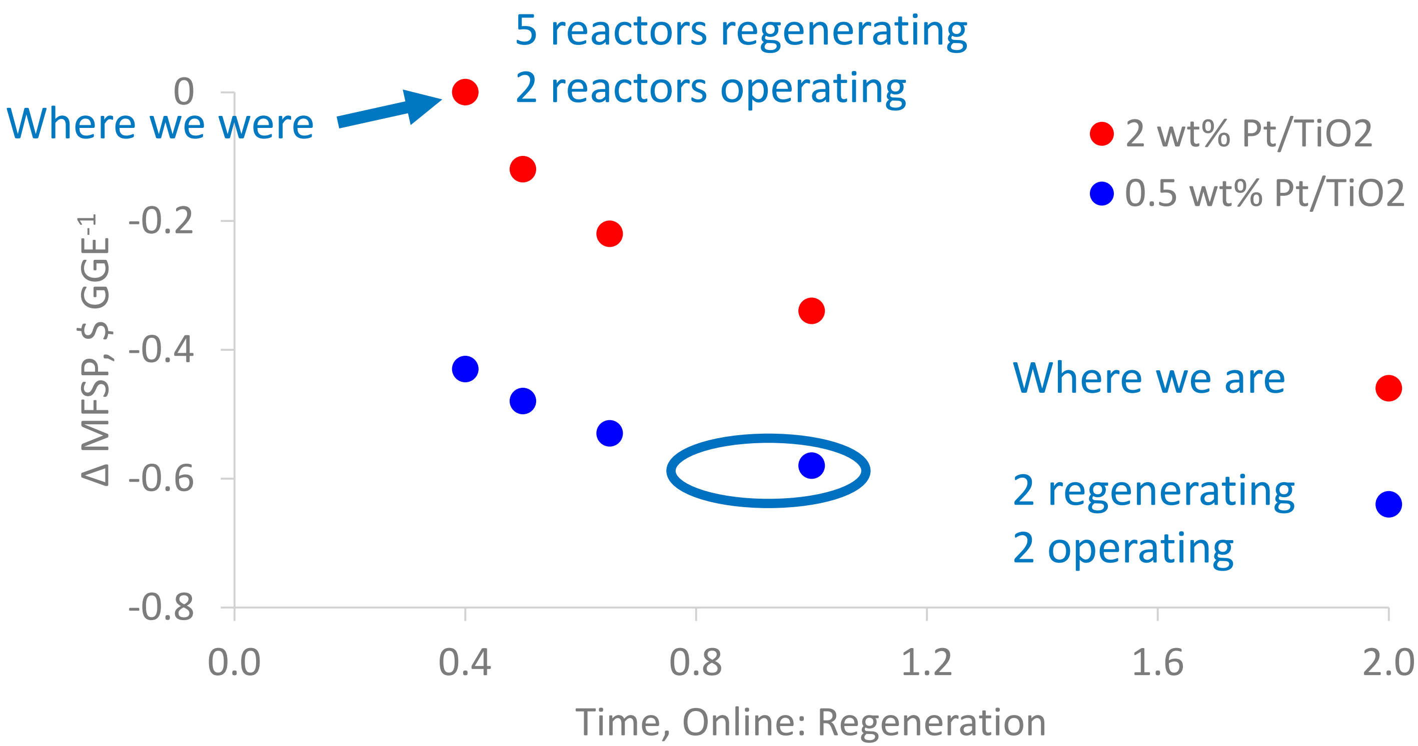
- Potential for even higher biomass: catalyst than shown

Higher pyrolysis temperature delays breakthrough



- Delayed onset of unreacted oxygenates
- Gives onstream: regeneration time of 0.75-1.1 by giving longer onstream time

Summary: How much progress have we made?



- Have improved cost substantially

Adapted from Griffin et al. E&ES, 2018, DOI: 10.1039/c8ee01872c

Conclusions& Future

- Conclusions
  - Lower-Pt catalyst performs comparably to higher-Pt catalyst
  - Regeneration shortening improves projected cycle time
  - Increasing hydrogen pressure decreases oxygen and methoxyphenols, increases phenols
  - Increasing pyrolysis temperature 500-550°C delays catalyst deactivation while giving comparable yield and oxygen, increasing time-on-stream

- Future:
  - Decrease catalyst cost
  - Higher B:C through higher pyrolysis temperature
  - Identify bad actors in pyrolysis oil
  - Lower-cost feedstock

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Questions?

Thank you!

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