(Progress toward) The Continuous-Flow Solid Acid Catalyst Hydrothermal Biorefinery

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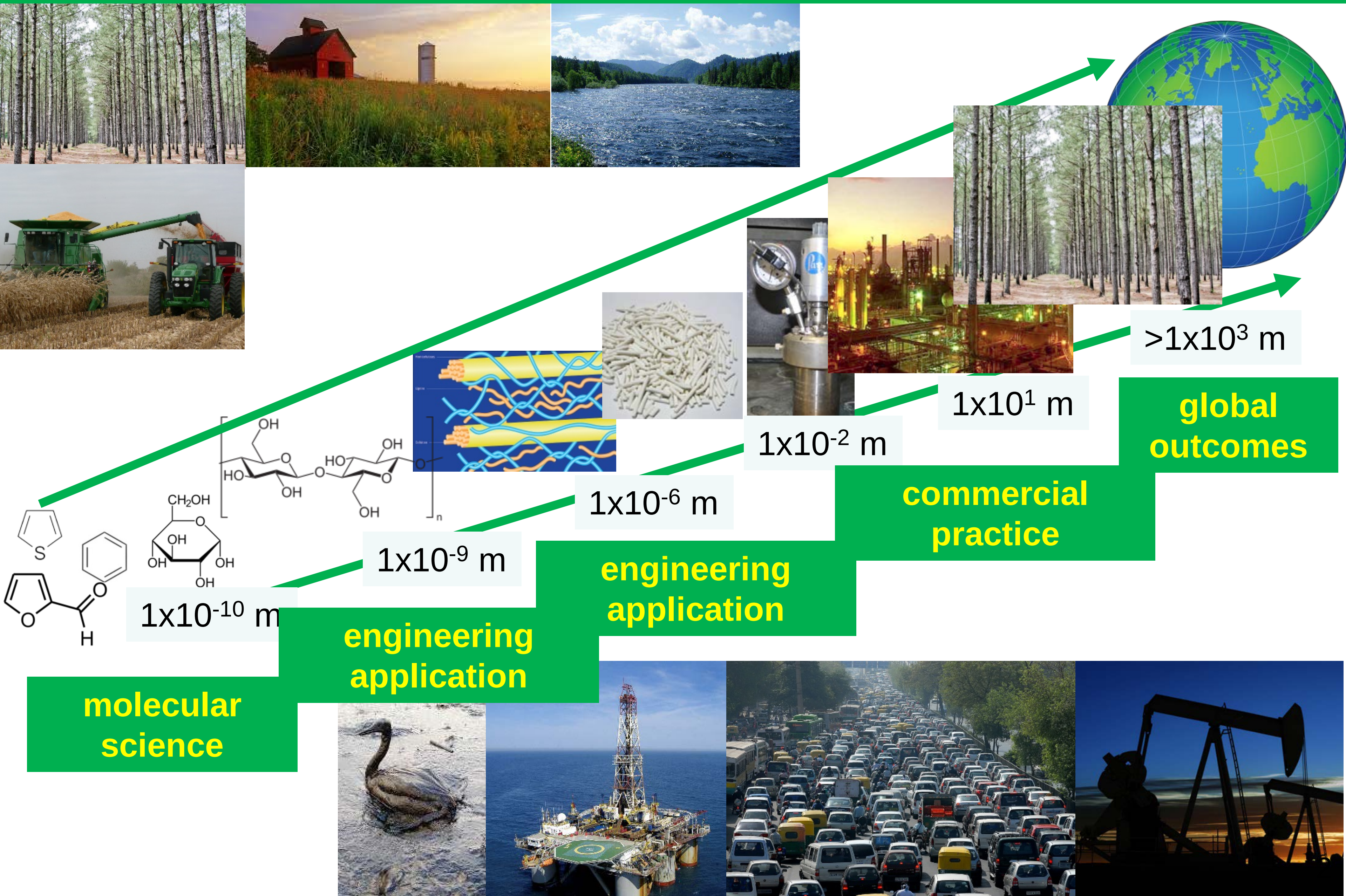
July 24

Catalysis and Reaction Engineering Research at WPI
Green Chemistry & Engineering Meets Sustainable Energy

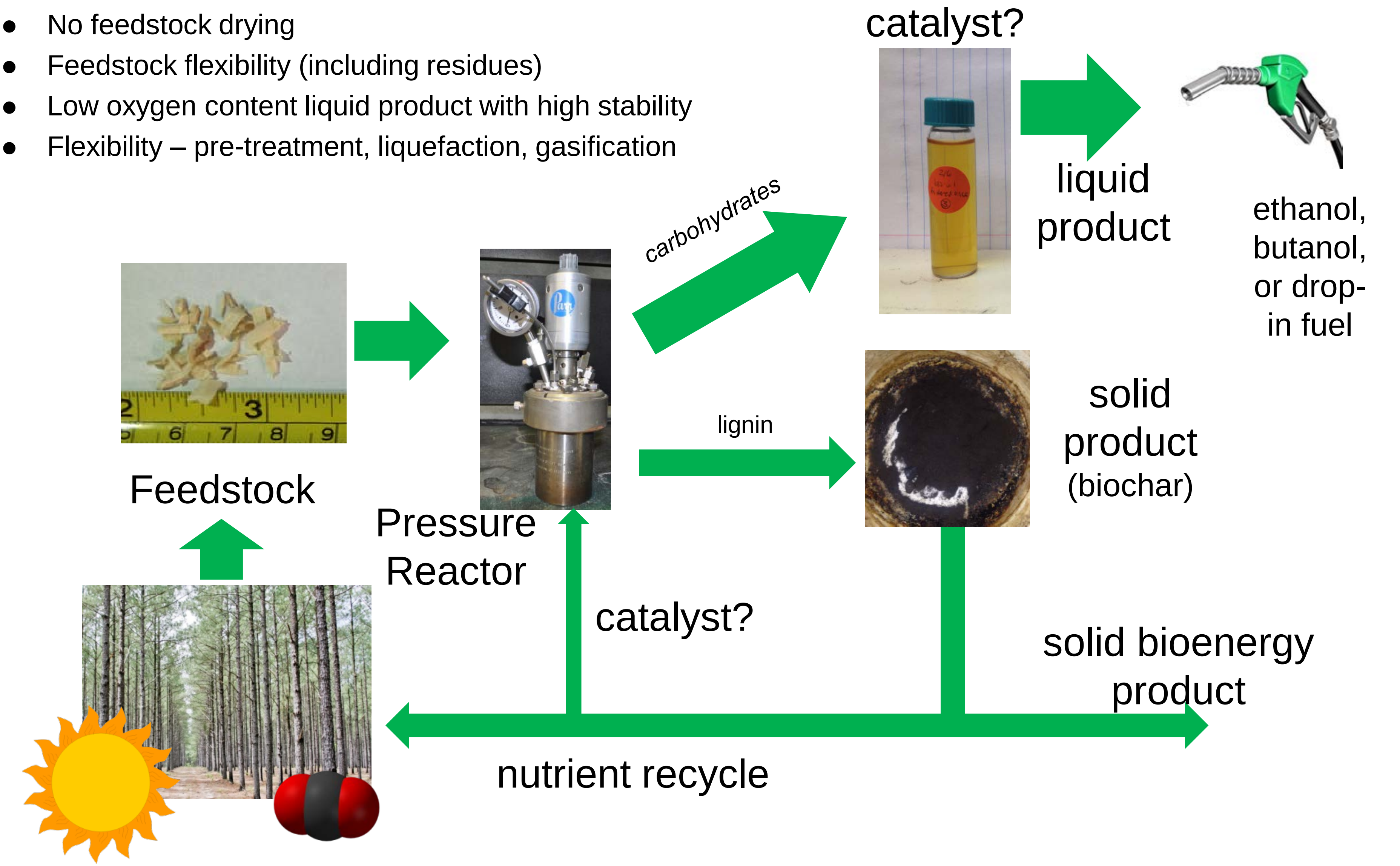


Bioenergy Challenges

- Capital costs of large-scale cellulosic biorefineries are massive (billions of $)
  - Low capital technologies are required
  - Technologies that leverage existing infrastructure are desirable
- Operating costs remain high (about double that for petroleum fuels)
  - Efficient technologies are required
  - Must be feedstock flexible and appropriate for waste biomass
  - Must make use of all biomass components
  - Multiple product streams ($) are required
- Making biofuel production sustainable has not been achieved
  - Land/water use rates
  - Waste production
- Transportation costs and energies remain high
  - Biomass is a distributed resource with low energy density grown in remote, rural areas
  - Small-scale, deployable biomass conversion may reduce transportation costs and energies

High Temperature Water Processes for Valorization of Renewable Resources

- Rapid reaction rates (small reactors)
- No feedstock drying
- Feedstock flexibility (including residues)
- Low oxygen content liquid product with high stability
- Flexibility – pre-treatment, liquefaction, gasification

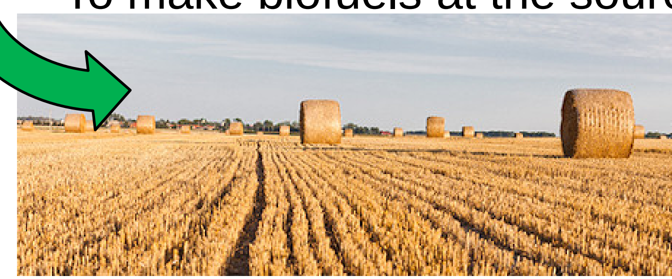


Deployable Biomass Conversion

Shrink this

and put it in here

To make biofuels at the source



Advantages:

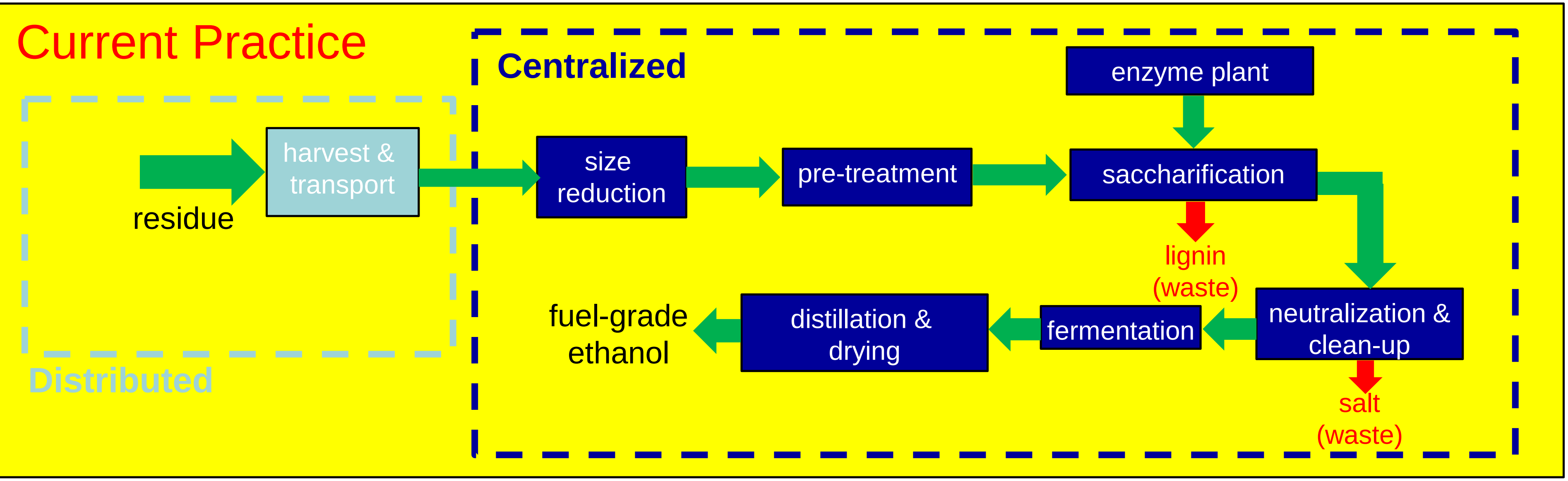
- Reduced capital costs
- Incremental costs of adding capacity
- Reduced transportation costs and energy consumption due to decreased liquid volumes to be shipped (compared to large solids volumes)
- Appropriate for remote rural areas

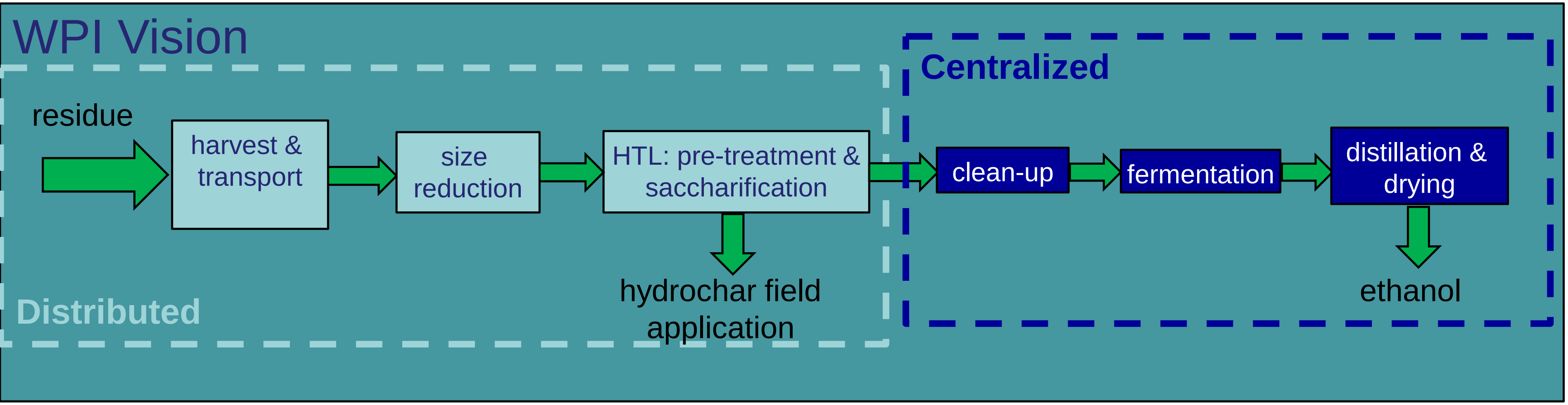
Challenges:

- Compact technologies (rapid reactions)
- Product stability and carbon utilization
- Solids handling & feedstock flexibility

Mobile biofuels production platform

Distributed Pre-treatment Concept: Reduced Operations and Capital Costs

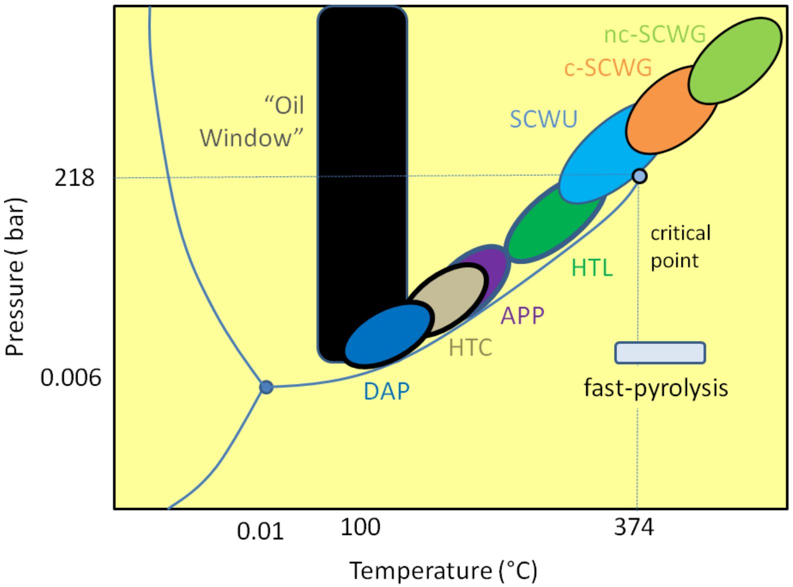




Why Hydrothermal? Techno-Economic Considerations

- Previous economic analysis suggests that pyrolysis ($2/gge) is more economical than either biochemical ($5/gge) or hydrothermal liquefaction (HTL) ($4/gge)
  Data from Wright et al., 2010 and Zhu et al. 2014
- Pyrolysis requires drying step and is limited by bio-oil product quality and stability
- HTL offers flexibility
  - Liquefaction to produce a bio-oil with superior properties compared to pyrolysis
  - Pre-treatment to maximize sugar yield for APP or fermentation

Primary Technical Challenge: Controlling chemistry during HTL



Timko et al. *J SCF*, submitted

Techniques to Control Reactivity

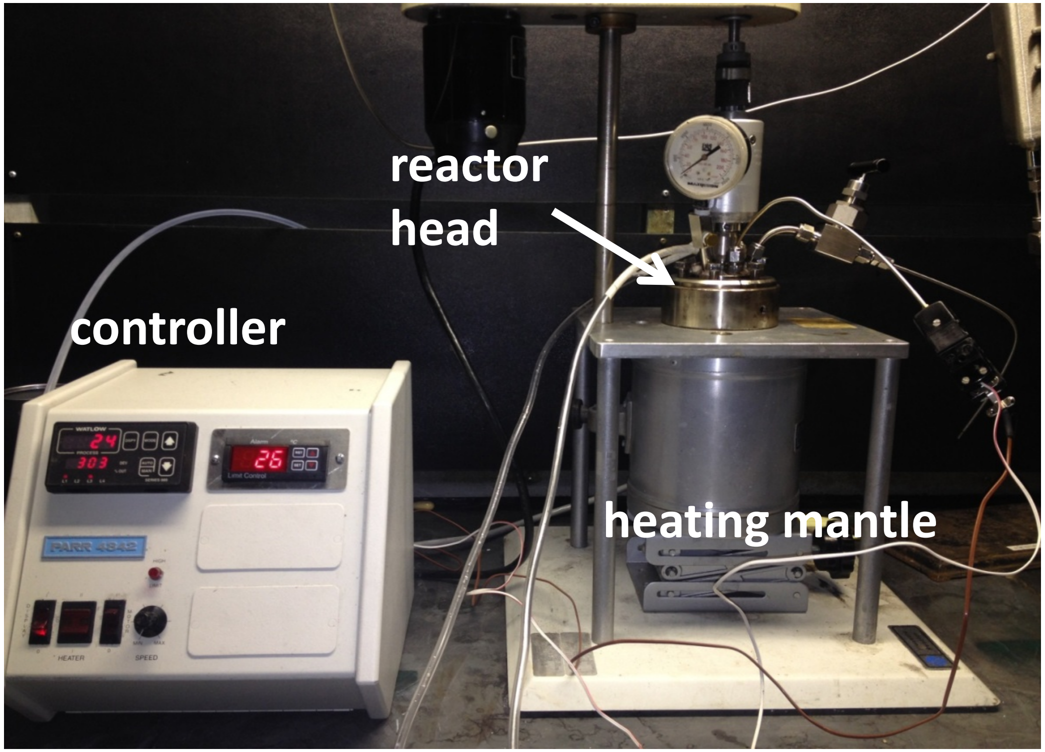
1) Reaction Engineering

- Heat rate
- Residence time control

2) Catalyst Engineering

- Making active catalysts stable
- Making stable materials active

Hydrothermal Batch Reactor

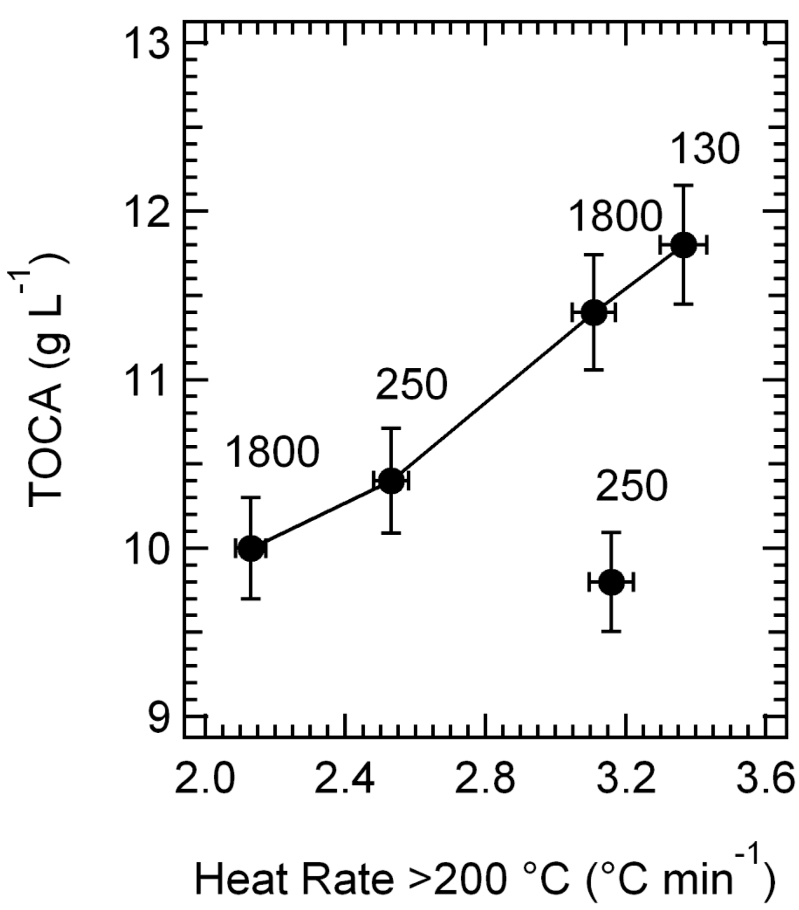


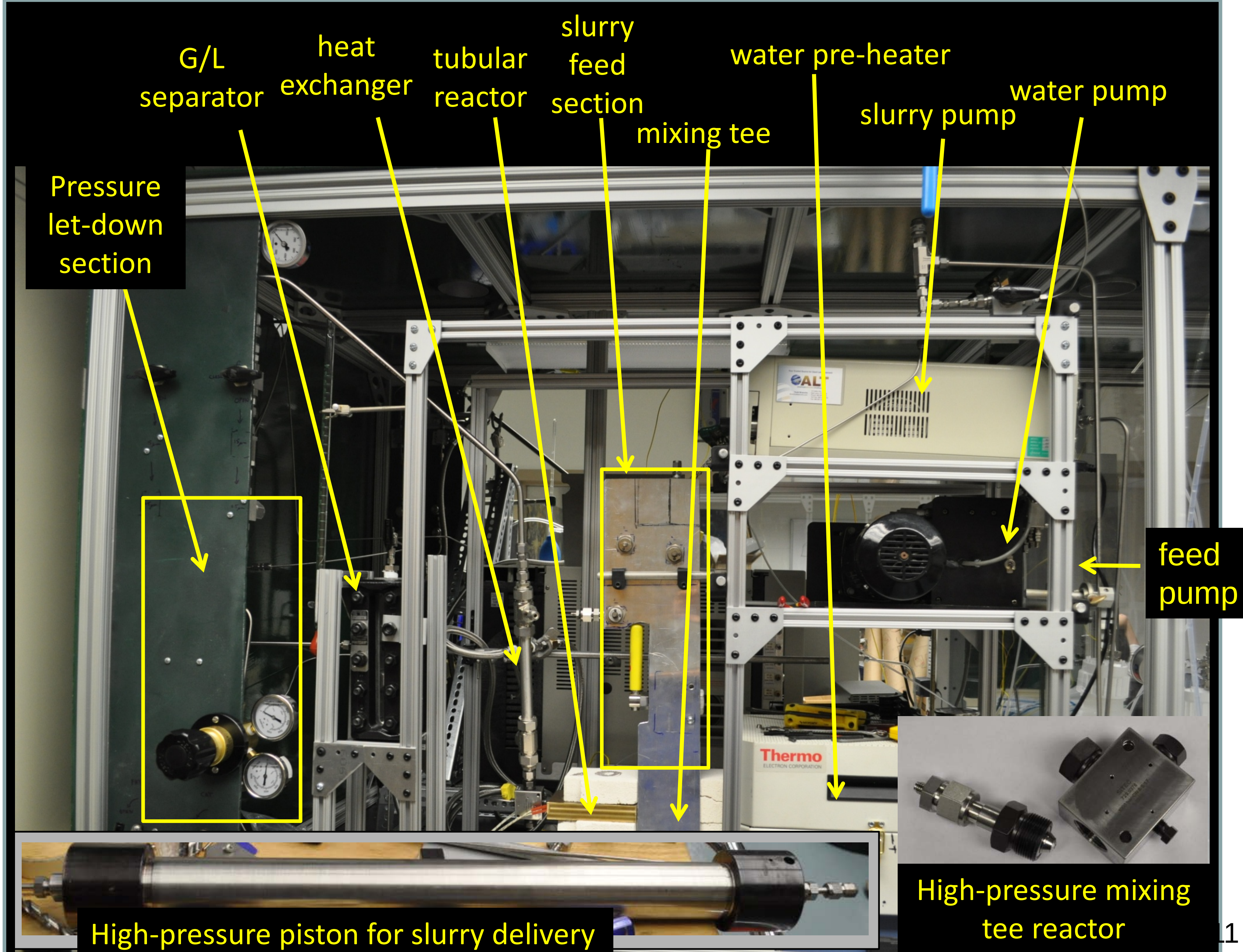
Reactor
500 mL 316-ss Parr reactor
rated to 2000 psi at 350 °C
experiments performed at 300 °C
reaction time = 10 min after heat up
agitation rate = 500 rpm

Feed
Size selected pine sawdust
10 wt% slurry

Organic Carbon Yield and Heat Rate

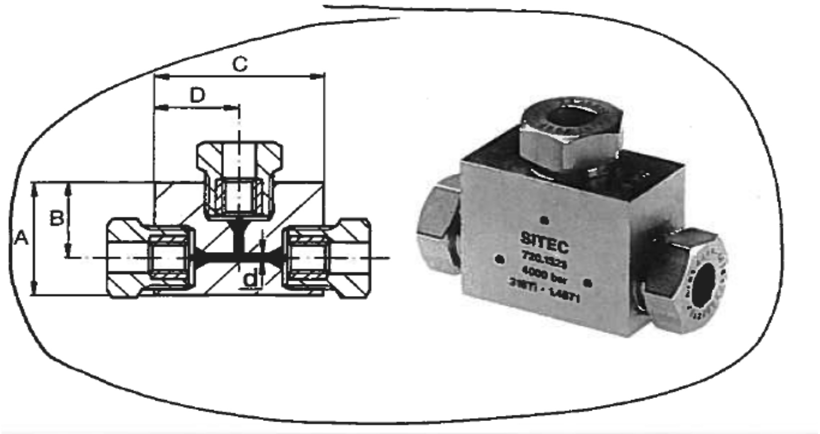
- Initially performed to investigate effect of particle size
- Instead, heating rate played an important role
- Qualitatively similar to HTL of grasses (Zhang et al. *J. Applied Anal. Pyrolysis,* 2009)
- Experiments in progress to investigate heating rate effects in batch reactor
- **Points to the importance of rapid heat rates in continuous flow reactors**

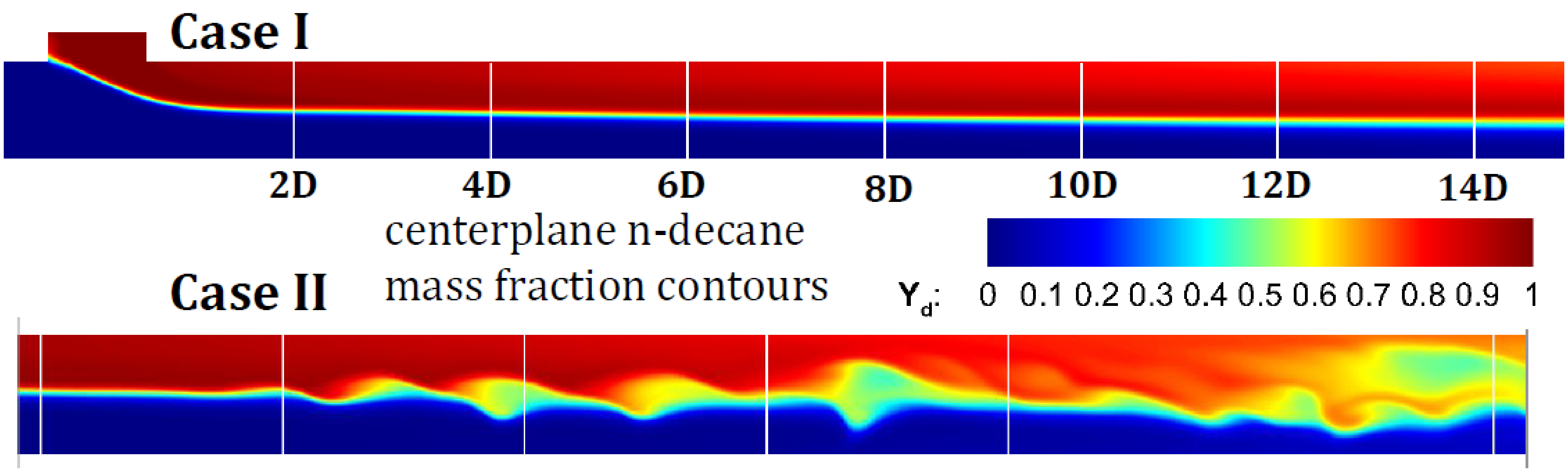



Pressure let-down section
G/L separator
heat exchanger
tubular reactor
slurry feed section
mixing tee
water pre-heater
slurry pump
water pump
feed pump
Thermo
High-pressure piston for slurry delivery
High-pressure mixing tee reactor

Heat Transfer Rate in Continuous Flow

- In collaboration with MIT in a separate study, the WPI team has been studying rapid heating in a mixing tee reactor
- Biomass fed cold from the top port
- Water superheated (>350 C) to achieve rapid heat rate

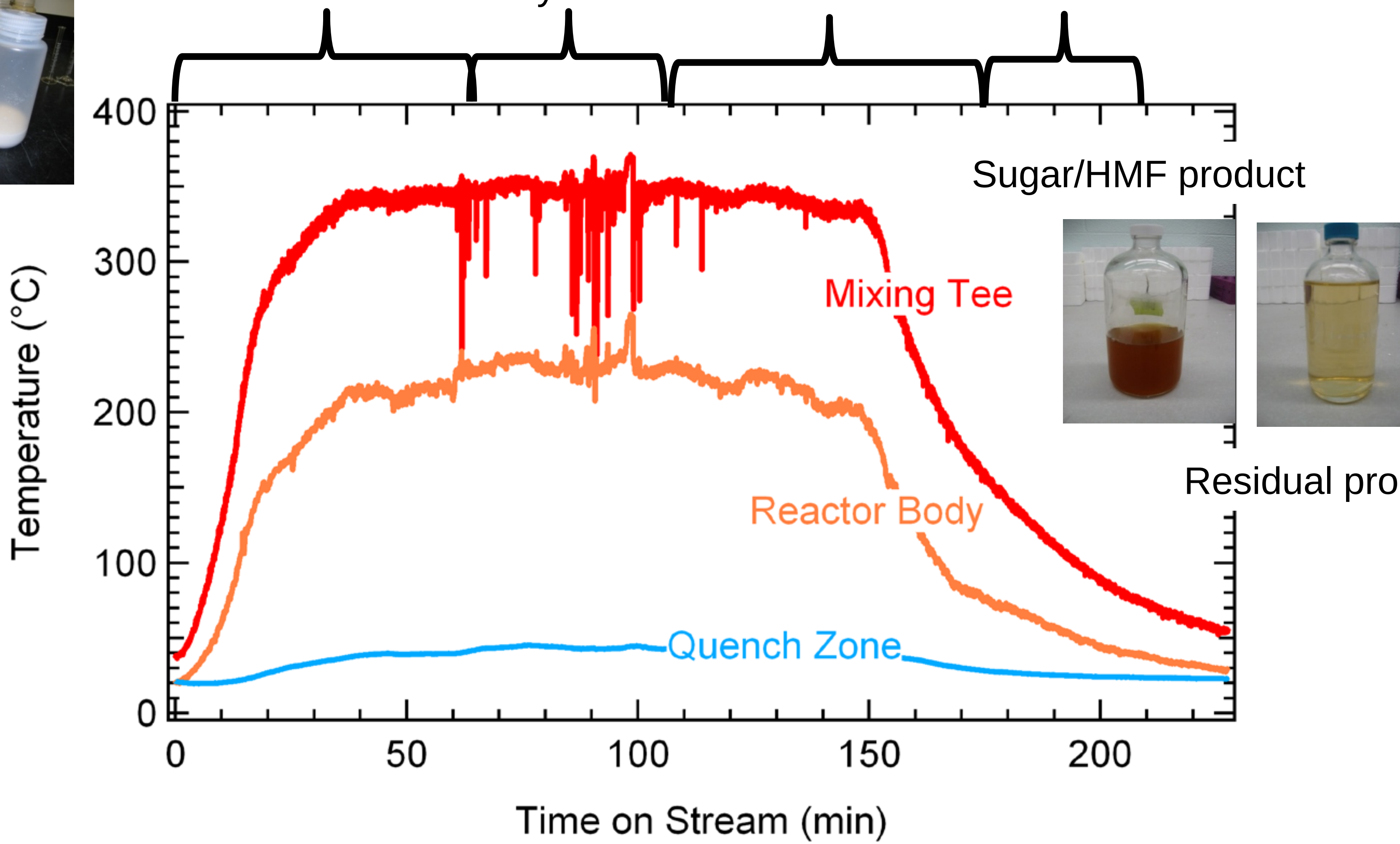




(Rhagavan et al. *J. Supercritical Fluids*, 2014)

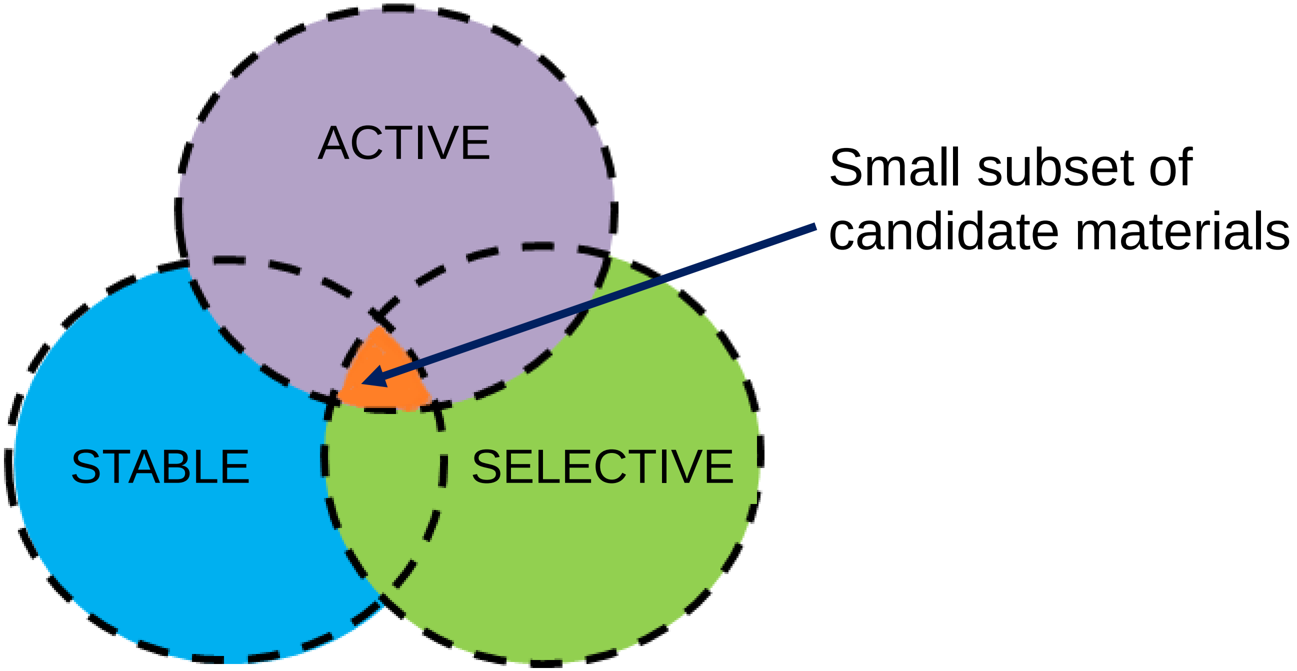
Temperature TOS Performance

Cellulose feed



Controlling Reactivity - Catalysis

- Catalyst allows temperature to be decreased, improving selectivity
- Catalyst must be – active, selective, and stable



- Additional requirements placed on the material for COST & SUSTAINABILITY

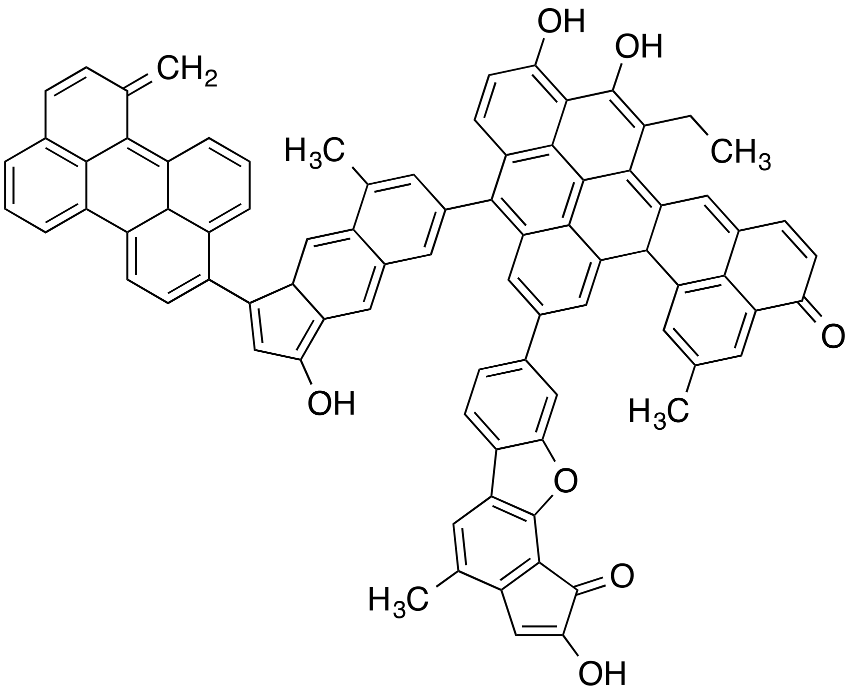
We address stability and activity 2 ways

- **Hydrothermal char** as a renewable catalyst material
  - The material itself is **stable**
  - **Need – impart activity**

- **Organic-modified zeolites** as a hydrothermally stable catalyst with well-defined pore structures
  - The material is **active and selective**
  - **Need – impart stability**

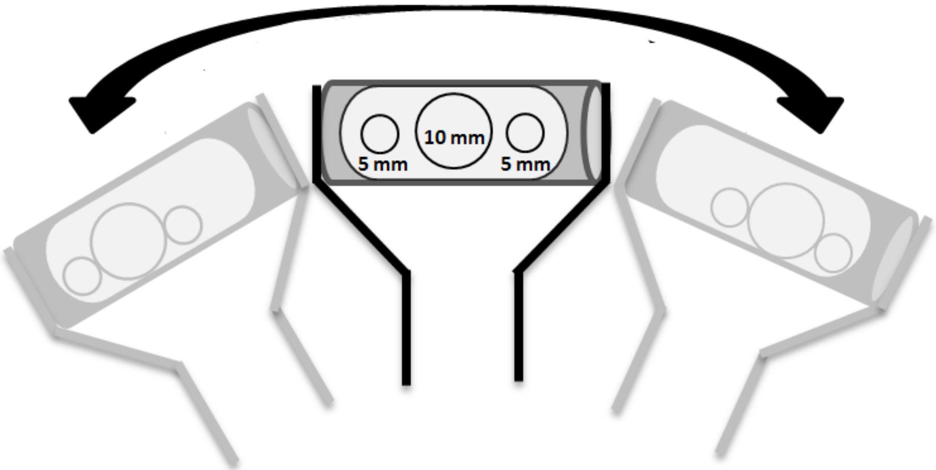
Char Materials as Catalysts

- ✓ *Renewable source (sugars, cellulose, hydrolyzates, biomass)*
- ✓ *Inherently stable in high-temperature water*
- ✓ *Can be functionalized (-OH, -SO_3, N)*
- x *Low intrinsic catalytic activity*
- x *Require harsh conditions to become catalytic (concentrated acid treatment)*



Here, I will focus specifically on hydrothermal chars formed by carbonaceous feedstocks in a water-rich environment

Ball-milling to activate hydrochars for catalyst applications

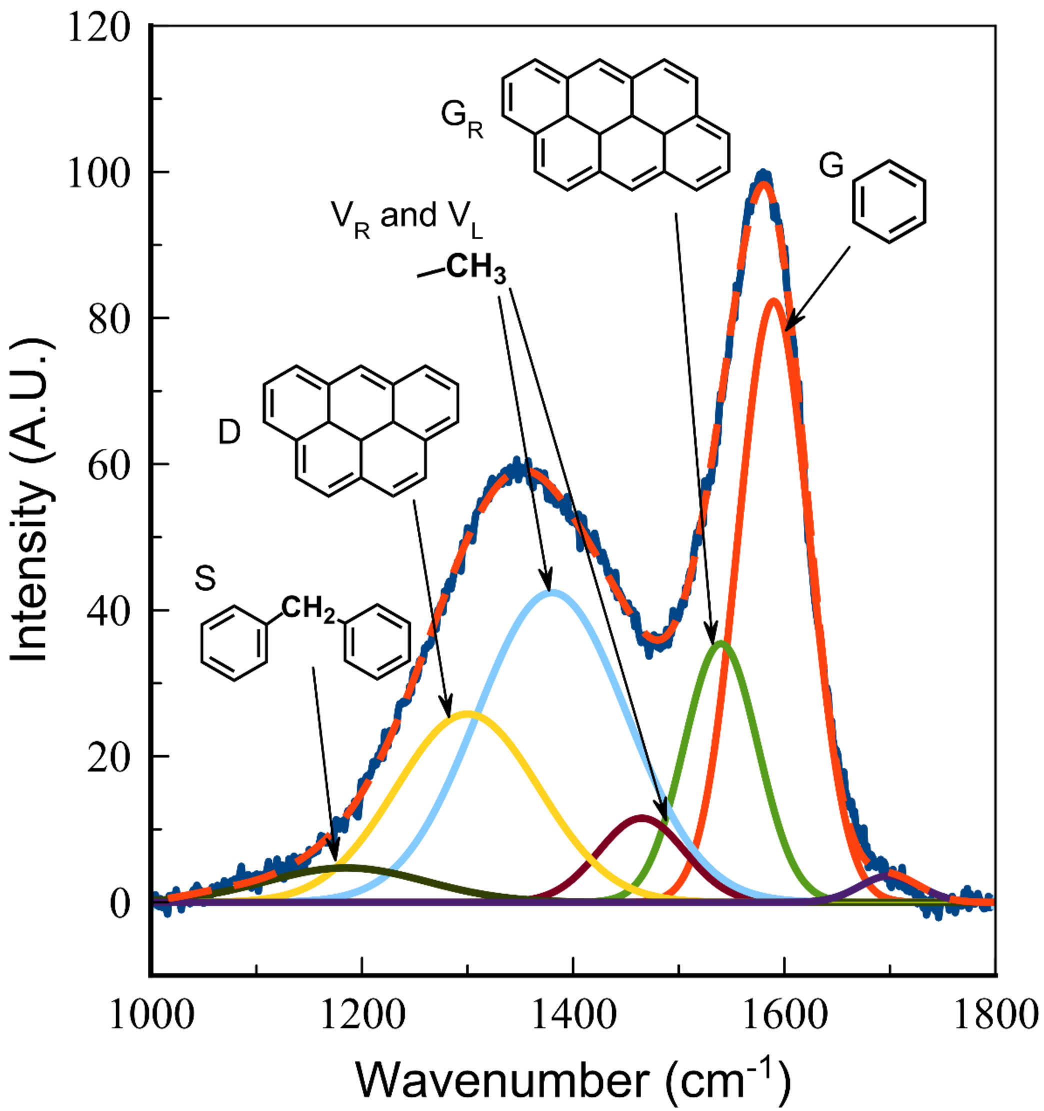


Ball-Milling

- ✓ *Energy imparted by ball impacts*
- ✓ *Solvent-free*
- ✓ *No need for downstream processing*
- x *Mechanism not understood*

We performed fundamental studies to improve our understanding of chemical processes that occur during ball milling

Raman Spectroscopy to Analyze Chars



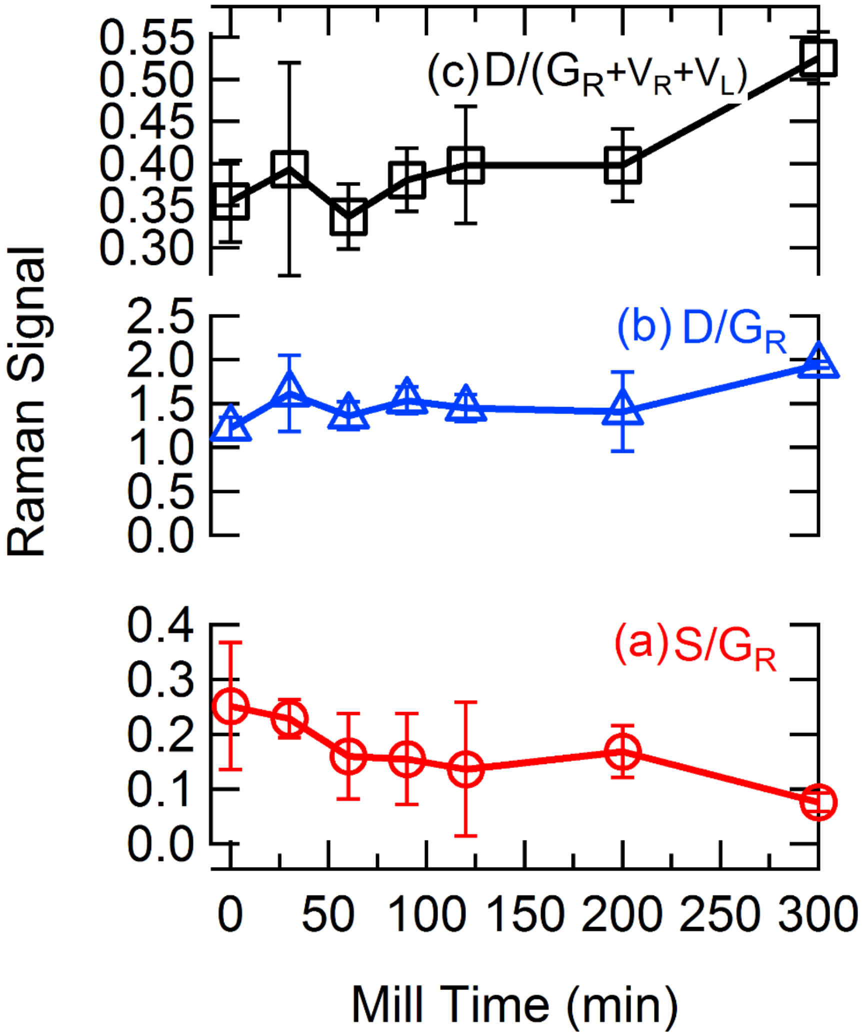
Assignments based on Li et al. (Fuel, 2006)

Vibrational spectra provide significant information on carbon-carbon connectivity

Subject char to ball milling and track structural changes to develop modification protocol

Tompsett et al., Carbon, submitted

Raman Shows Substantial Structural Changes during Ball Milling



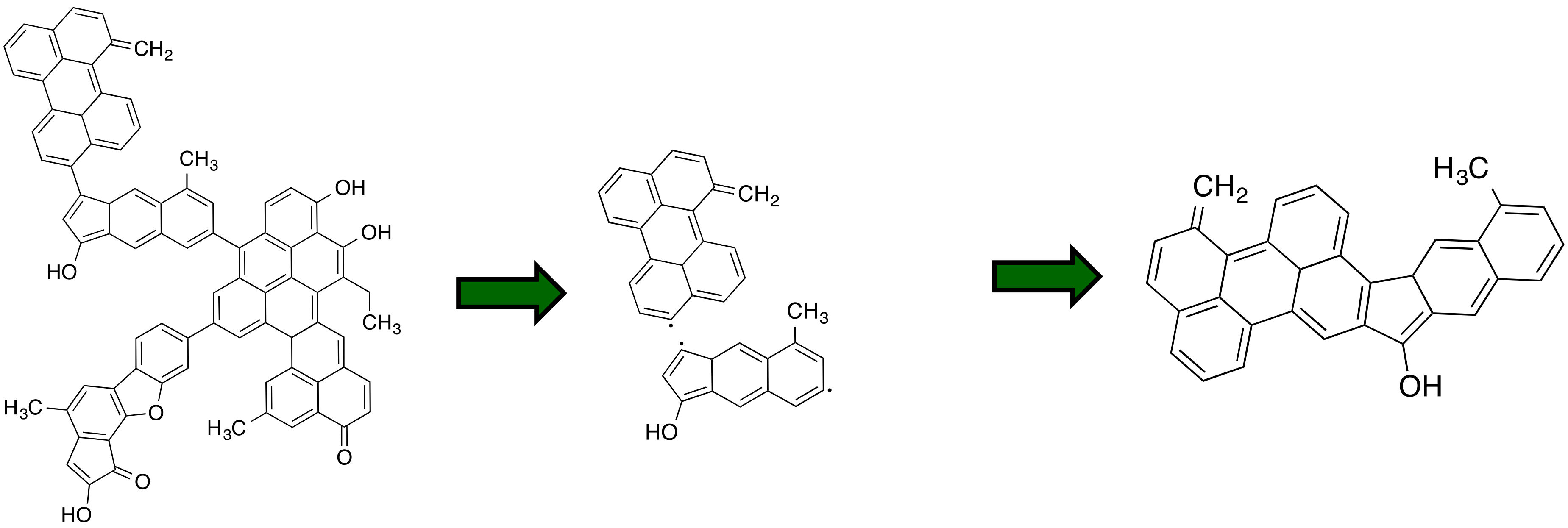
$D/(G_R+V_R+V_L)$ ↑ implies that alkyl chains disappear

D/G_R ↑ implies that small aromatic clusters form larger ones

S/G_R ↓ implies that bridgehead carbons disappear

Tompsett et al., Carbon, submitted

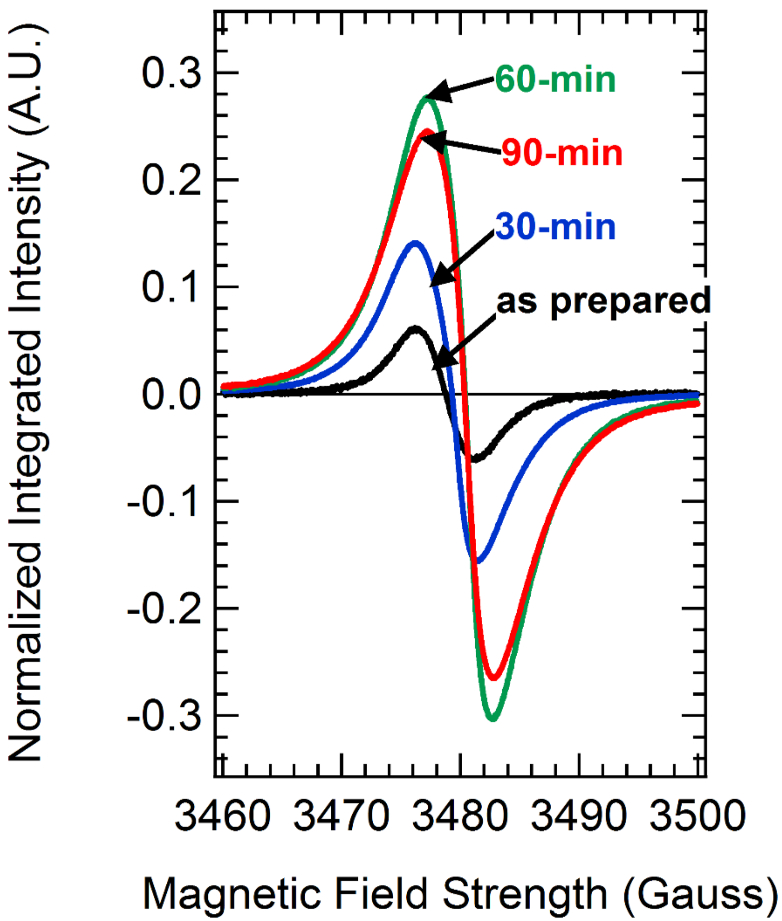
Char Reactions and Radical Intermediates

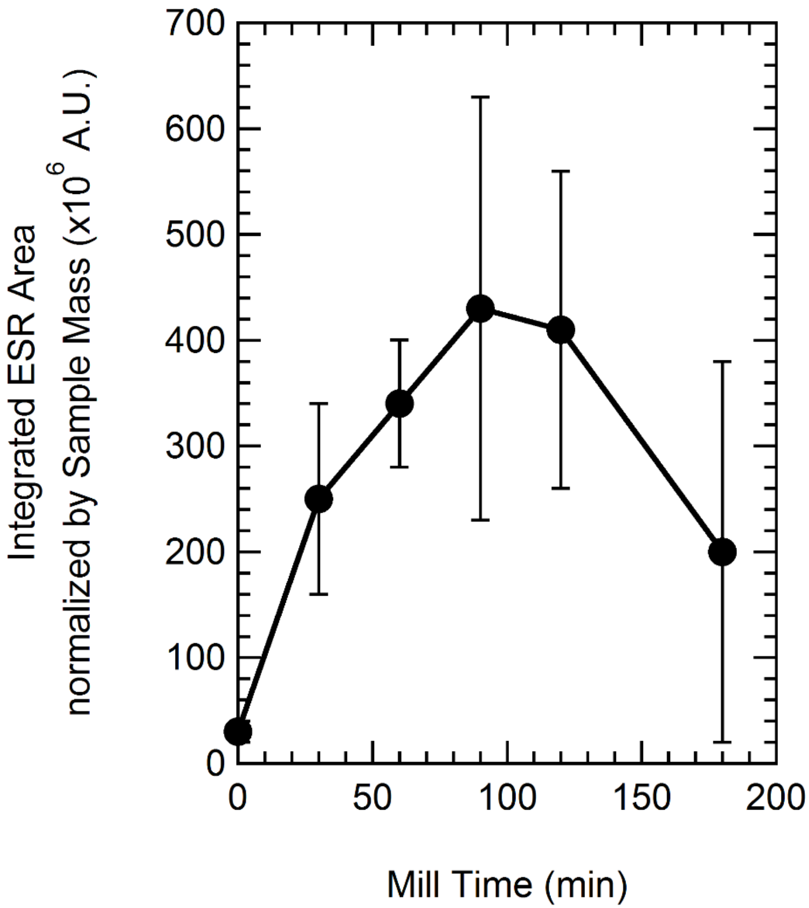


This mechanism explains loss of bridgehead carbons, disappearance of small aromatic clusters, and formation of larger aromatic clusters

Suggests formation of radical intermediates – ESR!

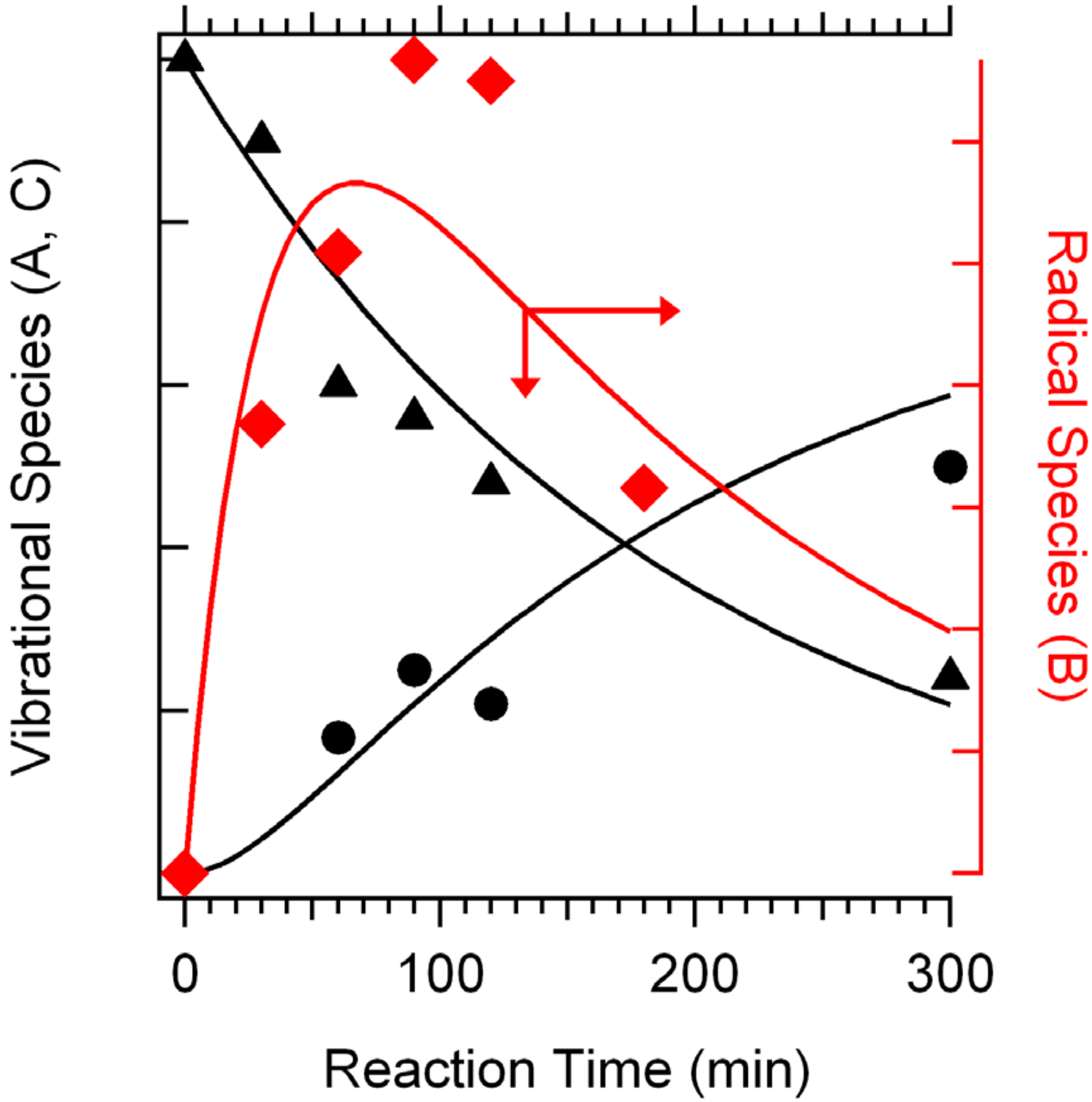
ESR Measures Radical Content





As predicted, radical signal rapidly increases and then decreases with larger milling times

Conceptual Kinetic Model



$A \xrightarrow{k_1} B$ Radical formation

$B \xrightarrow{k_2} C$ Radical recombination

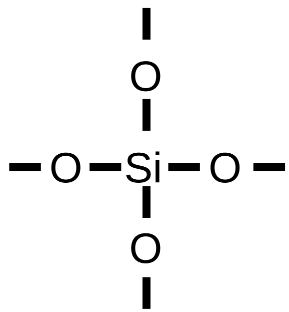
$B \xrightarrow{k_3} D$ Radical reaction with air

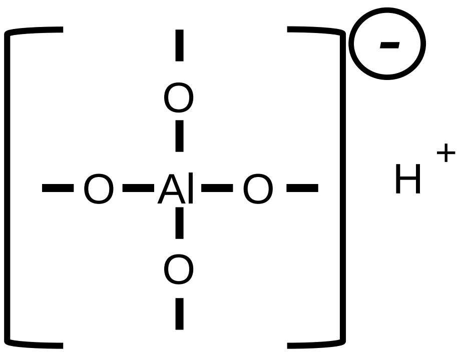
All rate constants on the order of $1x10^{-2}$ and $1x10^{-3}$ min^{-1}

Provides basis for reaction design

Organic-Modified Zeolites

Microporous material (<10 Å) with alumina substitution, zeolites are strong Brønsted acids



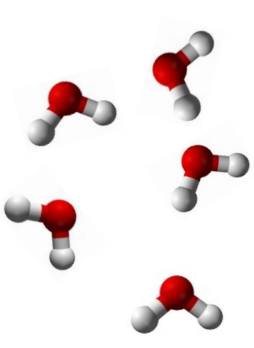


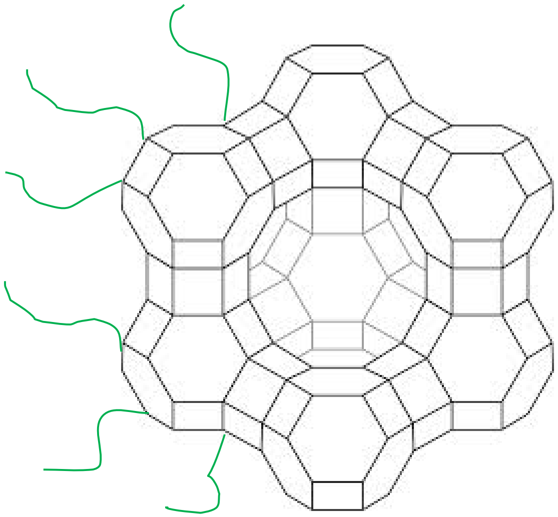
The more alumina, the more active – but the less water stable!

Solution proposed by Resasco et al. – kinetic stability using organic modifiers

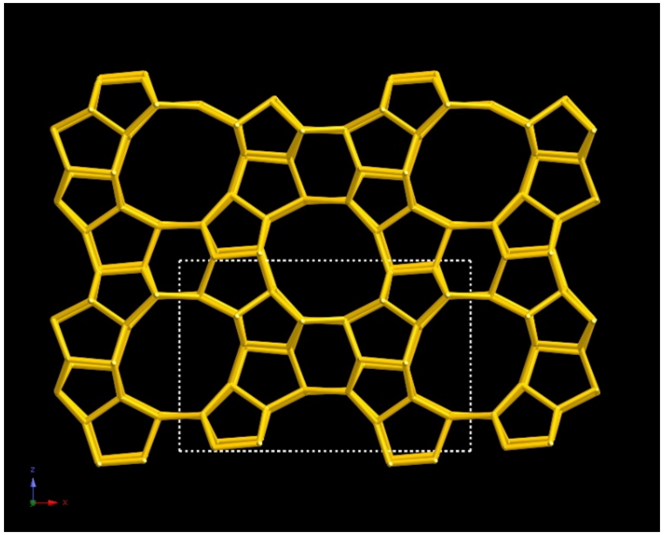
Water cannot enter the pores – zeolite remains stable

But, what about reactant access?





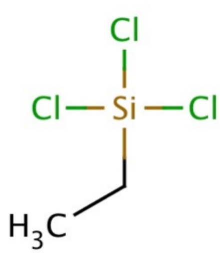
Organic-modified ZSM-5



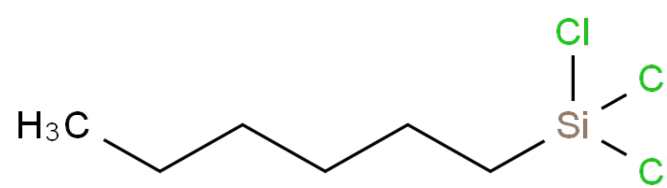
Common industrial zeolite with 4.46 Å pores and 6.36 Å cavities

Stable with high Al_2O_3 substitution ($\sim$40:1 SiO_2/Al_2O_3 ratio is commercial)

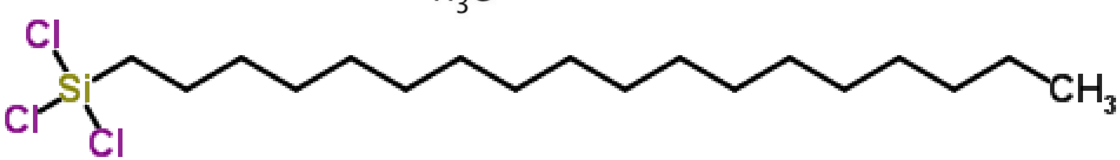
Use silanation chemistry to coat with hydrophobic molecules



ETS

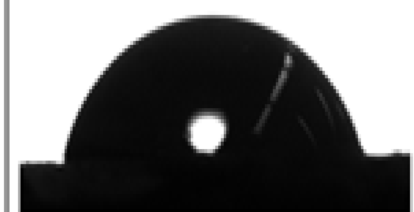
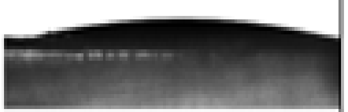
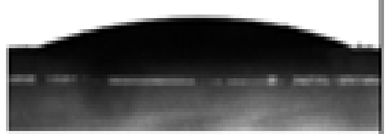
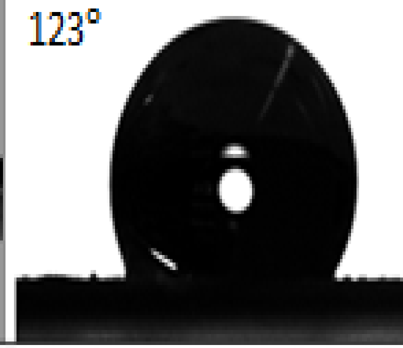


HTS



OTS

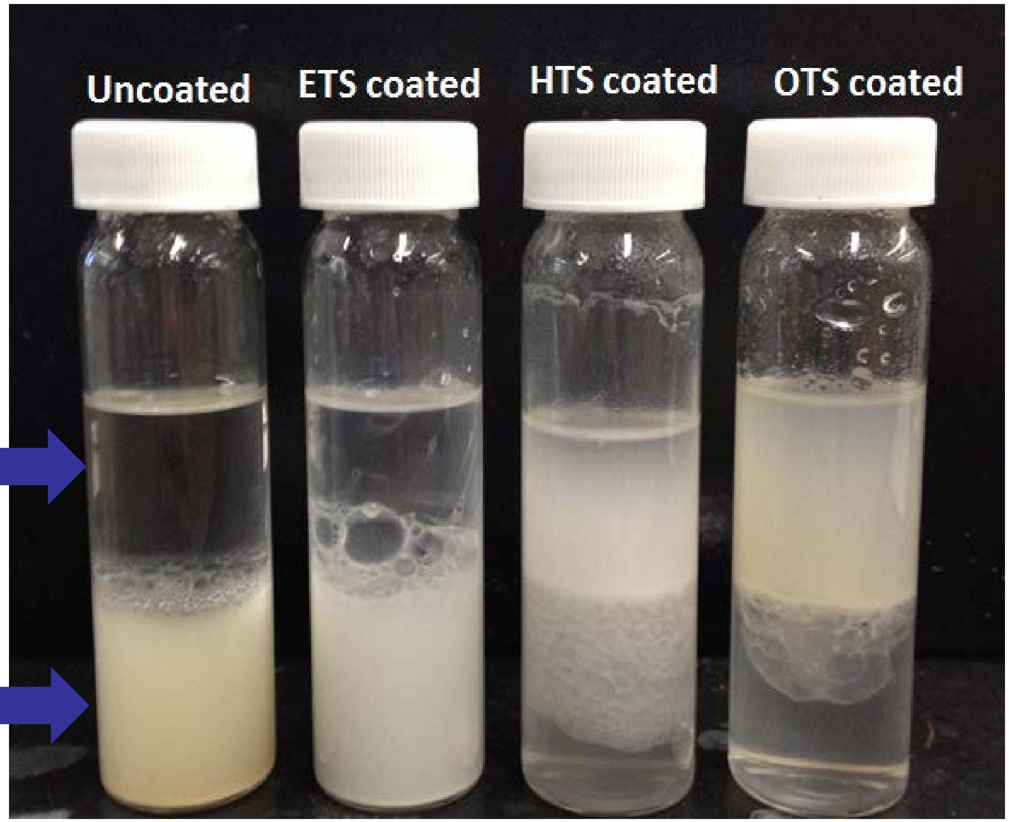
Contact Angle – confirms hydrophobic surface

	Uncoated	ETS modified	HTS modified	OTS modified
Modified Using Calcine Zeolite	*[Unable to capture photo because droplet absorbed into pellet instantaneously]*	*[Unable to capture photo because droplet absorbed into pellet instantaneously]*	80° 	100° 
Modified Using Uncalcine Zeolite			123° 	127° 

Phase behavior – confirms hydrophobic solution behavior

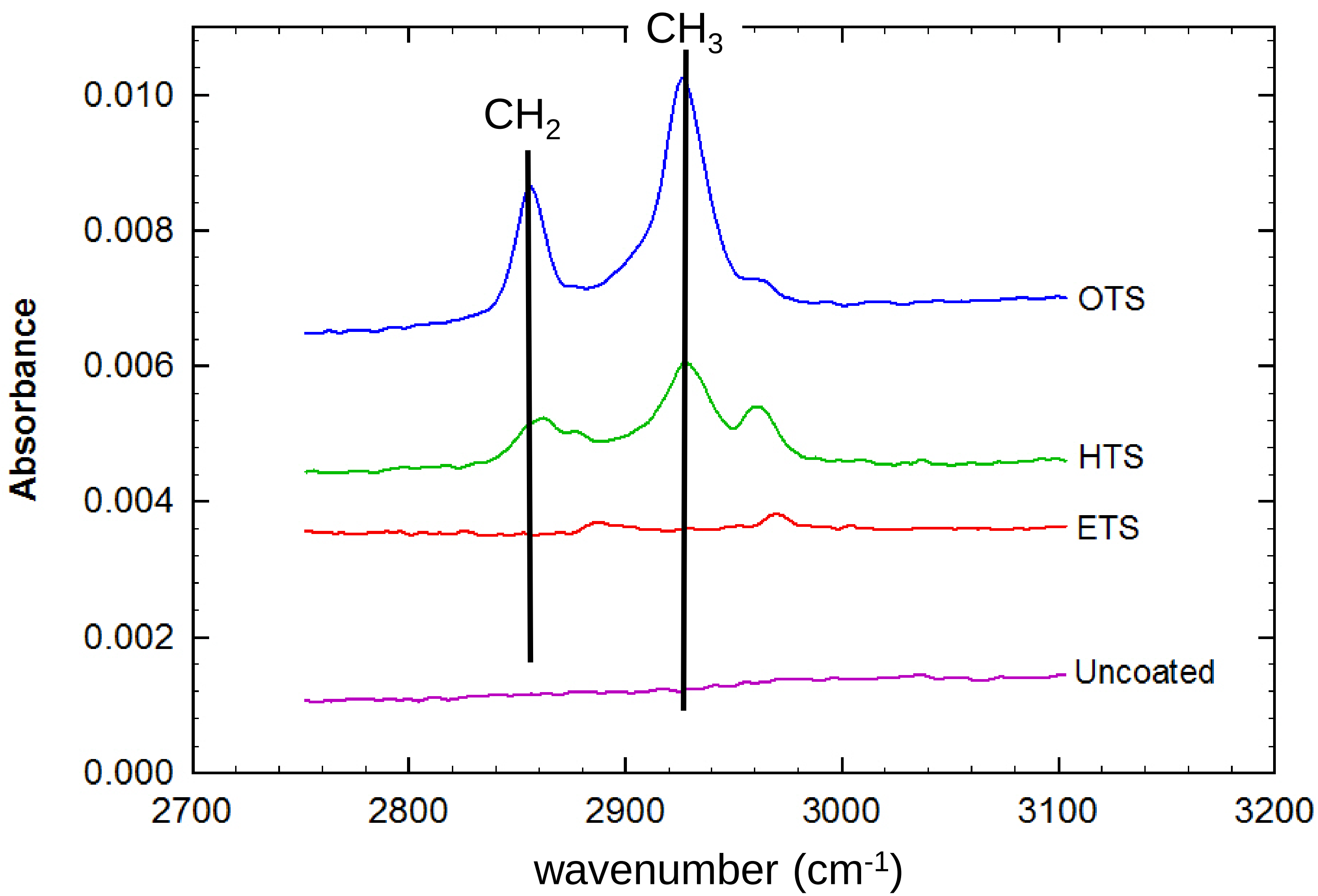
Toluene

Water

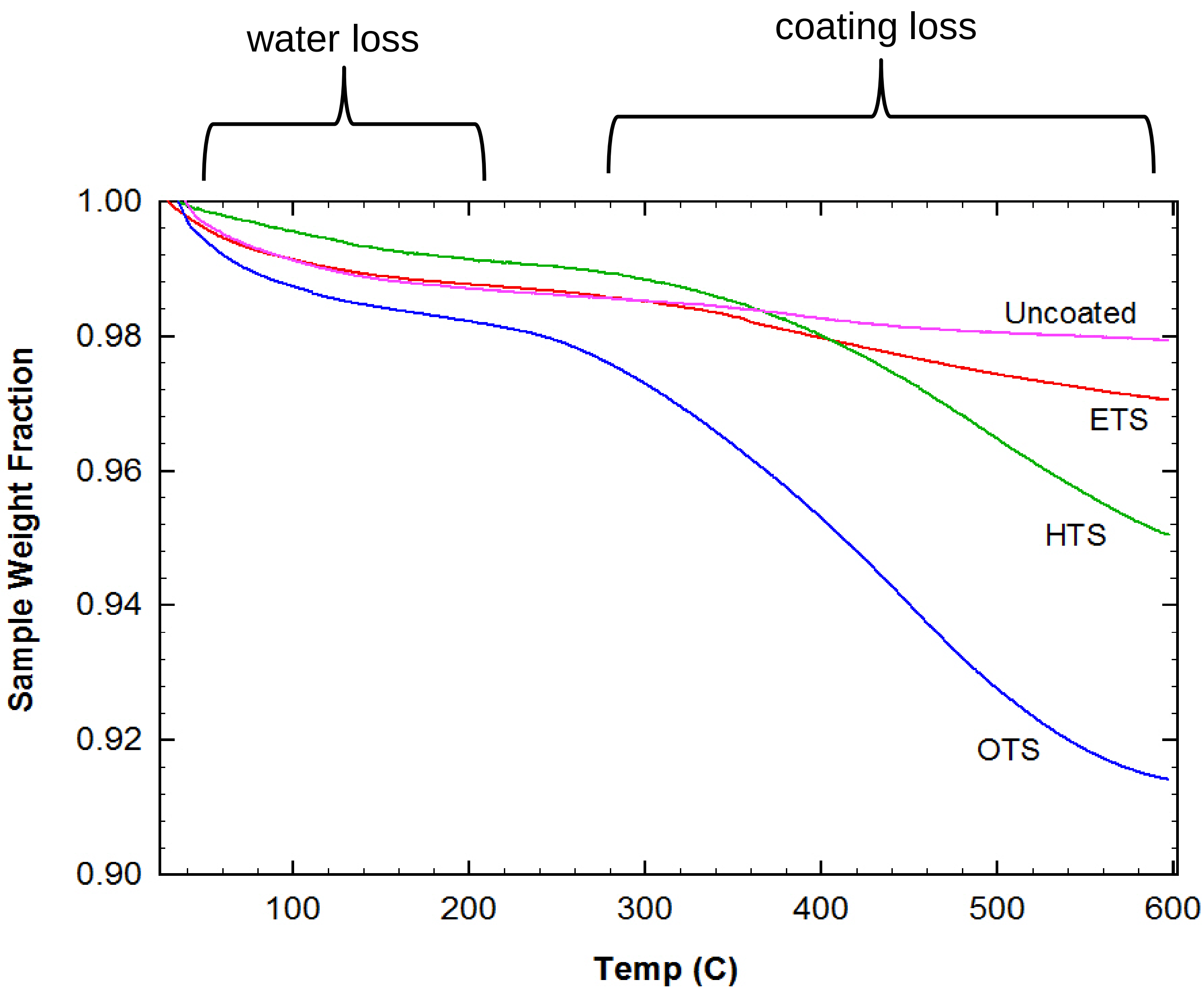


hydrophilic → **hydrophobic**

FTIR Confirms Presence of Alkyl Groups



TGA Confirms Thermal Stability



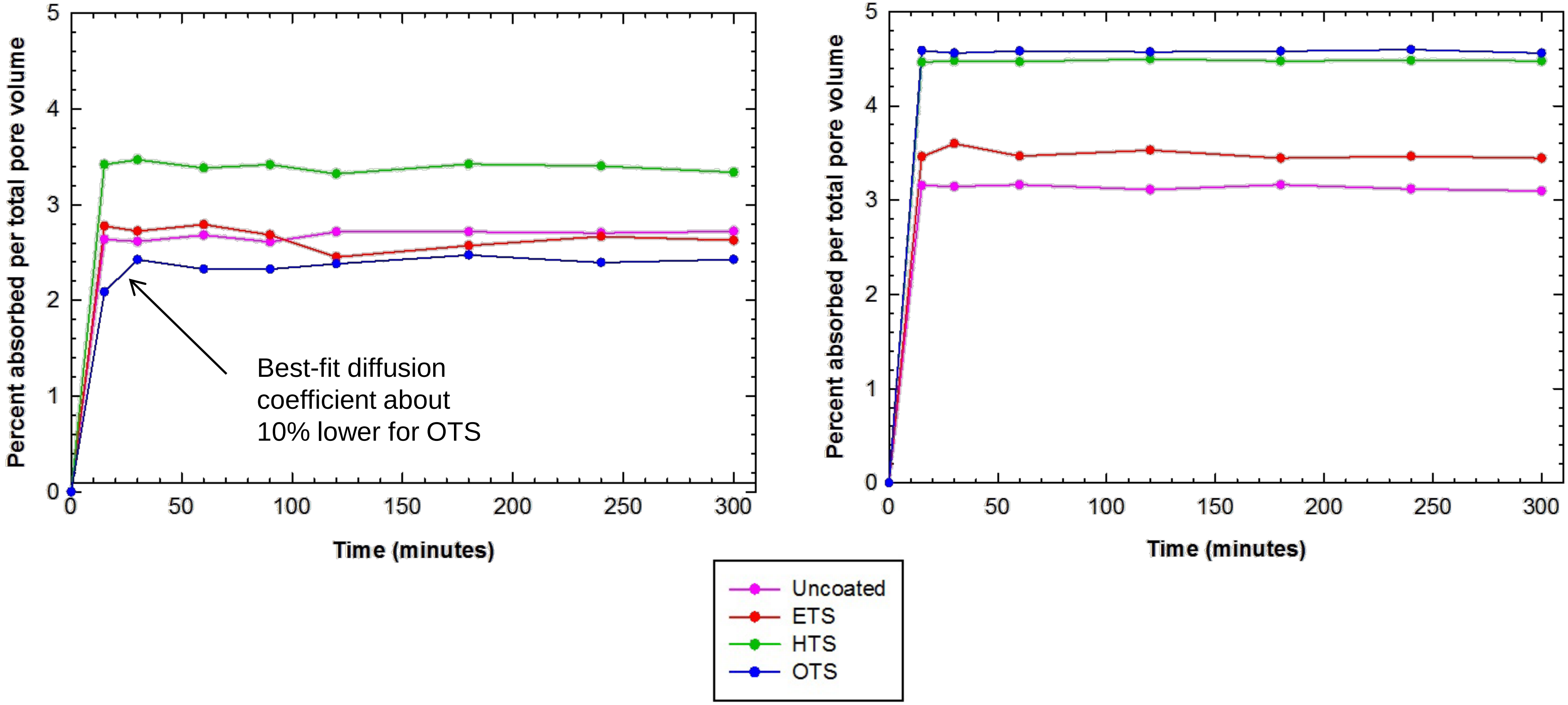
Sorption Experiments

Hexanol

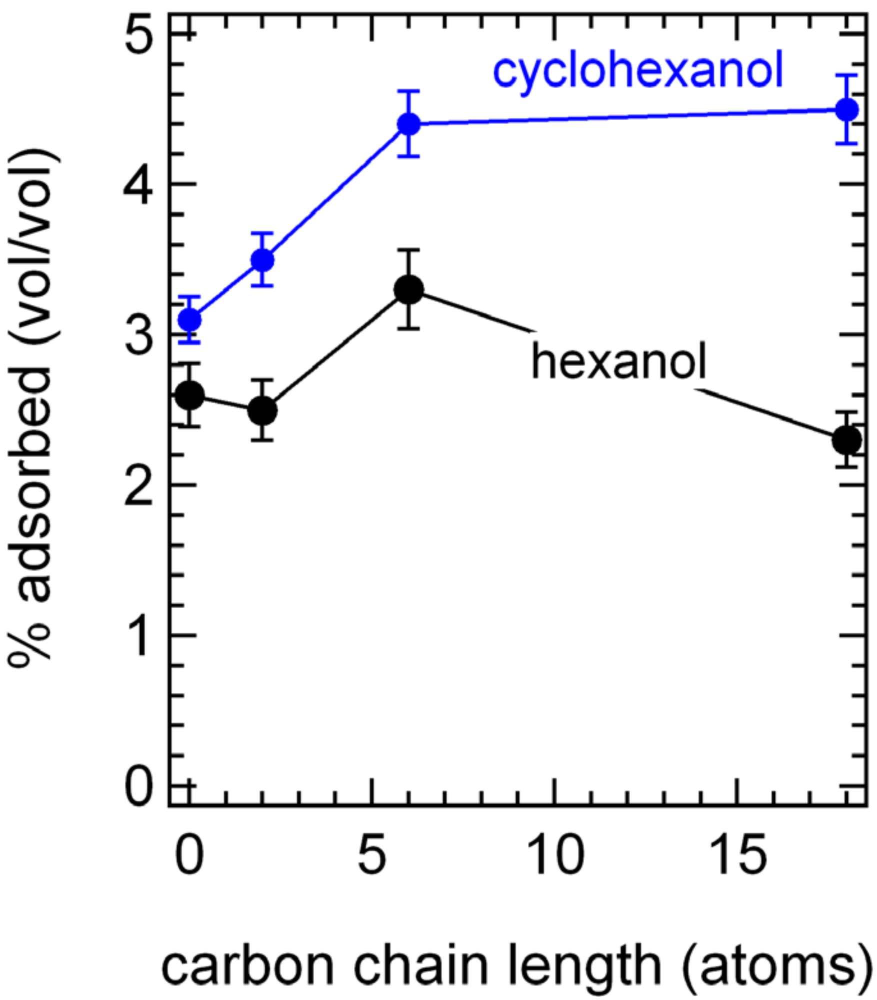
μ = 1.55 D $\quad$ S = 5.9 g L^{-1}

Cyclohexanol

μ = 1.46 D $\quad$ S = 0.36 g L^{-1}



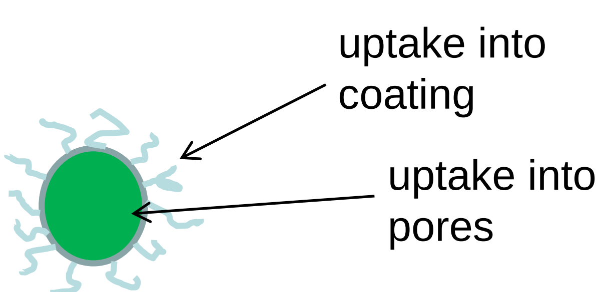
Equilibrium Uptake



Cyclohexanol uptake increases with coating thickness

Hexanol shows a more modest effect – need to investigate C_6 coating in more detail

Possible explanation, uptake into zeolite pores and into organic coating



Relative contributions depend on adsorbate sizes and polarities

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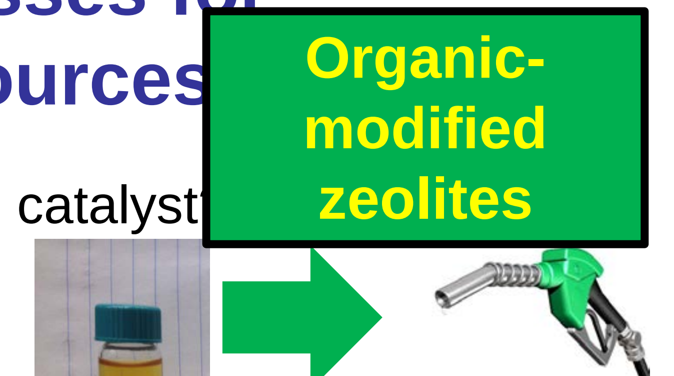

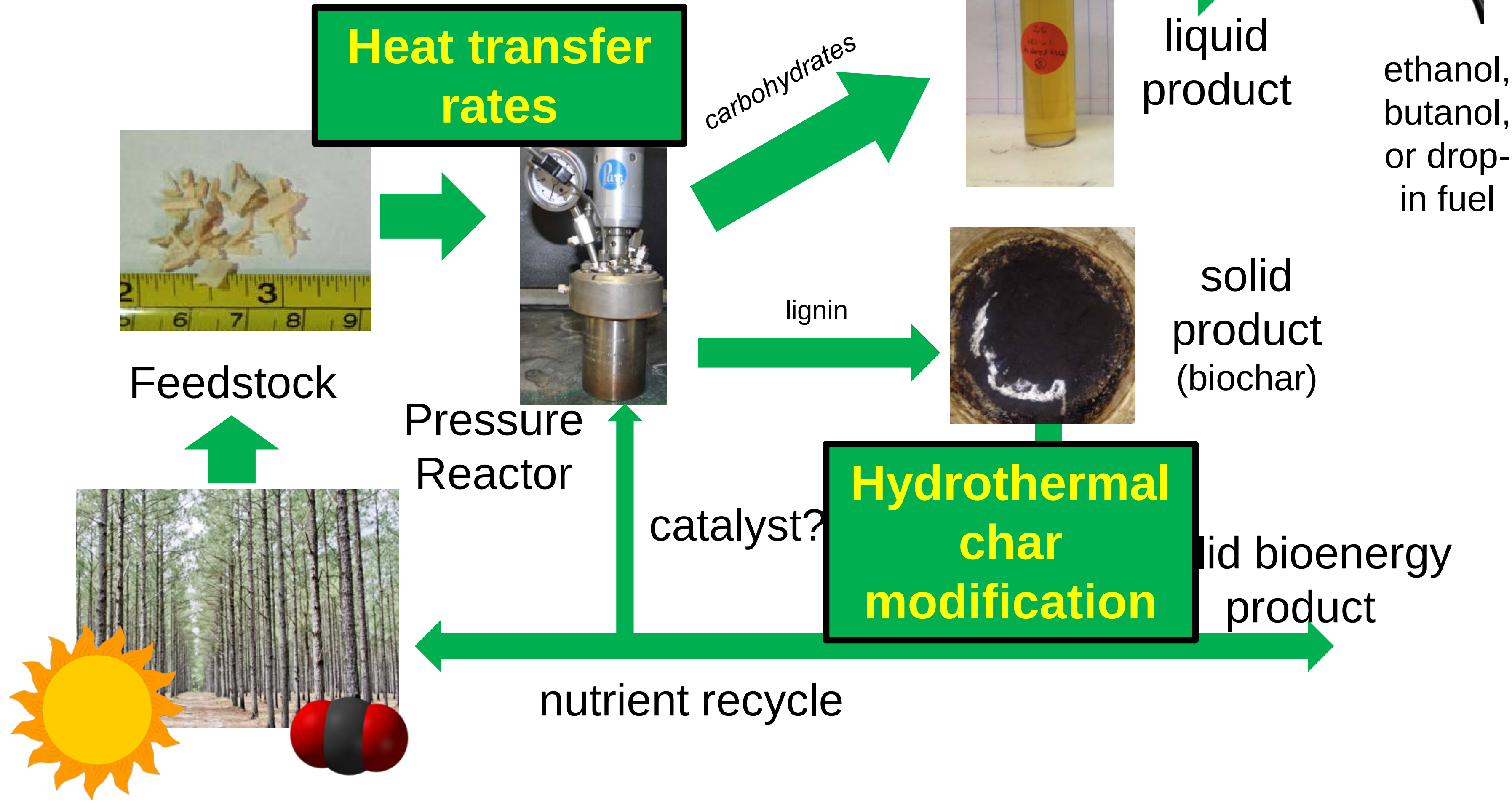

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- Conference c
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  - supported other areas (below)
- Juan V ey, Joseph T
  - Hydr research pr
- Alaina , Matt Cook
  - Zeolite modification senior research p
- Tatiana Loureiro, Joao Mauricio, and Matheus de Silva
- DOE STTR
- Start-up and departm
- Conference organize rd)

Obrigado!