Recent Advancements in Catalytic Fast Pyrolysis for the Production of Fuels and Chemicals from Biomass

Joshua A. Schaidle, NREL
ePYRO 2021
April 13th, 2021
NREL/PR-5100-79564
Emerging carbon conversion technologies need to be resilient and responsive to market and policy shifts

Challenge: How do we design carbon conversion technologies, including capex-intensive facilities, to succeed in tomorrow’s dynamic economy?
Opportunity: Designed Resilience

“It is not the strongest of the species that survives, nor the most intelligent, but the one most adaptable to change”

Leon C. Megginson

National Academy of Sciences Definition of Resilience: “The ability to prepare and plan for, absorb, recover from, and more successfully adapt to adverse events”


Goal: Enable the design of versatile catalytic carbon conversion technology platforms capable of nimbly responding to external stimuli

Critical Needs:
- Feedstock flexibility
- Adaptive process design and control
- Low conversion costs
- Product tunability

Porter's Five Forces

Exhibit Forces governing competition in an industry

- Threat of new entrants
- Bargaining power of suppliers
- The industry (jockeying for position among current competitors)
- Bargaining power of customers
- Threat of substitute products or services
Catalytic Fast Pyrolysis (CFP) Technology Platform

Potential for whole biomass conversion to drop-in hydrocarbon fuels at high yields (>75 gal/ton)

Advantages of the Technology:
- Cost of wood-based feedstock is de-coupled from petroleum price
- Vapor-phase catalytic upgrading provides control over product slate
- Reduces downstream hydrotreating costs as compared to fast pyrolysis
- Upgraded bio-oil could be co-processed in existing refinery infrastructure
- Produces a drop-in fuel blendstock, with co-product opportunities

In-Situ CFP Metal Oxide Catalysts

- Low capex requirements
- Harsh upgrading environment

Ex-Situ Entrained Bed CFP Zeolite Catalysts

- Controlled upgrading environment
- Higher capex required

Ex-Situ Fixed Bed CFP Metal-Acid Catalysts

- More diverse catalysts and chemistries possible
- Longer catalyst lifetimes required
Ex-situ Fixed Bed CFP: 2018 State-of-Technology

**Standard Conditions**
- Feedstock: Loblolly Pine
- Catalyst: 0.5-2.0 wt% Pt/TiO₂
- Pyrolysis Temperature: 500 °C
- Upgrading Temperature: 435 °C
- Catalyst Mass: 100 g
- WHSV: 1.4 g biomass/gcat*h
- Near Atmospheric Pressure
- Hydrogen Concentration: 83%
- Biomass:Catalyst Ratio: 3-13.2


---

**Improved carbon yields** compared to ZSM-5


The Pt/TiO₂ CFP-oil was hydrotreated using a single stage system for 80+ hours without fouling or plugging

---

**NiMo Sulfide, LHSV: 0.2-0.3, 13 MPa**

<table>
<thead>
<tr>
<th>Carbon yield %</th>
<th>H/C mol/mol</th>
<th>O wt.% dry</th>
<th>Density g ml⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>89</td>
<td>1.71</td>
<td>0.19</td>
<td>0.851</td>
</tr>
</tbody>
</table>

---

**Images and Diagrams:**
- Diagram of the pyrolysis and upgrading process
- Graph showing carbon yield, H/C, O, and density over oxygen content
- Graph comparing fuel, water, and gas densities over TOS, h
Bioenergy Technologies Office  

Progress on Reducing Biofuel Production Costs from CFP

Reduced modeled biofuel production costs by ca. $3/GGE since 2014 by improving carbon efficiency

*Targeted R&D on process optimization/durability and product diversification*

*24% 28% 36% 37% Carbon Efficiency to Fuels and Chemicals*

*Chemical Co-product Credits*

*Process Optimization and Durability*

Assessing Process Durability

**Standard Conditions**
- **Feedstock:** Loblolly Pine
- **Catalyst:** 0.5 wt% Pt/TiO₂
- **Pyrolysis Temperature:** 500 °C
- **Upgrading Temperature:** 435 °C
- **Catalyst Mass:** 100 g
- **WHSV:** 1.4 g biomass/gcat*h
- **Near Atmospheric Pressure**
- **Hydrogen Concentration:** 83%
- **Biomass:Catalyst Ratio:** 3

**Progress:** integrated experiments performed for 100+ reaction cycles reveal minimal impact on yields, oil-quality, and product composition

**Outcome:** improved confidence in catalyst and process durability, reduced risk for process model inputs, and support for technology transfer efforts

*Data gaps are from experiments performed under non-standard conditions*

**Conditions**

Feedstock: Loblolly Pine  
Catalyst: 0.5 wt% Pt/TiO₂  
Pyrolysis Temperature: 500 °C  
Upgrading Temperature: 435 °C  
Catalyst Mass: 100 g  
WHSV: 1.4 g biomass/gcat*h  
Near Atmospheric Pressure  
Hydrogen Concentration: 83%  
Biomass:Catalyst Ratio: 3-12

**Progress:** optimizing the size and shape of the catalyst support reveals improved deoxygenation activity and increased cycle length

**Outcome:** lower capital requirements, a $0.05/GGE reduction in MFSP, and improved operational efficiency
Catalyst characterization after reaction with forest residues revealed considerable potassium deposition at the leading edge of the catalyst bed.

Experiments performed with a 50:50 wt% blend of clean pine and forest residues for a cumulative time on stream of 32 h.

ICP-OES

- Potassium <100 ppm as prepared
- Phosphorous <50 ppm as prepared
- Iron 40 ppm as prepared
- Calcium 58 ppm as prepared

**Dark field STEM images and EDS maps indicate well-dispersed K on the surface of the post-reaction samples from the top of the bed.**

**Ongoing Research:**
Determine the impact of K on catalyst properties and performance.

**XPS Spectra of K 2p Region**
Confirm K deposition.
Progress: development of a new simulation framework that leverages DOE high performance computing capabilities for multiscale modeling to inform in-silico optimization and process scale up

Outcome: early identification of potential process disruption at the pilot scale due to thermal excursions during regeneration. Ongoing collaborative research targets alternative reactor designs to improve heat transfer capabilities at scale

Product Diversification
Expanding the Product Slate from CFP

- Catalytic Fast Pyrolysis
- Separation/Upgrading
- Thermal Recovery/WWT
- Hydrotreating
- Separations
- Carbonization
- Liquid Fuels
- Chemicals
- Materials
Valorizing the CFP Aqueous Waste Stream

Expanding product slate from CFP technology platform by developing separation strategies for chemical precursors

Separations Approach

Product Characterization


3wt% C
24 g/L
352 g/L

85-99 wt%
Bioinsecticides derived from CFP Bio-Oil

Fractions of CFP bio-oil exhibit activity as bioinsecticides, presenting an opportunity to improve sustainability in energy and food production sectors.

Extent of phenol alkylation appears to be correlated with mortality.
Early-stage results suggest that modifying the catalyst and process conditions enables the CFP product slate to be tuned towards olefins.

- Feedstock: Southern yellow pine
- Pyrolysis and catalysis temperature: 500°C
- Apparatus: Tandem micro-furnace pyrolyzer coupled to a GC-MS/FID
- Pressure: 115kPa
- B/C: 0.05
- Run in triplicate

Reduced Ga species (e.g., [Ga(OH)₂]⁺ and [GaH(OH)]⁺) appear to be responsible for improved olefin yield.

• **Designed resilience as a central theme** for emerging carbon conversion and management technologies

• **Critical Needs:**
  - Feedstock flexibility
  - Adaptive process design and control
  - Low conversion costs
  - Product tunability

• **Catalysis enables the development of versatile technology platforms** that meet these needs
Acknowledgements

Learn more about our research, our team and our capabilities at ChemCatBio.org

Contact Info: Joshua.Schaidle@nrel.gov
Thank you!
Recent Advancements in Catalytic Fast Pyrolysis for the Production of Fuels and Chemicals from Biomass

Joshua A. Schaidle, NREL
ePYRO 2021
April 13th, 2021