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DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review

New Technology for Hydroprocessing Bio-oils to Fuels

March 25, 2015
Bio-Oil Technology Area

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Goal Statement

- Goal: For hydrotreating bio-oils to fuel, demonstrate
  - Improved stability catalyst for the severe environment of hydrotreating
  - Ebullated bed reactor to address the complexity of bio-oil conversion

"Increased rates can also be achieved by better catalyst contacting to reduce diffusional limitations and reduce catalyst deactivation due to surface fouling. **An ebullated-bed reactor should be considered for hydrotreated biomass-derived oils**."

Baker, E.G. and D.C. Elliot **(1988)**. Catalytic Upgrading of Biomass Pyrolysis Oils In A.V. Bridgwater (Ed.), *Research in Thermochemical Biomass Conversion* (p 893). Netherlands: Springer.

Quad Chart Overview

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Timeline

- Award: 10/1/2011
- End: 9/30/2015
- Nearly complete

Barriers

- Barriers addressed
  - Tt-J Bio-oil upgrading to fuel
  - Tt-L Knowledge gaps in process
  - Tt-P Materials compatibility

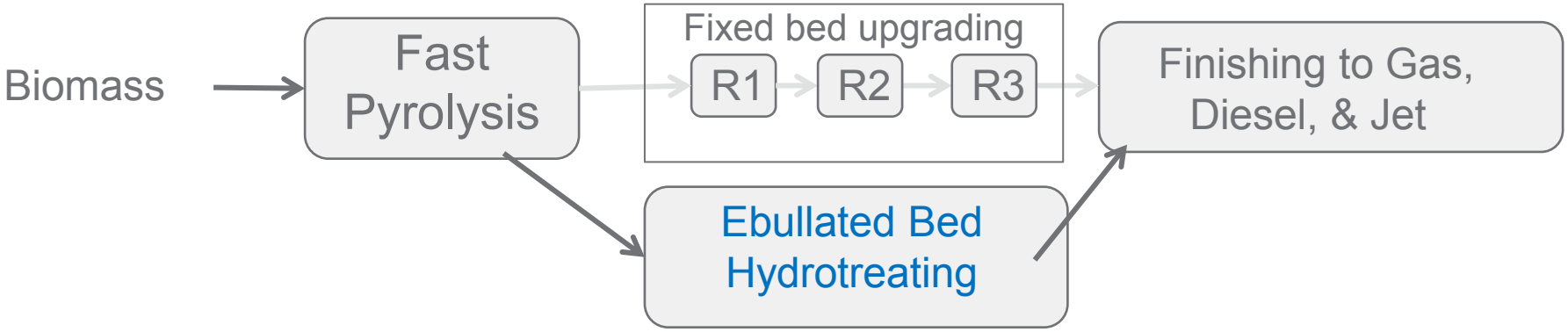
Budget

Peer Review FY10-12 Costs	Peer Review FY13 Costs	Peer Review FY14 Costs	Planned Funding (FY15-Project End)
$245,465	$202,803	$50,313	$1,001,419

Partners

- W.R. Grace (lead)
- PNNL
- VTT
- ORNL

1 - Project Overview



- Can a continuous ebullated bed upgrade bio-oil in a single step?
- Why an ebullated bed?
  - Handles some of the most difficult refinery feeds
  - Online catalyst replacement
  - Better hydrogen solubility and heat management
  - But, existing EB reactors are not designed for bio-oil upgrading
- Develop a stable catalyst for severe environment upgrading
  - Catalyst life is short in conventional hydrotreating
  - Existing EB catalysts are not compatible with bio-oil upgrading

2 – Approach (Technical)

- Bio-Oil Production : Fast pyrolysis of high quality bio-oil from wood and crop residue feeds at 20kg/h scale (VTT)
- Novel Support Development: Novel hydrotreating supports produced and screened in high throughput, micro-scale stability testing. (Grace and PNNL)
- Novel Catalyst Scale-up: Catalysts are formed/extruded at both lab (100 g) and pilot (1-5 kg) scale for stability and application testing (Grace)
- Ebullated Bed (EB) Testing: Scaled catalysts are performance-tested in EB reactor (~0.5 L catalyst volume) with actual bio-oil (PNNL)
- Corrosion Analysis: Performed both *in situ* and *ex situ* to evaluate required materials of construction for bio-oil ebullated bed systems (ORNL)
- Process evaluation: Techno-economic and lifecycle analyses to measure improvement over petroleum and fixed bed hydrotreating (PNNL, Grace)

- **Top potential challenges**
  - **Technical 1: reactor and process compatibility with bio-oil**
  - **Technical 2: balancing catalyst stability and activity requirements**
  - **Non-technical: reluctance of refineries to embrace biofuels**

2 – Approach (Management)

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- Project Management
  - Report progress to DOE in quarterly with quantifiable milestones
  - Progress reviewed in monthly managerial reviews within each organization, and results are shared in joint quarterly meetings
- Critical Success Factors:
  - Technical:
    - Demonstrate long life catalyst stable in severe upgrading (1000h)
    - Robust demonstration of an EB reactor with bio-oil
  - Market: Emergence of pyrolysis vs. other biofuels
  - Business: Competitive economics of overall route
- Success in this project will:
  - Introduce next-generation catalysts with improved net economics through longer life (widely applicable to many biomass upgrading routes)
  - Yield higher visibility of EB hydrotreating option for biomass

3 – Project Context

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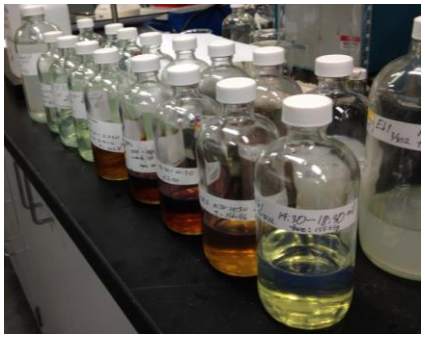
Prior accomplishments through FY2013:

- Bio-oil produced at pilot scale from wood and crop residue
- Completed severe environment support screening
  - Lowered support leach rate by up to 70%
- Performed pilot scale extrusion of 9 candidate supports
- Completed 9 ebullated bed tests, longest time on stream of 50h
- Demonstrated hydrocarbon product at ~2wt% oxygen
- Preliminary TEA and LCA. Drivers are catalyst maintenance and yield



3 – Catalyst Development

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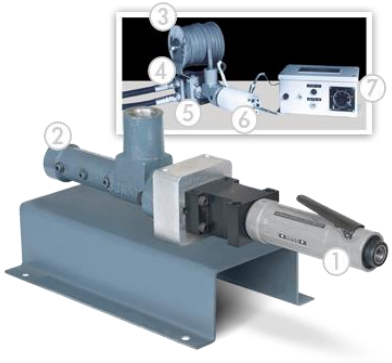
Objective: Develop a stable catalyst for severe environment upgrading

Accomplishments:

- Developed novel support that resists high acid, high temperature, liquid water environment, and kinetic environment of EB
- Also has the positive characteristics of oxide support
- 8 different catalyst formulations prepared on that support



Impact: Catalyst has broad application for high temperature, liquid water, and strong acid environments, which frequently occur when upgrading biomass derived compounds to fuels or chemicals

3 – Reactor Progress

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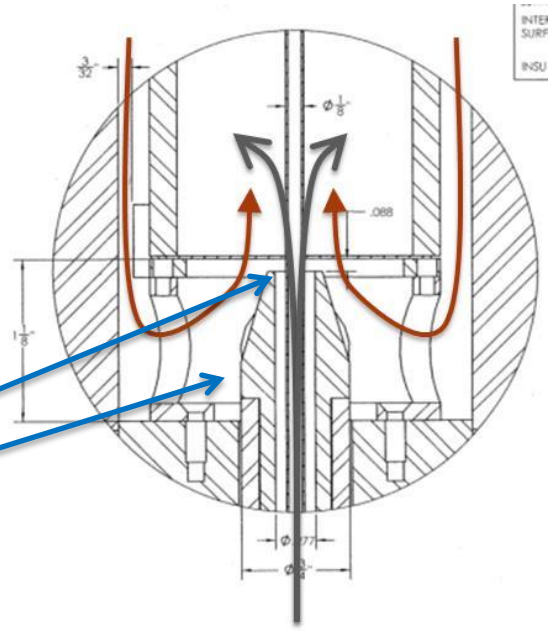
Objective: Can a continuous ebullated bed upgrade bio-oil in a single step?

Accomplishments:

- Total of 18 campaigns, wide range of operating strategies and mods
- Modifications increased sustained operation out to 100 hours
- 80-90% of bio-oil converts to high quality product
- Remaining bio-oil forms segregated phase, impairing operation

- Process modifications
  - Injector temperature
  - Catalyst/mobile phase temperature
  - Liquid recycle rate
  - Reduced thermal gradient
  - Increased thermal gradient
  - Co-solvent injection (multiple solvents tested)
  - Catalyst type
- Physical modifications
  - Injector/catalyst interface
  - Catalyst bed depth



3 – Insights on bio-oil in an EB

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Findings:

- Upgrading bio-oil to hydrocarbon in a single stage is difficult
  - Thermal instability causes polymer formation, mitigation affects heat balance
  - Bio-oil upgrading intermediates phase separate from both bio-oil and the final fuel/water product
  - There are at least 2 separable liquid phases in bio-oil HDO intermediates that are both separable from the fuel product.
  - Multiphasic flow is disruptive to the EB

- These challenges are not common to petroleum EB applications
  - Thermal stability window for petroleum is wider
  - Feed/product insolubility is not common in petroleum upgrading
  - Heavy polymer analogue (asphaltene) formation is avoided

Opportunity: Modifying an EB for part of the conversion process may avoid these issues and use the advantages that an EB provides.

- Transitioned to mitigation plan: Fixed bed upgrading to evaluate the performance of the novel catalyst

3 – Upgrading Progress

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Objective: Evaluate novel catalyst performance in fixed bed upgrading

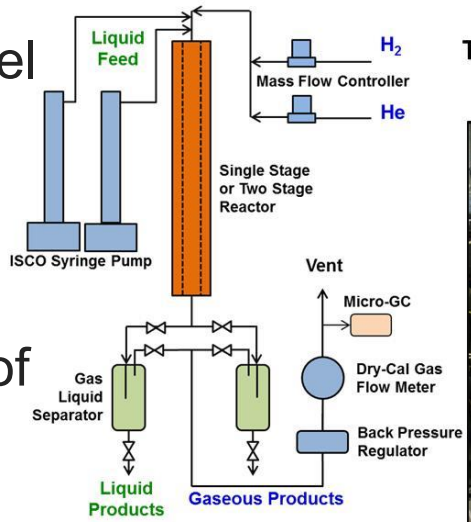
Accomplishments:

- Total of 9 campaigns performed
- Evaluated 8 different catalysts versus baseline technology
- Novel catalyst variant tested in both hydrotreating and hydrocracking beds

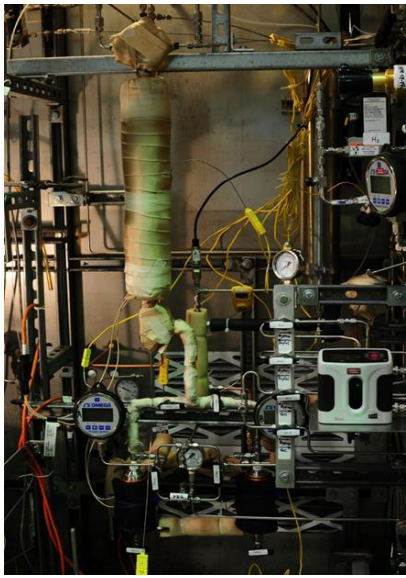
- First bed: RuS/novel
- Second bed: promoted-MoS/novel
- Run length: 100h per catalyst
- Feed: baseline pine bio-oil

- Initial results demonstrate that product quality is similar to state of the art catalyst under identical conditions

- Detailed results including lifetime estimate are pending



Two-stage reactor



4 – Relevance, 5 – Future Work

- To the BETO goal of developing enabling bioenergy technology
  - Catalyst development for upgrading, a large cost driver to bio-oil upgrading
  - A broadly applicable catalyst stable to the severe environment typical to liquid biomass conversion
  - Advancing the knowledge of the complex multiphasic nature of bio-oil upgrading
  - Assessment of unique upgrading technology
- Applications of the Expected Outputs
  - Use of novel catalyst support to extend lifetime of bio-oil upgrading
  - Application of this support in other severe environment systems
  - Use of ebullated bed upgrading as a part of biomass refining to fuels
- Technology Transfer
  - Catalyst prepared on industrially relevant pilot tools
  - Currently capturing IP
  - Existing Grace customers have expressed interest in project outcomes
- Project is wrapping up

Summary

- Developed a catalyst for upgrading bio-oil that is stable in severe environments
- Completed initial assessment of single step EB upgrading
  - Produces a high quality fuel
  - Concept needs modification for sustained operation
- Contributed to the understanding bio-oil conversion, intermediate characteristics, and technology needs.
- Project is nearly complete

Additional Slides

Responses to Previous Reviewers' Comments

"Concerned about catalyst screening. It is not clear to me what criteria are being used because of proprietary concerns."

- We are looking at it similarly to traditional alumina support in terms of strength and porosity, combined with greatly reduced rate of leaching in acidic env.

"This appears to be a technically sound approach with a fair chance of success, although the hurdles of catalyst activity maintenance and corrosion remain."

- We agree that those are the 'killer variables,' along with stable operation of the reactor and its complex three- or four-phase dynamic mixture.