

DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review

Bio-oil Upgrading with Novel Low Cost Catalysts

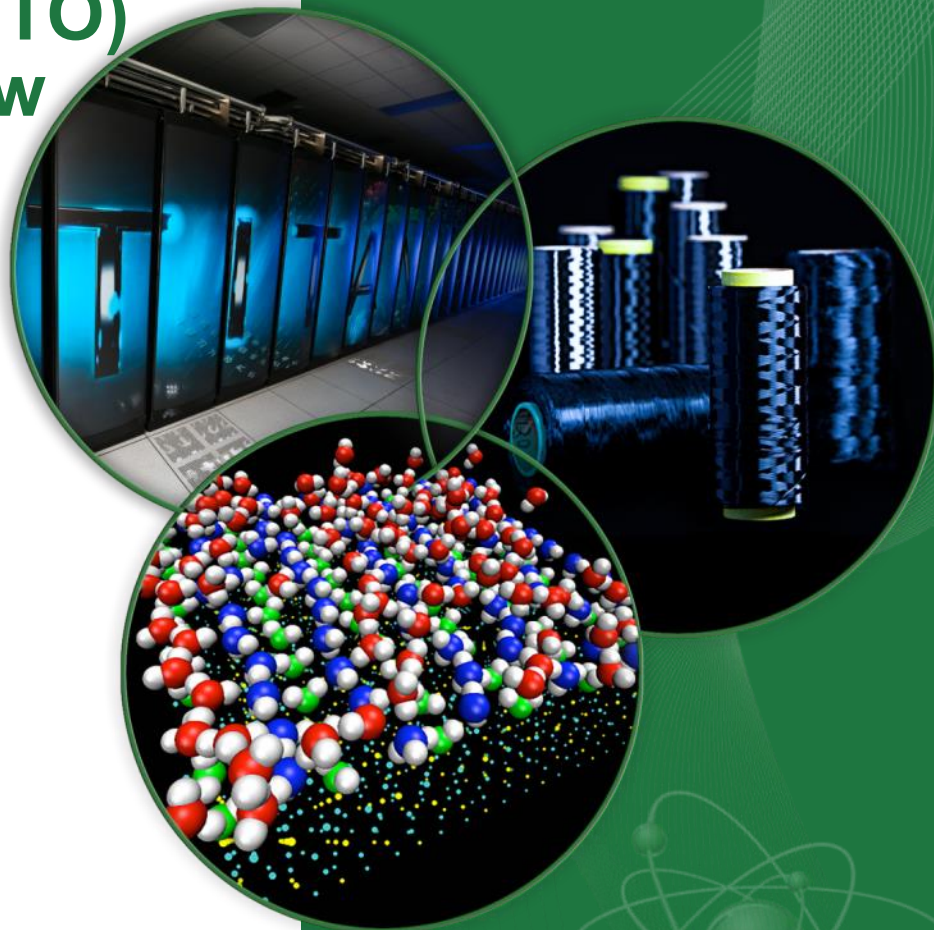
March 24, 2015

Bio-oil Technology Area Review

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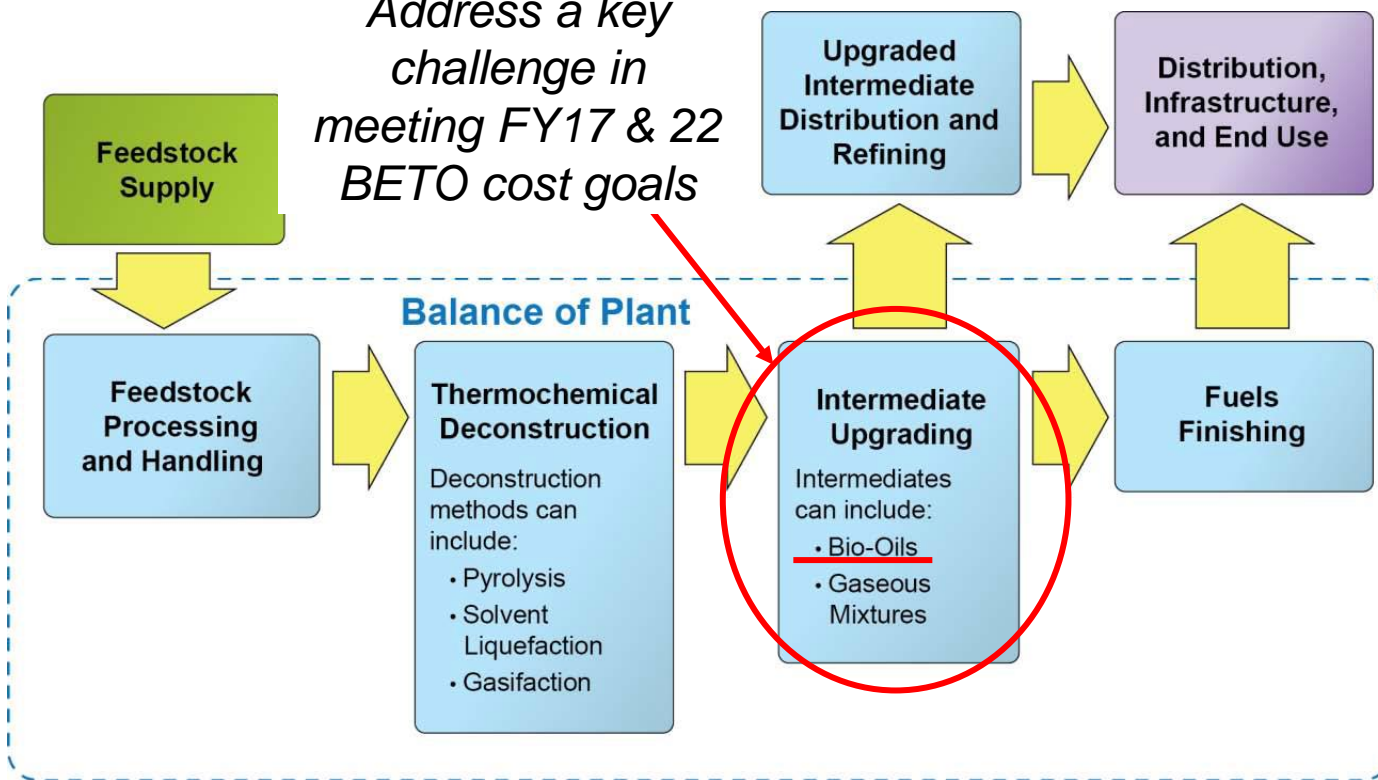
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Goal Statement

- Develop novel catalysts effective for bio-oil intermediate upgrading that are **less expensive and more durable** than the state of technology (SOT)

Address a key challenge in meeting FY17 & 22 BETO cost goals



Commercially viable technologies available for U.S. industry for producing renewable gasoline, jet & diesel from biomass

Thermochemical conversion process steps for biomass to biofuels

DOE Bioenergy Technologies Office Multi-Year Program Plan (MYPP), November 2014.

Quad Chart Overview

Timeline

- Project start date: October 1, 2012
- Project end date: September 30, 2017
- Percent complete: 50%

Budget

| | Total Costs FY 10 – FY 12 | FY 13 Costs | FY 14 Costs | Total Planned Funding (FY 15) |
|-----------------------------|---------------------------|-------------|-------------|-------------------------------|
| DOE Funded | \$0 | \$463,765 | \$456,557 | \$580,000 |
| Project Cost Share (Comp.)* | N/A | N/A | N/A | N/A |

Barriers

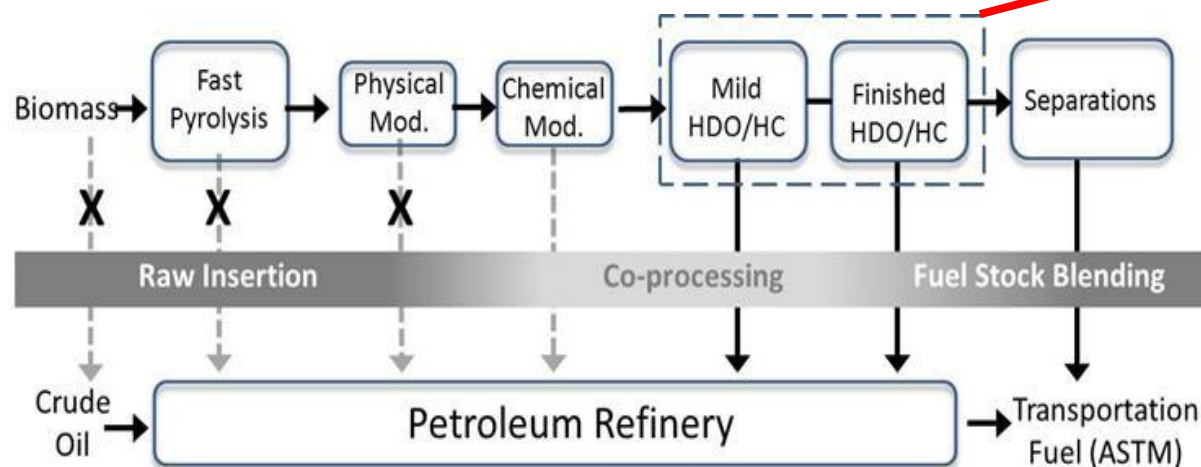
- Tt-H. Bio-oil intermediate stabilization
- Tt-J. Catalytic upgrading of bio-oil intermediates to fuels and chemicals
- Tt-L. Knowledge gaps in chemical processes

Partners

- Pacific Northwest National Laboratory
 - WBS: 2.3.1.302
 - Alan Zacher (PI)
 - Reactor evaluation with real bio-oils
 - Techno-economic analysis (Sue Jones)
- Center for Nanophase Materials Sciences
 - DOE SC User Facility at ORNL
 - Viviane Schwartz

1 - Project Overview

**focus of this work:
hydroprocessing of
fast pyrolysis bio-oil**



Zacher, et al., Green Chemistry 16 (2014) 491-515.

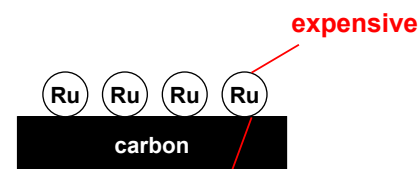
- SOT: multi-step catalytic processes**

- 1st step: stabilization (mild hydrogenation)**

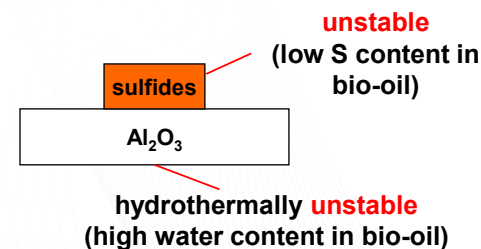
- Low temperature (150-250 °C)
- Ru/C type catalysts

- 2nd step: deep hydrogenation and hydrocracking**

- High temperature (350-400 °C)
- Sulfided Ni(Co)Mo/Al₂O₃ type catalysts



**weak metal-support interaction (leaching)
under reducing conditions**

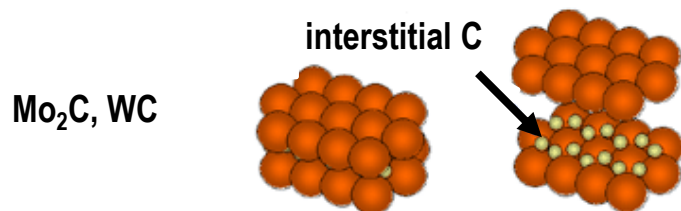


**coking ubiquitous, but
regeneration proven difficult**

Need for novel catalysts “compatible” with bio-oil & regenerable

2 – Approach (Technical): Develop novel bio-oil catalysts based on transition-metal carbides

- Transition metal carbides exhibit precious-metal-like catalytic properties (Mo_2C - Ru, WC - Pt...)

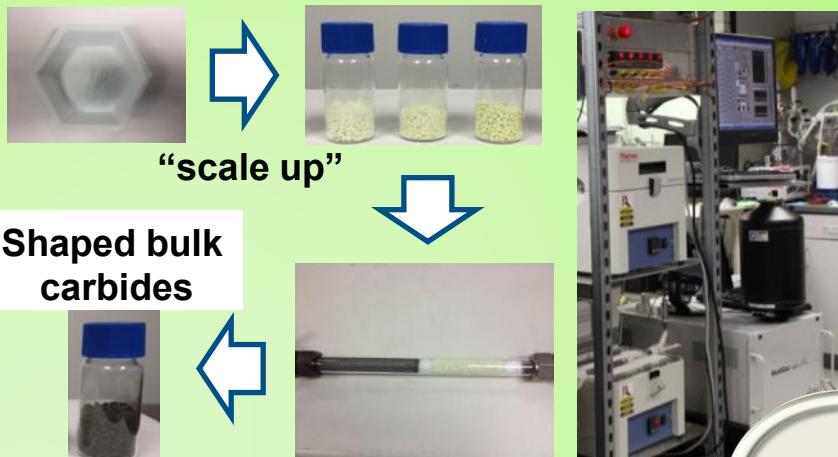


Theory: C insertion to parent metal lattices makes metal electronic structures closer to those of precious metals

- Carbides are active under petroleum hydrotreating conditions
 - No need for sulfiding agents (cf. CoMo/ Al_2O_3)
- Carbides can be prepared with high surface area
 - No need for supports to disperse active phases (cf. Ru/C, CoMo/ Al_2O_3) => mitigate issues associated with supports
- Performance unproven in real bio-oil upgrading involving hot aqueous-phase & oxygenate-rich environments
 - Catalytic reactivity
 - Stability (hydrothermal, oxidation, coking)

2 – Approach (Technical)

Catalyst design & synthesis



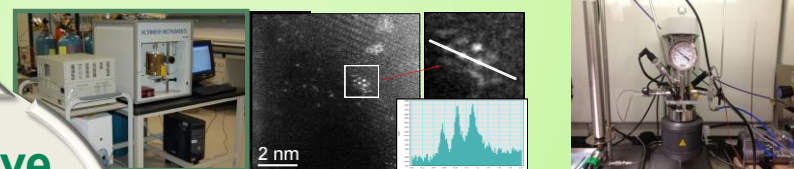
Characterization



- Understand correlations between synthesis conditions, structures & performance
- Leverage SC & univ. capabilities

Micro-scale analysis

Model compound study



Iterative process

Reactor evaluation with real bio-oils



- Activity
- Selectivity
- Stability
- Regenerability

2-stage hydrotreater



Techno-economic analysis



- Assess cost reduction potential
 - Carbides vs. Baseline
 - Catalyst cost, regeneration interval, H₂ consumption, oil yield
- Input for project decision making
 - Research priority
 - Go/No-Go decision

2 – Approach (Management)

- **Critical success factors**

- Demonstration of large-scale, long-term operability in real bio-oil hydroprocessing to hydrocarbon fuels
- Effective coordination with other areas including feedstock, separation, reactors, techno-economic analysis, and end use

- **Challenges to be overcome**

- Limited information and industry experience available in implementing carbide catalysts in bio-oil conversion processes
- Need to understand and control the impact of and interplay among multiple parameters to fully assess and harness the catalysts' potential in a timely manner

- **Key project management tools**

- Meetings and updates between ORNL and PNNL for timely feedback and coordination
- Milestones and Go/No-Go decision points in line with BETO MYPP FY17 validation timeline and performance targets

3 – Technical Accomplishments/Progress

| Milestone | Planned Completion Date | Status |
|--|-------------------------|--------|
| Synthesis & characterization of Mo & W carbides with controlled structures (12 formulations) | Mar 2013 | √ |
| Perform initial evaluation of upgrading performance (12 formulations, model & real bio-oils) | June 2013 | √ |
| Perform in-depth kinetic study (4 down-selected formulations, model bio-oil) | Sept 2013 | √ |
| Develop a method of large-scale synthesis of bulk carbide catalyst beads | Sept 2013 | √ |
| Synthesize & characterize at least six formulations of W and Nb carbides | Dec 2013 | √ |
| Establish if bulk carbide pellets can be optimized for long term testing in a packed bed mini pilot reactor | Mar 2014 | √ |
| Evaluate down-selected catalysts for bio-oil hydrotreating performance (activity, degree of deoxygenation, hydrogen consumption and stability) | June 2014 | √ |
| Assess strategies for mitigating catalyst deactivation and develop a protocol for catalyst regeneration | Sept 2014 | √ |

3 – Technical Accomplishments/Progress

| Milestone | Planned Completion Date | Status |
|---|-------------------------|-------------|
| Assess the impact of promoter loading on the hydroprocessing performance of Mo carbides | Dec 2014 | √ |
| Demonstrate that Mo carbide catalysts have cost advantage over the FY14 SOT by at least 10% in modelled cost (Go/No-Go) | Mar 2015 | in progress |
| Assess the impact of porosity on the hydroprocessing performance of Mo carbides | June 2015 | |
| Determine coking/decoking characteristics of Mo carbides as a function of promoter loading and porosity | Sept 2015 | |
| Demonstrate that Mo carbide catalysts have cost advantage over the FY15 SOT by at least 10% in modelled cost are hence a viable alternative for the FY2017 validation | Sept 2016 | |
| Demonstrate that Mo carbide catalysts have cost advantage over the FY15 SOT by at least 30% in modelled cost (Stretch) | Sept 2016 | |
| Demonstrate that Mo carbide catalysts have cost advantage over the FY16 SOT by at least 10% in modelled cost | Sept 2017 | |
| Publish a technical report summarizing the project results and recommendations on future directions for carbide catalysts in the context of bio-oil pathways | Sept 2017 | |

3 – Technical Accomplishments/Progress

- **Selected Mo (vs. W & Nb) system for further optimization through synthesis, characterization and model compound study**
- **Began optimizing bulk Mo carbide synthesis**
- **Evaluated Mo carbides in 2-stage hydroprocessing of real bio-oils**
- **Performed initial techno-economic analysis**
- **Initiated long-term stability evaluation and regenerability with real bio-oils**
- **Started generating fundamental insights into carbide structure-performance relationships**

Identified that several properties of Mo carbide are potentially advantageous for bio-oil hydroprocessing & paths for optimization

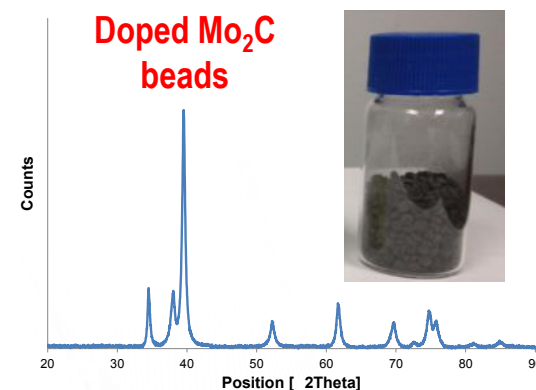
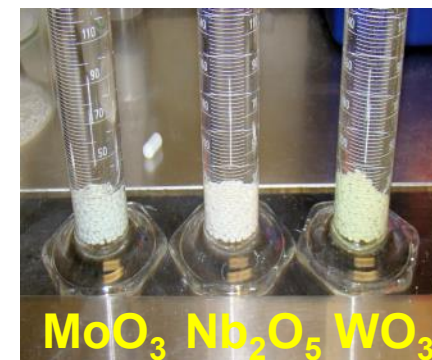
Continued bulk carbide formulation, characterization & model compound study

- **50+ oxide precursor beads synthesized**

- Variable: oxide metal type (Mo, W, Nb), oxide loading, dopant type, binder type and loading

- **70+ bulk carbide beads synthesized & characterized**

- Variable: oxide precursor type, carburization temperature, post-synthesis treatment
- Analysis tools: XRD, surface area, porosity, XRF, ICP, XPS, microscopy, TGA, TPR/TPO, model compound upgrading (furfural, acetic acid, guaiacol)



Mo carbides selected for optimization
easier synthesis & property control
better performance in model compound conversion

Began optimizing bulk Mo carbides

- **Goal**

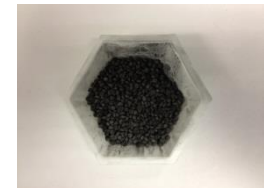
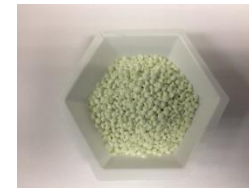
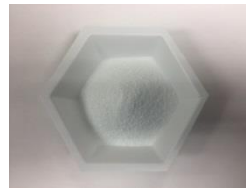
- Enhanced performance: activity, coking & oxidation resistance, regenerability
- Ability to control catalyst structures: mechanical strength, porosity, dopant loading

Developed bulk carbide bead synthesis method enabled the real bio-oil testing under relevant conditions

(no commercial product available)

- **Synthesis variables**

- Dopant type & loading
- MoO₃ loading
- Binder type & loading



- **Detailed characterization & model compound study guided sample selection for real bio-oil study at PNNL**

- 1st series (BC01-04): assess the impact of dopant type
- 2nd series (BC05-08): assess the impact of dopant loading
- 3rd series (BC09): study the impact of catalyst loading & regenerability

↑
catalyst code

Performance of Mo carbides evaluated with real bio-oil in 2-stage hydrotreater

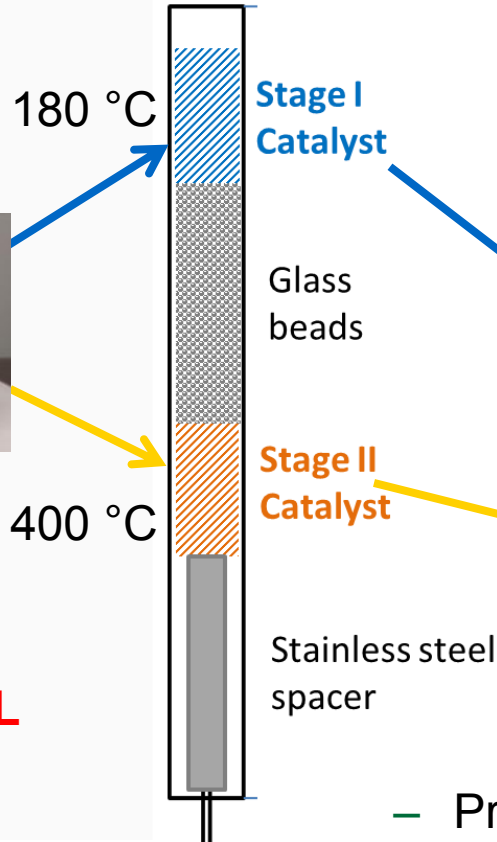
- 9 Mo carbide formulations (BC01-09) studied with raw bio-oil (pine wood, conventional fast pyrolysis)

Two-stage reactor (40 ml)

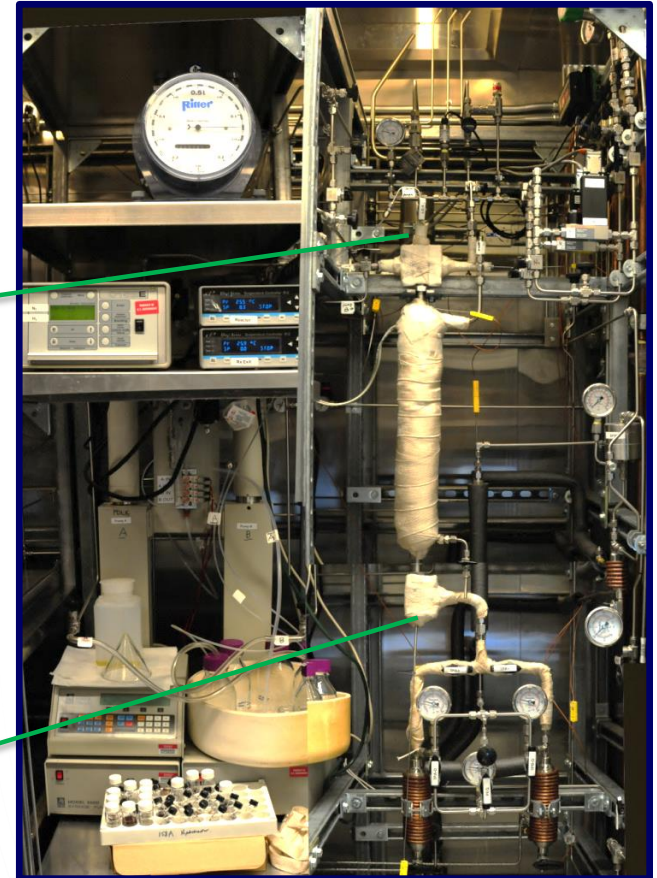
Baseline
sulfided
Ru/C
+
sulfided
promoted
Mo/Al₂O₃



vs.



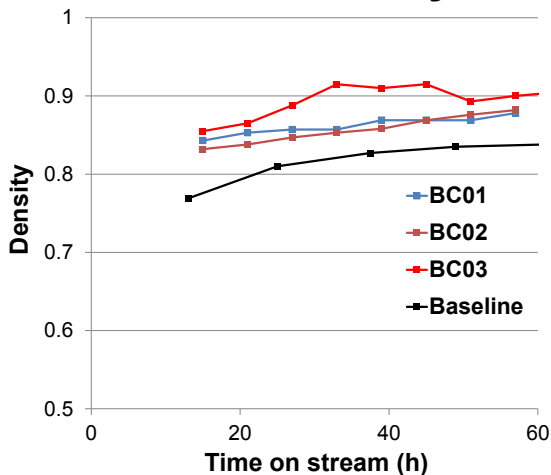
work done at PNNL



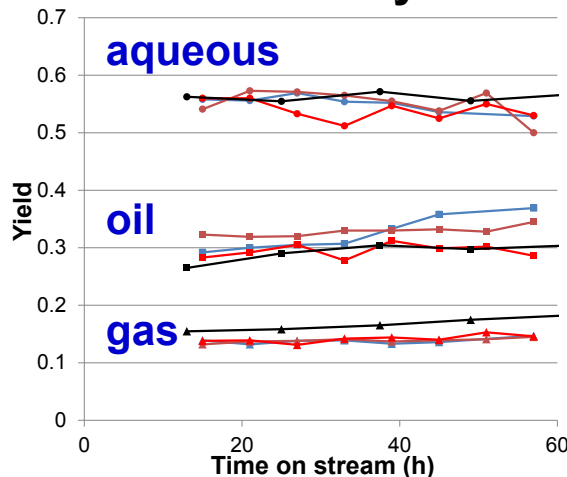
- Pressure: 1750 psi
- H₂/bio-oil: 1700 cc/cc
- WHSV : 0.146 g/g_{cat}/h

Obtained first of a kind data on bulk Mo carbides in hydroprocessing raw bio-oil

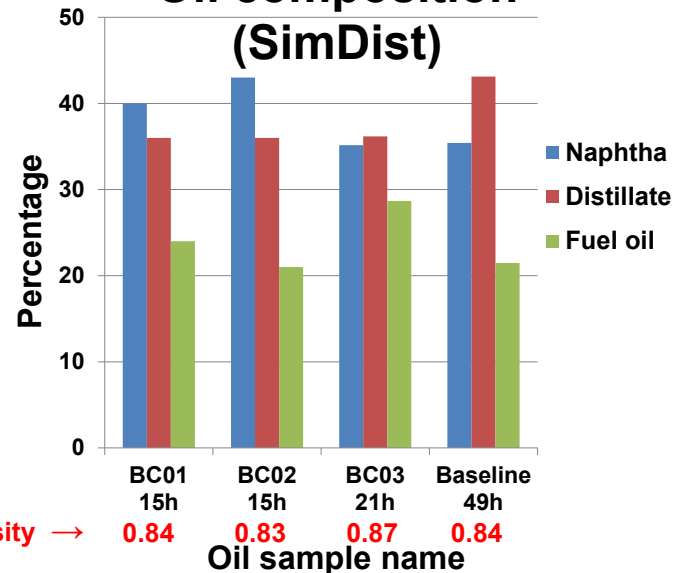
Oil density



Product yields



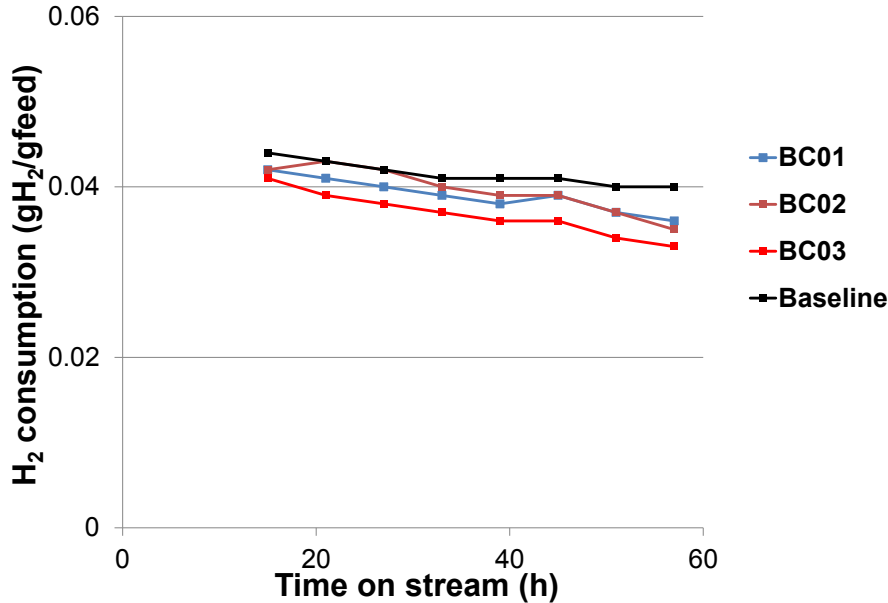
Oil composition (SimDist)



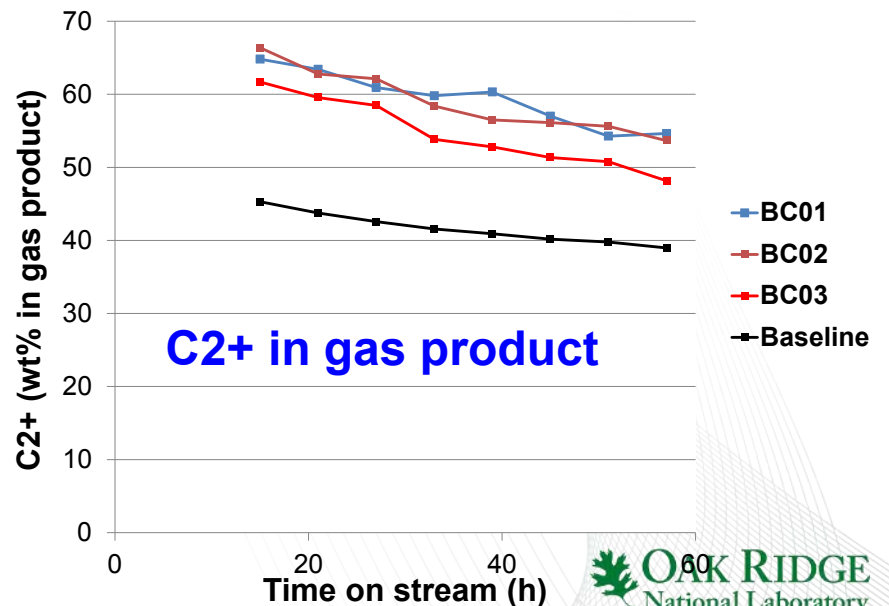
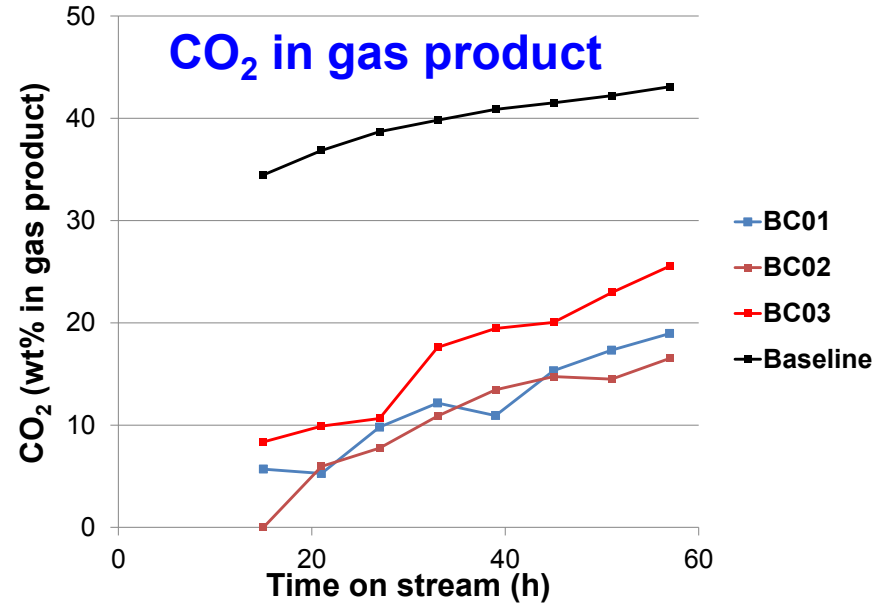
- **Overall Mo₂C can achieve performance similar to Baseline!**
 - Oil density (degree of deoxygenation: activity)
 - Global product yields
 - Oil composition (fuel product distribution)
- **Higher activity for Baseline vs. slightly higher oil yield for Mo₂C**
- **BC03 less efficient than the other Mo₂C samples (see oil density)**
 - Highlight possibility of enhancing Mo₂C performance by controlling formulation and structure

Carbides presented potentially advantageous properties: better H and C economy

H₂ consumption



- Less H₂ consumption than Baseline
- Carbides retain more gas-phase C in HCs (C1-C5 alkanes) than as CO₂

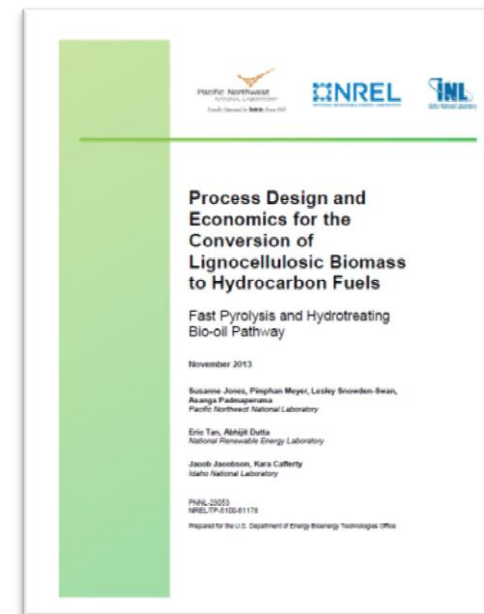


Techno-economic analysis

work done at PNNL

- **TEA performed to assess cost reduction potential of carbide catalysts**

- PNNL performance and cost models being updated with carbide catalyst results
- Data derived from PNNL 40 ml hydrotreater system
- Results being prepared for Go/No-Go decision (3/31/15) comparing the carbide catalyst performance to that reported in the MYPP

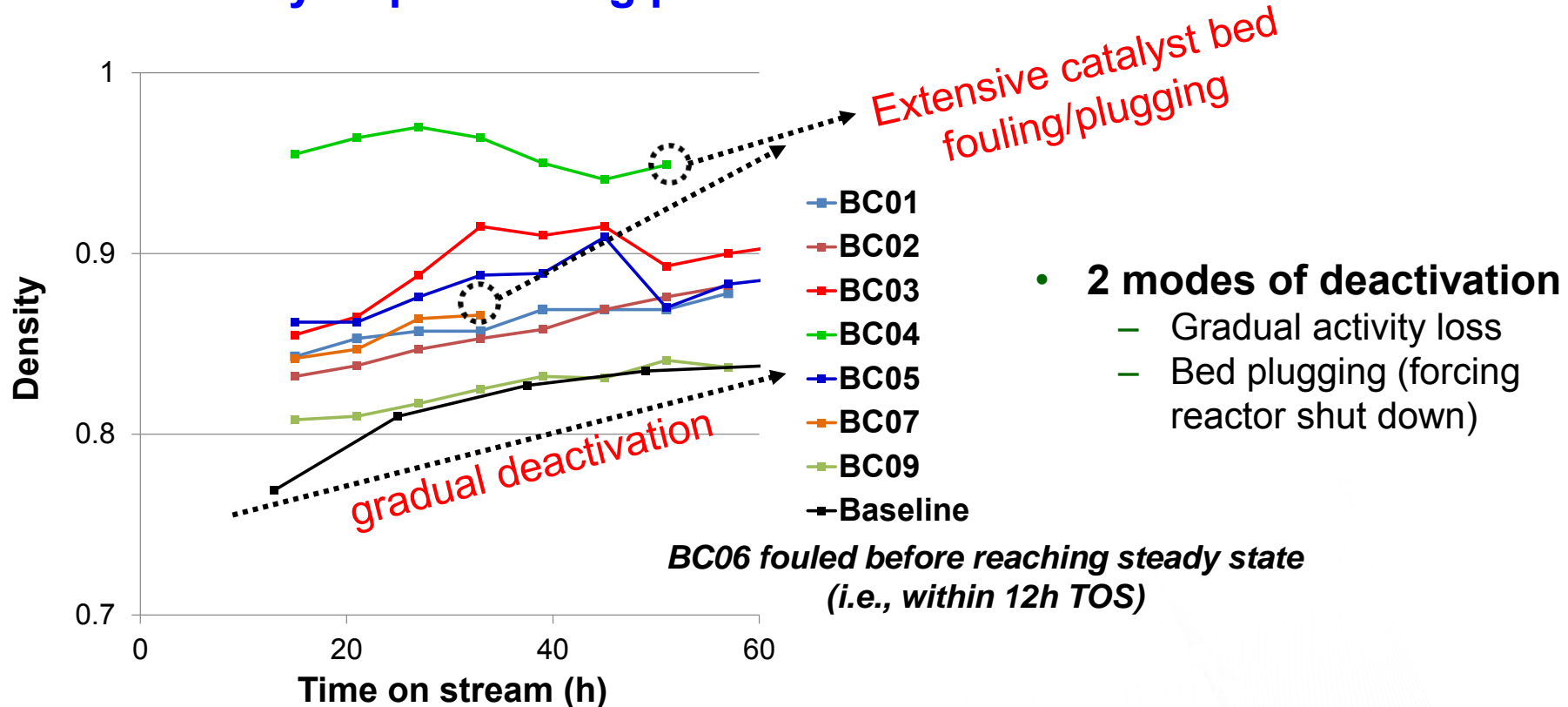


- **Key cost drivers for carbide catalysts**

- Potential advantages: no precious metal, no sulfiding agent, less H₂ consumption, less carbon as CO₂
- Weakness: less active
- Recommended research areas
 - Enhance activity
 - Confirm regenerability & develop regeneration strategies

Carbide stability shown sensitive to formulation

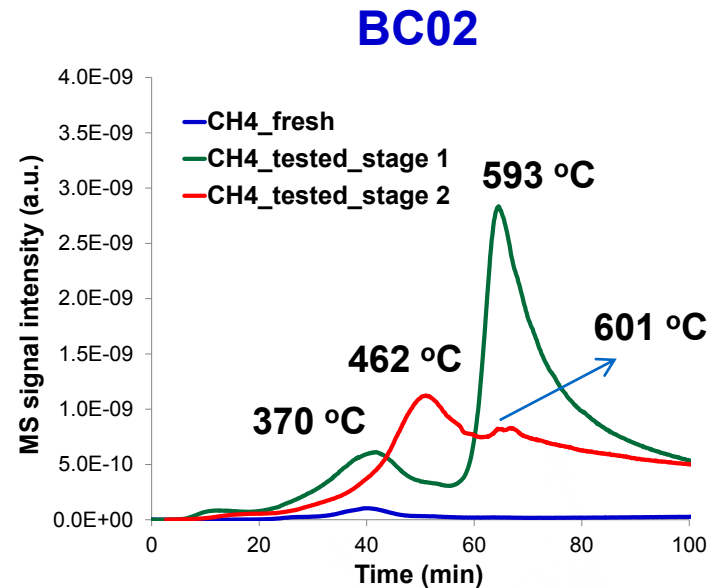
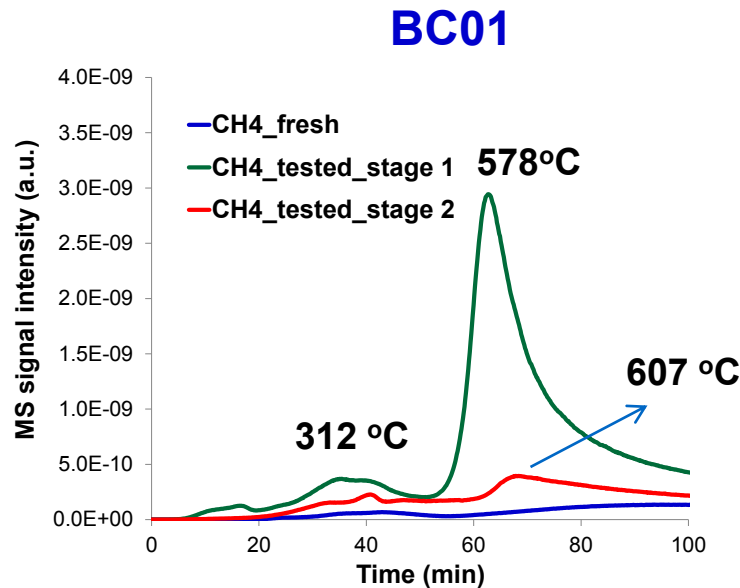
Hydroprocessing performance with time on stream



- **Bed plugging occurred during 60-h run only for some formulations**
 - BC04 of BC01-04 series (dopant type)
 - BC06 & 07 of BC05-08 series (dopant loading)
- **Elucidating structure-stability relationship could help extend the length of operation (work in progress)**

Coking appears to be a major deactivation mechanism

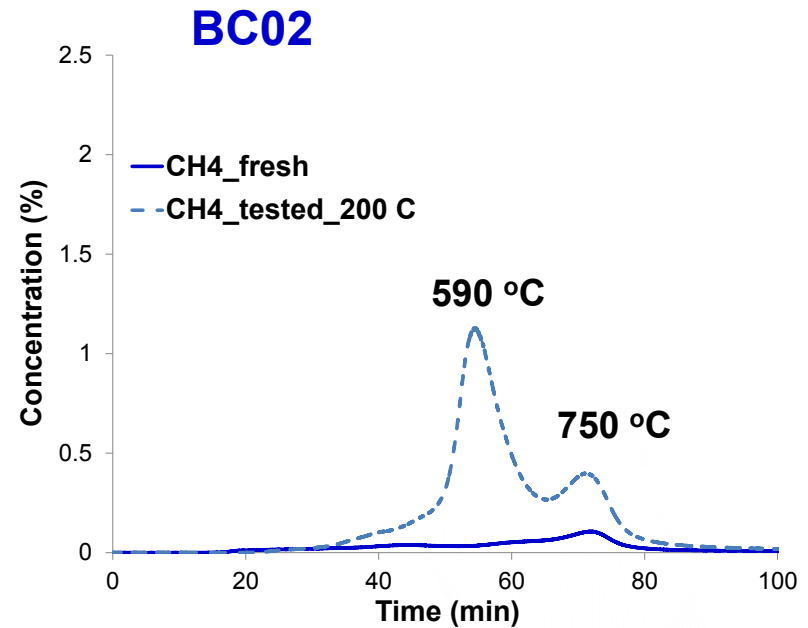
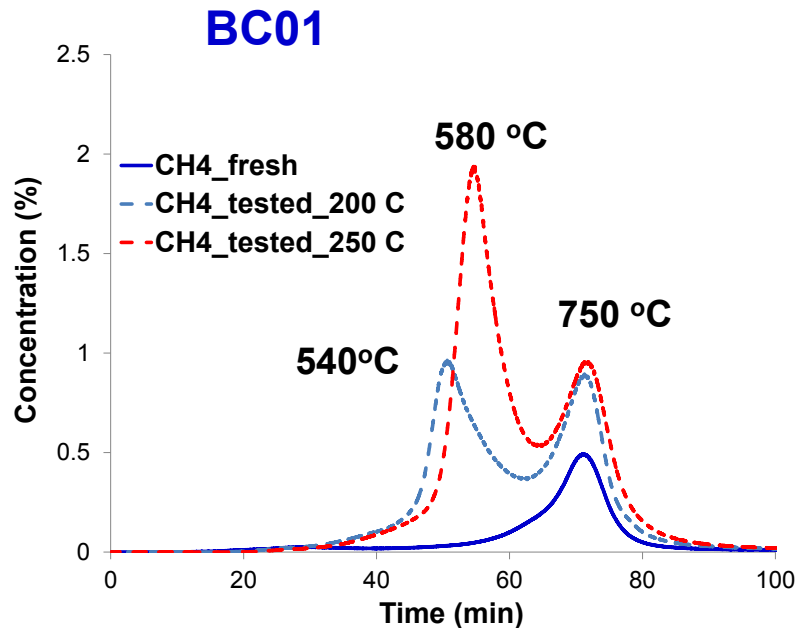
TPR (temperature programmed reduction) profiles before and after 2-stage hydroprocessing of **real bio-oil**



- **Carbon deposits more significant in Stage 1 than Stage 2**
 - Stage 1 “protects” Stage 2
- **BC01 seems to be less prone to coking than BC02**
 - Less CH₄ from Stage 2
- **Deposited C quite reactive => possibility of regeneration with H₂**
 - Leading to extended catalyst life & reduced conversion cost

Characterization further supports the possibility of decoking via reduction

TPR profiles before and after hydroprocessing of **model bio-oil** (furfural, acetic acid, guaiacol in water) in a batch reactor



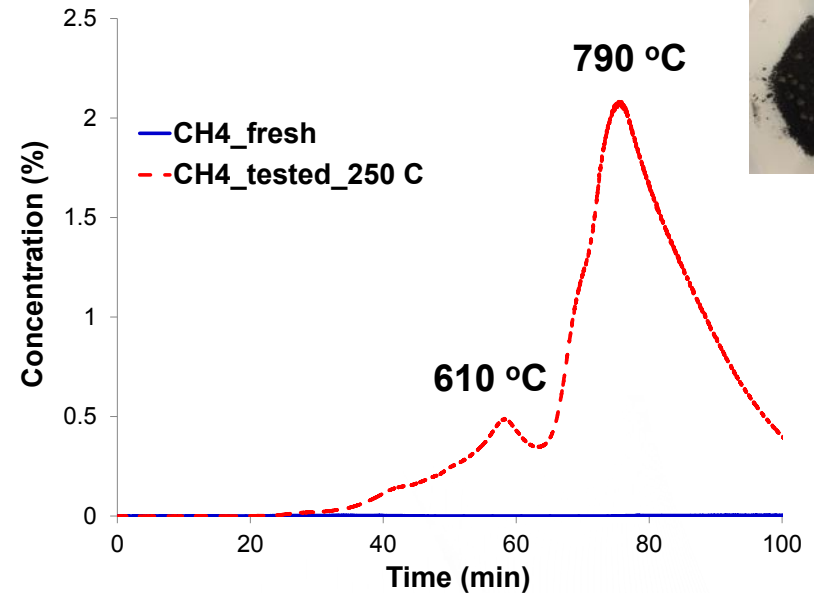
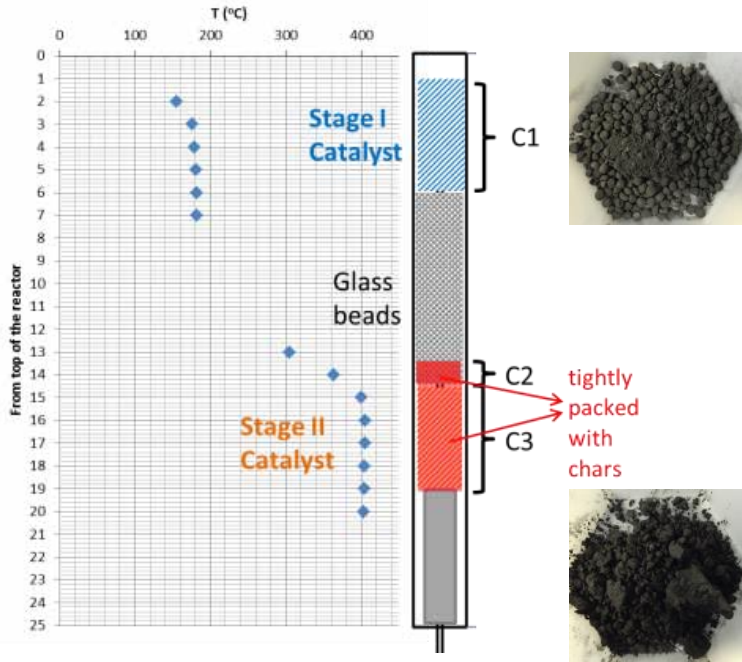
- **Two types of coke deposits evidenced by H₂ treatment**
 - “Reactive” carbon (530-570 °C)
 - “Refractory” carbon (740-760 °C)
- **Build up of reactive C more important than that of refractory C**

Regeneration needs to be initiated before catalyst-bed fouling (plugging)

Bed fouling location during **real bio-oil** upgrading

BC04

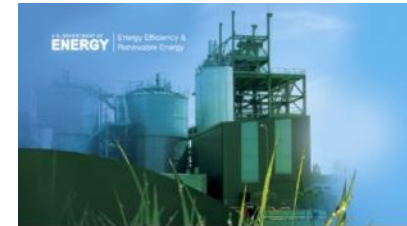
TPR profiles before and after hydroprocessing of **model bio-oil** in a batch reactor



- **Bed plugging makes in situ regeneration difficult**
 - Large pressure drop => restricted gas flow
 - Mainly “refractory” carbon (deposited on catalysts & free carbon/char)
- **High temperatures needed to remove refractory carbon can compromise carbide structure**

4 – Relevance

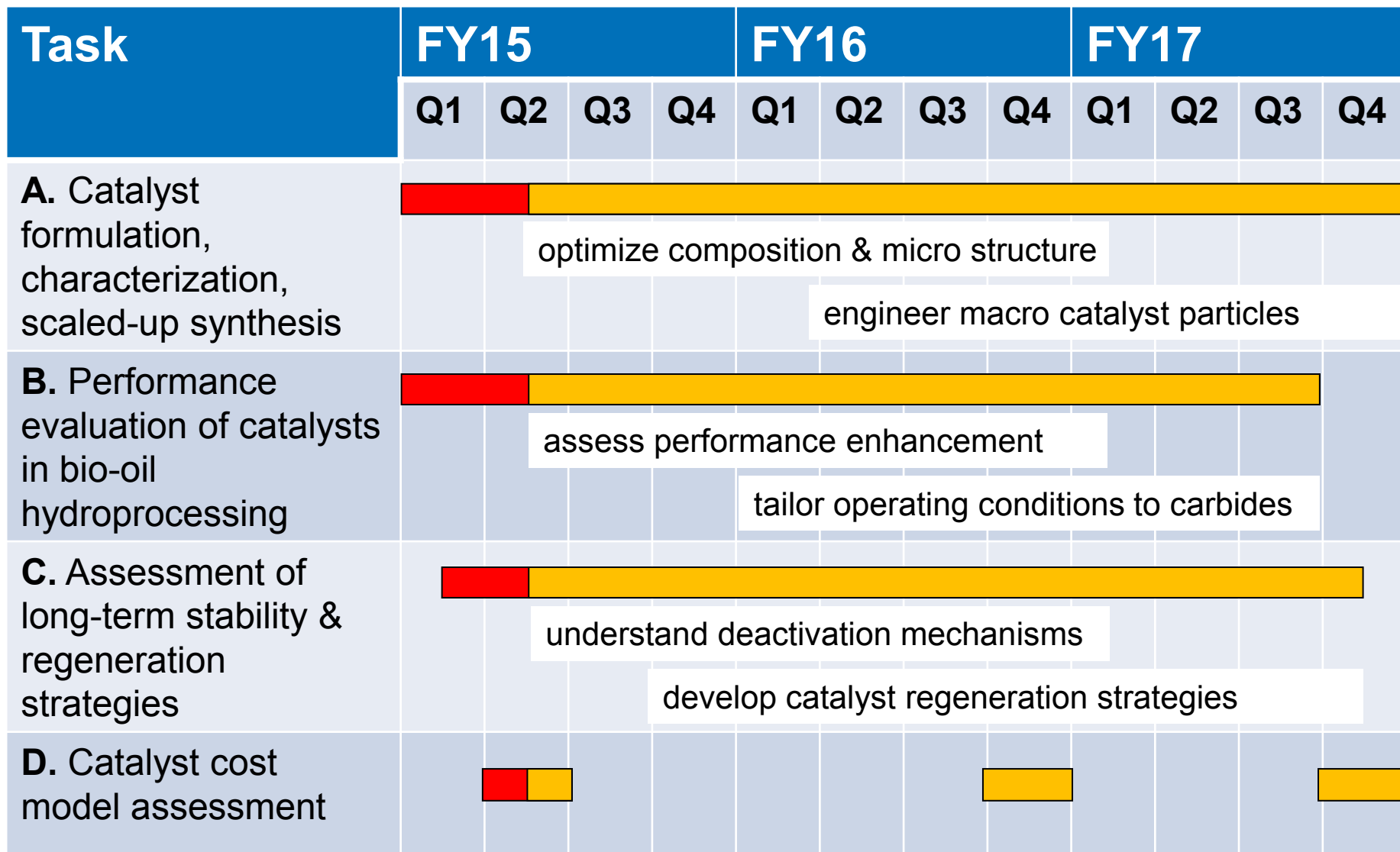
- **Project outcome (novel catalysts) directly contributes to meeting the DOE thermochemical conversion R&D goals**
 - **Commercially viable technologies for converting biomass into renewable gasoline, jet and diesel**
 - **BETO performance goal (nth plant modeled cost)**
FY17: \$2.50/GGE of conversion cost
 - **Project goal**
FY17: 30-50% catalytic upgrading cost reduction potential demonstrated vs. SOT
- **Research addresses critical techno-economic barriers**
 - **High conversion cost especially due to limited catalyst durability**
 - **Pursuing alternatives to SOT catalysts de-risks bio-oil technology**
- **IPs being developed, protected and disseminated (patents, publications, presentation etc.) and industry collaboration opportunities being pursued to maximize the impact on the bioenergy industry**



5 – Future Work

- **Optimize Mo carbide composition and micro-structure**
 - Enhance activity & durability
 - Variable: dopants, Mo/C ratio, surface area, porosity
- **Engineer catalysts particles at macro-scale**
 - Enable large-scale synthesis, evaluation, and validation
 - Option: existing gelling method, use of supports or substrates
- **Continue performance evaluation in hydroprocessing**
 - Monitor performance enhancement being achieved
 - Tailor operating conditions (T, P, catalyst combination)
- **Develop catalyst regeneration strategies**
 - Extend the length of catalyst operability
 - Variable: gas composition, temperature, duration, frequency
- **Techno-economic analysis**

5 – Future Work



 completed  remaining

Summary

• Overview

- Project develops novel catalysts effective for bio-oil hydroprocessing that are less expensive and more durable than the state of technology

• Approach

- Develop catalysts specifically tailored to the requirements of bio-oil hydroprocessing
- Optimize carbides as practical catalysts guided by fundamental characterization and analysis at ORNL and real bio-oil evaluation and techno-economic analysis at PNNL

• Technical Accomplishments/Progress/Results

- Performance of Mo carbide catalysts assessed via 2-stage hydroprocessing of real bio-oil and techno-economic analysis
- Potential advantages of Mo carbides identified: less expensive, regenerable, lower H₂ consumption, lower CO₂ formation, higher oil yield
- Micro-scale characterization continued enabling further development of synthesis methods

• Relevance

- Project addresses critical technical barriers (BETO MYPP) to the development of commercially viable thermochemical conversion technologies: need for lower cost and more durable catalysts

• Future Work

- Optimize catalysts and reactor operating conditions to enhance catalyst activity and durability
- Elucidate deactivation mechanisms and develop mitigation strategies

• Status

- 2013: carbide synthesis method developed & catalyst evaluation with model compounds started
- 2015: carbides evaluated with real bio-oils and initial techno-economic analysis done

Additional Slides

Responses to Previous Reviewers' Comments

- Mo & W are expensive metals, especially as unsupported catalysts, so there should be some work to understand if those metals can be easily recovered & recycled when the catalysts are spent.

Answer: We agree that metal recovery is an important aspect of catalyst development and conjecture that metal recovery from bulk Mo and W carbides could be relatively straightforward (e.g., via oxidation back to precursor oxides) in contrast to the more conventional supported catalysts. The project is at TRL2-4 focusing on demonstrating and proving the performance of carbides as bio-oil upgrading catalysts. We plan to investigate this topic in a more systematic way, if the project outcome warrants further development beyond TRL4.

Responses to Previous Reviewers' Comments (cont.)

- There seems to be a fundamental weakness in this work. It focuses on hydrotreating of light oxygenates. Hydrotreating of acetic acid will indeed reduce the acid#, but it only produces low-value ethane. And furfural and guaiacol are not acidic, and hydrotreating them will consume substantial hydrogen. This does not seem to be the most effective approach to stabilization & upgrading.

Answer: Since the last review, our carbide catalysts were evaluated with real bio-oils and one of the potential advantages observed was reduced H₂ consumption compared to Baseline catalysts (Ru/C + sulfided catalysts). The hydrotreating of light oxygenates mentioned by the reviewer has been used as a characterization tool for rapid initial screening and understanding catalyst structure-function relationships.

Responses to Previous Reviewers' Comments (cont.)

- Not clear how tech transfer would occur if successful. Not clear if there is IP being developed, and if there is, how that is being protected. Perhaps an industry partner needs to be brought to the project. (?)

Answer: Since the last review, we filed a patent application on a novel catalyst synthesis method and will continue patenting as new IPs are developed. We have been exploring industrial collaboration opportunities with some informal exchanges made with a couple of catalyst companies. As more real bio-oil reactor testing as well as techno-economic analysis data become available, we plan to more actively engage industry partners (process industry, biorefinery, catalysts) for input on our project and potential collaborations.

Publications, Patents, Presentations, Awards, and Commercialization

Publications

- Jae-Soon Choi, Viviane Schwartz, Eduardo Santillan-Jimenez, Mark Crocker, Samuel A. Lewis, Sr., Harry M. Meyer, III, Karren L. More, “Structural evolution of molybdenum carbides in hot aqueous environments and impact on low-temperature hydroprocessing of acetic acid”, *Catalysts* **5** (2015) 406-423.
- Jae-Soon Choi, Viviane Schwartz, Eduardo Santillan-Jimenez, Mark Crocker, Samuel A. Lewis, Sr., Harry M. Meyer, III, Karren L. More, “Catalytic performance of molybdenum carbides in aqueous-phase hydrotreating of acetic acid”, *Preprints of Papers-American Chemical Society, Division of Energy and Fuels Preprints* **58** (2013) 1103-1104.

Patent

- Jae-Soon Choi, Beth L. Armstrong, and Viviane Schwartz, “Method of synthesizing bulk transition metal carbide, nitride, and phosphide catalysts”, U.S. Patent Application No. 14/069,514 (November 1, 2013).

Presentations

- Jae-Soon Choi, Alan H. Zacher, Huamin Wang, Mariefel V. Olarte, Viviane Schwartz, I. Ilgaz Soykal, Beth L. Armstrong, Michael J. Lance, Raynella M. Connatser, Samuel A. Lewis Sr., “Performance of molybdenum carbide catalysts in 2-stage hydroprocessing of fast pyrolysis bio-oil”, to be presented at the 24th North American Catalysis Society Meeting (NAM), Pittsburgh, PA, June 14-19, 2015.
- Jae-Soon Choi, Viviane Schwartz, Beth L. Armstrong, Raynella M. Connatser, Samuel A. Lewis Sr., I. Ilgaz Soykal, Alan H. Zacher, Huamin Wang, Mariefel V. Olarte, “Developing molybdenum carbide catalysts for bio-oil hydroprocessing”, oral presentation at the Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products (TCS2014), Denver, Colorado, September 2-5, 2014.
- Viviane Schwartz, I. Ilgaz Soykal, Beth L. Armstrong, Samuel A. Lewis Sr., Raynella M. Connatser, Jae-Soon Choi, “Novel class of molybdenum carbide catalysts for bio-oil upgrading”, oral presentation at the 8th International Conference on Environmental Catalysis, Asheville, North Carolina, August 24-27, 2014.

Publications, Patents, Presentations, Awards, and Commercialization (cont.)

- Viviane Schwartz, Jae-Soon Choi, Eduardo Santillan-Jimenez, Mark Crocker, Samuel A. Lewis Sr., Raynella M. Connatser, Harry M. Meyer III, Karren L. More, "Transition-metal carbides as novel class of catalysts for bio-oil upgrading", invited presentation at the IEEE East Tennessee Section Meeting, Oak Ridge, Tennessee, November 14, 2013. Invited
- Jae-Soon Choi, Viviane Schwartz, Eduardo Santillan-Jimenez, Mark Crocker, Samuel A. Lewis Sr., Raynella M. Connatser, Harry M. Meyer III, Karren L. More, "Catalytic performance of Mo₂C in aqueous-phase hydroprocessing of model bio-oils", poster presentation at the 12th Annual Symposium of the Southeastern Catalysis Society, Asheville, North Carolina, September 29, 2013.
- Jae-Soon Choi, Viviane Schwartz, Eduardo Santillan-Jimenez, Mark Crocker, Samuel A. Lewis, Sr., Harry M. Meyer, III, Karren L. More, "Catalytic Activity and Stability of Molybdenum Carbides in Aqueous Phase Hydrotreating of Acetic Acid", oral presentation at the 23rd North American Catalysis Society Meeting (NAM), Louisville, KY, June 2-7, 2013.
- Jae-Soon Choi, Viviane Schwartz, Eduardo Santillan-Jimenez, Mark Crocker, Samuel A. Lewis, Sr., Harry M. Meyer, III, Karren L. More, "Catalytic performance of molybdenum carbides in aqueous-phase hydrotreating of acetic acid", invited presentation at the 245th ACS National Meeting & Exposition, New Orleans, Louisiana, April 7-11, 2013.

Acknowledgements

- **DOE BETO technology managers**
 - Nichole Fitzgerald, Melissa Klembara
- **PNNL collaborators**
 - Alan Zacher (PI)
 - Reactor study: Huamin Wang, Mariefel Olarte, Daniel Santosa
 - TEA: Susanne Jones
- **ORNL collaborators**
 - Catalyst synthesis and characterization: Viviane Schwartz, Beth Armstrong, Ilgaz Soykal, William Brookshear, Josh Pihl, Michael Lance, Harry Meyer, John Henry, Kevin Cooley
 - Reactor study and analytical chemistry: Raynella Connatser, Samuel Lewis, Andrew Lepore
- **DOE Office of Science User Facility Program**
 - Access to ORNL's Center for Nanophase Materials Sciences