2.3.1.303
Novel and robust catalysts for bio-oil hydrotreating

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Thermochemical Conversion

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Goal Statement

**Challenge:** Catalyst deactivation by various mechanisms during bio-oil hydrotreating limits catalyst life, operation stability, and cost reduction.

**Goal:** Address catalyst deactivation issues by
- Advancing the understanding of bio-oil hydrotreating chemistry,
- Developing new generation catalysts with maximized lifetime and functionality over conventional systems.

Enable the commercially viable thermochemical process for biomass conversion to biofuels. Supports BETO’s upgrading process goals and targets (develop bio-oil stabilization technologies; develop improved catalysts for hydrotreating) and BETO’s $2.50/GGE conversion cost goals by 2017 via a thermochemical pathway.
Quad Chart Overview

Timeline
- Project start date: 10/1/2013
- Fund received: 2/3/2014
- Project end date: 9/30/2017
- Percent complete: 18%

Barriers
- Barriers addressed
  - Tt-J: Catalytic Upgrading of Bio-Oil Intermediates to Fuels and Chemicals
  - Tt-L: Knowledge Gaps in Chemical Processes
  - Tt-H: Bio-Oil Intermediate Stabilization and Vapor Cleanup

Budget

<table>
<thead>
<tr>
<th></th>
<th>Total Costs FY 10 –FY 12</th>
<th>FY 13 Costs</th>
<th>FY 14 Costs</th>
<th>Total Planned Funding (FY 15-Project End Date)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOE Funded</td>
<td>0</td>
<td>0</td>
<td>206 K</td>
<td>1,573 K</td>
</tr>
<tr>
<td>Project Cost Share (Comp.)</td>
<td>0</td>
<td>0</td>
<td>0</td>
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</tbody>
</table>

Partners
- PNNL CORE pyrolysis project 2.3.1.302
- Bio-oil samples from:
  - Battelle Columbus
  - VTT
1 - Project Overview

- Lower the cost associated with bio-oil hydrotreating catalysts by addressing catalyst deactivation issue, the largest challenge in the bio-oil hydrotreating, and exploring novel and inexpensive catalysts.

- PNNL developed a promising non-sulfided catalyst line, offering alternatives to catalysis technology being developed under the PNNL CORE pyrolysis tasks. Improvement of non-sulfided catalysts is still required.

- **Focus:** Development of new generation of non-sulfided catalysts for the two step hydrotreating process for bio-oil upgrading based on novel and inexpensive catalytic materials.

- **Focus:** Understanding of the correlation between catalyst formulation and catalytic performance.

- **Focus:** Understanding of the correlation between bio-oil properties and hydrotreating performance.
2 – Approach

- **Catalyst design, synthesis, and characterization.**
  - Novel non-sulfided catalysts with improved robustness and activity by extensively varying the components.
  - Identifying novel catalytic materials for bio-oil hydrotreating. Leveraging PNNL’s material science expertise.
  - Catalyst characterization by advanced technologies. Leveraging EMSL-PNNL’s advanced material characterization facilities.

- **Catalyst evaluation via bio-oil hydrotreating test.**
  - Testing in hydrotreaters with various scales in PNNL using real bio-oil with extended time on stream.
  - Understanding activity and lifetime as a function of catalyst, bio-oil feedstock, and process parameters.

- **Correlation development between hydrotreating performance, catalyst components, and bio-oil qualities.**
  - Effect of each components (such as active metal, support, and second function) of catalysts on hydrotreating performance.
  - Impact of bio-oil properties (such as content of contaminates or active coking species) on hydrotreating performance.
2 – Approach

► Critical success factors
  - Reduce the cost associated with catalysts in bio-oil hydrotreating by employing new catalysts with improved activity and lifetime.
  - Identify robust and inexpensive catalytic materials suitable for bio-oil hydrotreating.
  - Provide knowledge on bio-oil hydrotreating chemistry to direct the further catalyst and process development.

► Potential challenges
  - Deactivation of non-sulfided metal catalysts by sulfur poisons in bio-oil.
  - Balancing catalyst performance requirements and catalyst production cost.
  - Complexity of bio-oil resulting in difficulties for correlating with performance.

► Management Approach – Approved Project Management Plan
  - Quarterly internal milestones, quarterly report to BETO, and annual deliverables.
  - Regular meeting with PNNL CORE pyrolysis team and PNNL team of Computational Pyrolysis Consortium.
  - Go/No Go in Q2 FY16 to assess the new generation non-sulfided catalysts.
## Technical Progress Milestones

<table>
<thead>
<tr>
<th>Milestone</th>
<th>Planned Completion Date</th>
<th>Completion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline testing with current catalysts.</td>
<td>31-Mar-14</td>
<td>✓</td>
</tr>
<tr>
<td>Synthesis of at least six new catalysts.</td>
<td>30-Jun-14</td>
<td>✓</td>
</tr>
<tr>
<td>Characterization of the six newly prepared catalysts.</td>
<td>30-Sep-14</td>
<td>✓</td>
</tr>
<tr>
<td>Complete the testing of at least two catalysts by bio-oil hydrotreating and annual report.</td>
<td>30-Sep-14</td>
<td>✓</td>
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<tr>
<td>Complete hydrotreating testing of catalysts developed in FY14.</td>
<td>31-Dec-14</td>
<td>✓</td>
</tr>
<tr>
<td>Identify the most likely principle correlations between bio-oil properties and hydrotreating performance.</td>
<td>31-Mar-15</td>
<td>Underway</td>
</tr>
<tr>
<td>Complete testing of principle correlations identified in Q2.</td>
<td>30-Jun-15</td>
<td>Underway</td>
</tr>
<tr>
<td>Establish/define principle corollary relationships and deliver annual report.</td>
<td>30-Sep-15</td>
<td>On schedule</td>
</tr>
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</table>
3 – Technical Progress
Baseline catalysts and process

Two bio-oil hydrotreating catalyst lines developed in PNNL

- Reduced metal catalysts are required for low temperature stabilization of bio-oil by hydrogenation to eliminate gunk/coke formation and enable long-term operation.
- Reduced metal catalyst for high temperature HDO showed advantages of better activity, lower reaction temperature, and regenerability compared to sulfided catalysts, however, sulfur poisoning presents a significant challenge.
PNNL’s two-step process using non-sulfided bi-functional catalysts demonstrated promising performance.

Deactivation of catalysts was still a significant challenge.

Analysis of spent catalysts showed existence of substantial amounts of inorganics (Ca, Mg, K, Fe), sulfur, and coke, indicating poisoning is the major deactivation mode for the catalysts.
3 – Technical Progress
Catalyst design - to improve stability and activity

Property metrics for the bi-functional catalysts:

- **Metal**
  - HDO/hydrogenation ability
  - Sulfur resistance
  - Sintering resistance

- **Support**
  - Accessibility/pore structure
  - Surface area/metal dispersion
  - Hydrothermal stability

- **Acid function**
  - Acidity
  - Accessibility/pore structure
  - Hydrothermal stability

Other novel catalysts have also been considered and tested with a focus on inexpensive base metal catalysts.
Catalyst synthesis: varying the components
- Four metals, including mono- or bi-metallic, noble or base metals.
- Five supports, including metal oxides or their composite.
- Eight solid acids, including zeolites with various acidity and pore structure, metal oxide composites, stabilized metal oxides.
- Other catalysts: bulk base metal based bimetallic catalysts.

Catalyst characterization: compare different materials, compare fresh and spent catalysts.
- Metal: model compound HDO testing, electron microscope, x-ray diffraction, x-ray photoelectron spectroscopy.
- Support and solid acids: surface area, pore volume, pore distribution, acidity by NH$_3$ desorption, hydrothermal stability by batch hydrothermal treatment under conditions much more severe than typical bio-oil hydrotreating tests.
Preferred solid acids, and oxide supports were identified for hydrotreating tests.

Critical parameters, such as Al site contents, that effect the hydrothermal stability of the materials were determined.

It is critical to balance accessibility, acidity, and hydrothermal stability.

Preferred metals were identified based on model compound HDO tests.
3 – Technical Progress
Bio-oil hydrotreating tests - accomplished

**Condition matrix:** pressure of 1500-1800 psig, temperature of 160-170 °C for step I and 320-340 °C for step II, LHSV of 0.4 to 0.8 L/L h, TOS of 40-100 h.

**Feed and product analysis:** CHN, O, S, inorganic content, water content, density, simulation distillation, GC-MS, total acid number, $^{13}$C NMR.

30 ml x 2 capacity, 2000 psig, 450 °C, unattended operation approved.
Metal identity has a dramatic effect on the stability and product distribution.

Significant gap between model compound test results and real bio-oil hydrotreating test results.

Substantial amounts of sulfur and inorganics were found in the spent catalysts.

The resistance to poisons such as sulfur is the major factor that effects the stability of active metal in hydrogenation (stabilization) and HDO of real bio-oil.

Tuning final oil yield could be achieved by choosing appropriate metal functions in the hydrotreating catalysts.

Metal used in step I - step II catalyst
Baseline oxide support and zeolite as solid acid

M1-M2
Ru–Ru (baseline)
Ru–Pd
Ni-X – Ni-X
Pd–Pd

T step I: 160 °C, T step II: 320 °C,
H₂ pressure: 1500 psig, H₂/bio-oil: 2700 L/L
LHSV: 0.40 L/L h for each step
The step II HDO catalysts with different solid acid function showed minimal difference regarding stability and product yields.

The pore structure, which related to the accessibility of the active site in zeolite, played a more important role than the acidity of the zeolite as the solid acid component in the second stage bifunctional catalysts for bio-oil hydrotreating.

Metal oxide composites showed poorer performance than zeolites, probably because of its low surface area.

Baseline metal and oxide support with various solid acids
Cleaned bio-oil; T step I: 170 °C, T step II: 340 °C, H₂ pressure: 1500 psig, H₂/bio-oil: 2700 L/L
WHSV: 0.37 g/g h (0.36 LHSV) for step I,
1.20 g/g h (0.65-1.2 LHSV) for step II.
Increase metal to solid acid ratio resulted in a significant increase of catalyst activity and minimal change in stability.

Doping zeolite with metal to eliminate coke formation on zeolite did not result in a difference in performance.

Metal poisoning by contaminants in bio-oil, such as sulfur, appears to be a primary deactivation mode for bio-oil hydrotreating.

The metal to solid acid ratio will be further optimized.

Baseline metal and oxide support
Cleaned bio-oil (inorganic removed);
T step I: 170 °C, T step II: 340 °C,
H₂ pressure: 1500 psig, H₂/bio-oil: 2700 L/L
WHSV: 0.37 g/g h (0.36 LHSV) for step I,
1.20 g/g h (0.70-0.77 LHSV) for step II.
Bio-oil properties, such as contents of potential contaminants and active coking species, play a critical role on the stability of catalysts for the bio-oil hydrotreating.

Detailed evaluation of the effect of each property parameter is ongoing.

Development of bio-oil cleaning protocol to control content of certain poisons in the bio-oil is ongoing.
4 – Relevance

- Contributes to the overall MYPP bio-oil pathway goal: “by 2017, achieve an nth plant modeled conversion cost of $2.50/GGE via a thermochemical pathway.”
  - Reduce cost associated with bio-oil hydrotreating catalysts by addressing catalyst deactivation issues through advancing the understanding of bio-oil hydrotreating chemistry and developing new generation catalysts with improved lifetimes and functionality.

- Applications of the expected outputs from this project:
  - Novel catalysts and catalytic materials; Methods for catalyst synthesis, characterization, evaluation by bio-oil hydrotreating, and bio-oil pre-treatment.
  - Knowledge of the correlations between hydrotreating performance, catalyst components, and bio-oil qualities to direct the further catalyst and process development.

- The successful project will have:
  - Developed new generation bio-oil hydrotreating catalysts with lower bio-oil production cost associated with catalysts.
  - Improved the understanding of bio-oil hydrotreating chemistry to narrow the knowledge gap in bio-oil upgrading processes.
5 – Future Work

<table>
<thead>
<tr>
<th>TASKS</th>
<th>FY2014</th>
<th>FY2015</th>
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<tbody>
<tr>
<td></td>
<td>Q1</td>
<td>Q2</td>
</tr>
<tr>
<td>A Catalyst design, synthesis, and analysis</td>
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<tr>
<td>B Catalyst evaluation via bio oil hydrotreating testing</td>
<td></td>
<td></td>
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<tr>
<td>C Correlation development between performance, catalyst components, and bio oil qualities</td>
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<tr>
<th>Milestone</th>
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<td>B.ML.3</td>
<td>Complete hydrotreating testing of catalysts developed in FY14. 31-Dec-14</td>
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<tr>
<td>C.ML.1</td>
<td>Identify the most likely principle correlations between bio oil properties and hydrotreating performance. 31-Mar-15</td>
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<tr>
<td>C.ML.2</td>
<td>Complete testing of principle correlations identified in Q2. 30-Jun-15</td>
</tr>
<tr>
<td>C.DL.1</td>
<td>Establish/define principle corollary relationships and deliver annual report. 30-Sep-15</td>
</tr>
</tbody>
</table>

Go/No Go in Q2 FY16 to assess the lifetime of the new generation non-sulfided catalysts.
5 – Future Work

► Catalyst development
  ■ Further develop and evaluate new catalytic materials by characterization and bio-oil hydrotreating.
  ■ Transition to inexpensive base metal catalysts.
  ■ Evaluate advanced zeolite with enhanced stability and accessibility.

► Understand the correlations
  ■ Further understanding the effect of the properties of bio-oil (content of sulfur, inorganics, or carbonyls) on the bio-oil stabilization and hydrodeoxygenation on the non-sulfided catalysts.
  ■ Assess pretreatment methods to eliminate identified problematic species in bio-oil.

► Demonstrate long-lifetime bio-oil hydrotreating
► Utilize TEA to identify most promising opportunities and provide data to TEA.
**Summary**

- **Overview:** Address bio-oil hydrotreating catalyst deactivation issue by advancing the understanding of bio-oil hydrotreating chemistry and developing new generation catalysts.

- **Approach:** Catalyst development and evaluation; Understanding the correlation between hydrotreating performance, catalyst formulation, and bio-oil properties.

- **Technical Progress:** Developed catalysts with extensively varied components; catalytic material synthesis and detailed characterization; bio-oil hydrotreating testing in a 2x30 ml hydrotreater; established correlations, effect of metal identity and solid acid on the performance of hydrotreating catalysts.

- **Relevance:** Driving pyrolysis/upgrading technology towards MYPP goals and targets. Barriers addressed: Tt-J, Tt-L, Tt-H.

- **Success factors:** Identify robust catalytic materials with lower overall cost; provide knowledge on bio-oil hydrotreating to direct further development.

- **Challenges:** Catalyst poisoning; balance material cost and catalyst performance; bio-oil complexity.

- **Future Work:** Further development of novel catalysts; further understanding of correlations; demonstrate long lifetime; economic analysis.

- **Technical transfer:** Disseminate knowledge that is industrially relevant; publication of peer-reviewed manuscripts and presentation in conferences.
Additional Slides
Responses to Previous Reviewers’ Comments

The project presented herein is a new project in FY2014 and were not peer reviewed in 2013.
Huamin Wang, et al., “Reduced metal catalysts for bio-oil hydrotreating in a two-step process”, to be presented (oral) at the 24\textsuperscript{th} North American Meeting (NAM) of the Catalysis Society, June 2015, Pittsburgh, PA.