DOE Bioenergy Technologies Office (BETO)
2015 Project Peer Review

2.3.1.303
Novel and robust catalysts for bio-oil hydrotreating

March 24, 2015
Thermochemical Conversion

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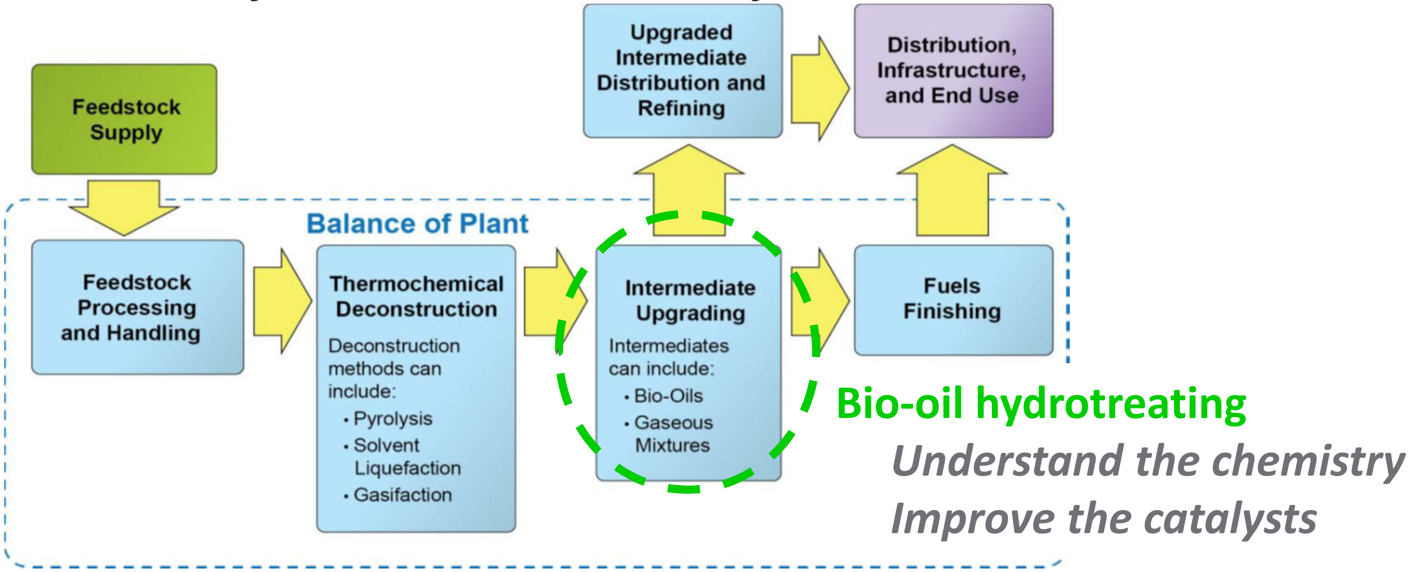
Goal Statement

- **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

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Timeline

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

Budget

	Total Costs FY 10 –FY 12	FY 13 Costs	FY 14 Costs	Total Planned Funding (FY 15-Project End Date
DOE Funded	0	0	206 K	1,573 K
Project Cost Share (Comp.)	0	0	0	0

Barriers

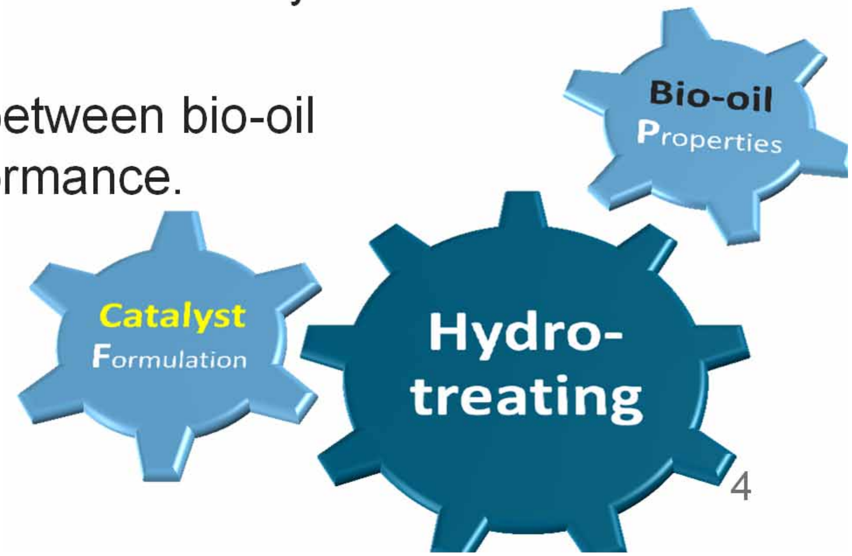
- Barriers addressed
  - Tt-J: Catalytic Upgrading of Bio-Oil Intermediates to Fuels and Chemicals
  - Tt-L: Knowledge Gaps in Chemical Processes
  - Tt-H: Bio-Oil Intermediate Stabilization and Vapor Cleanup

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

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- **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.

3 – Technical Progress
Milestones

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

Baseline catalysts and process

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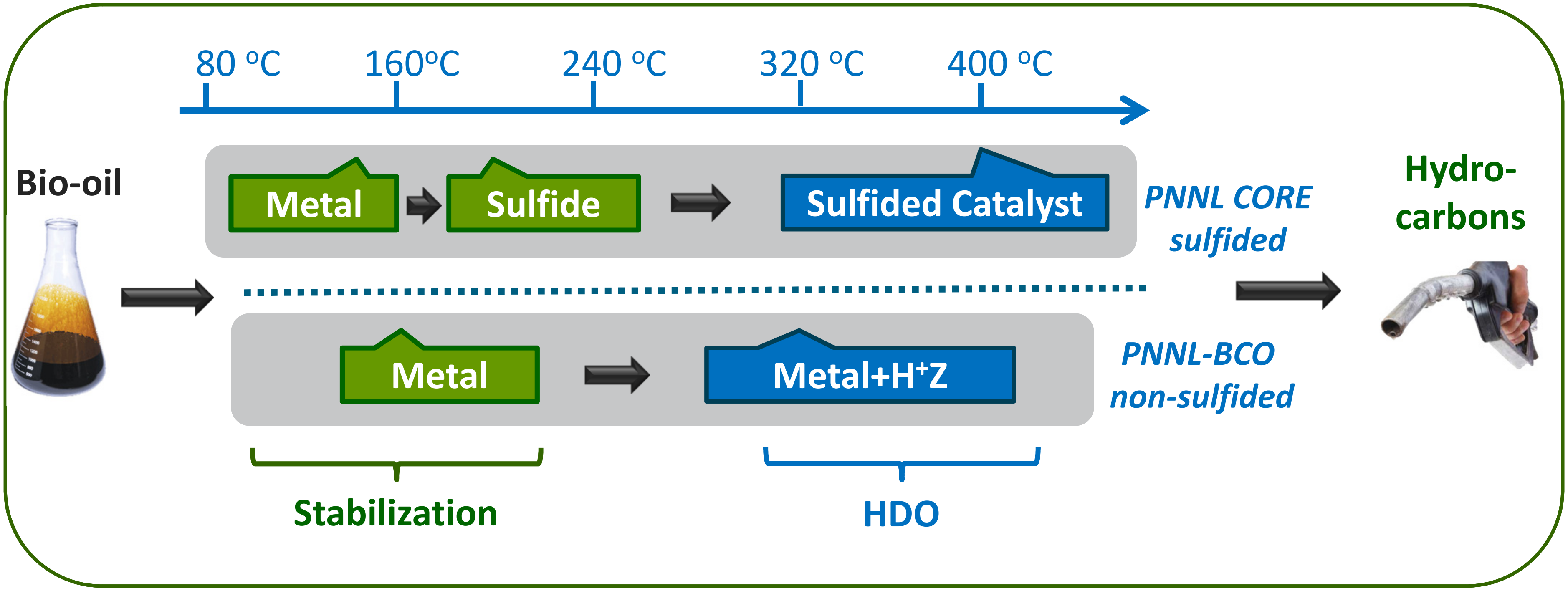
Two bio-oil hydrotreating catalyst lines developed in PNNL



- 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.

3 – Technical Progress
Baseline catalysts and process - deactivation

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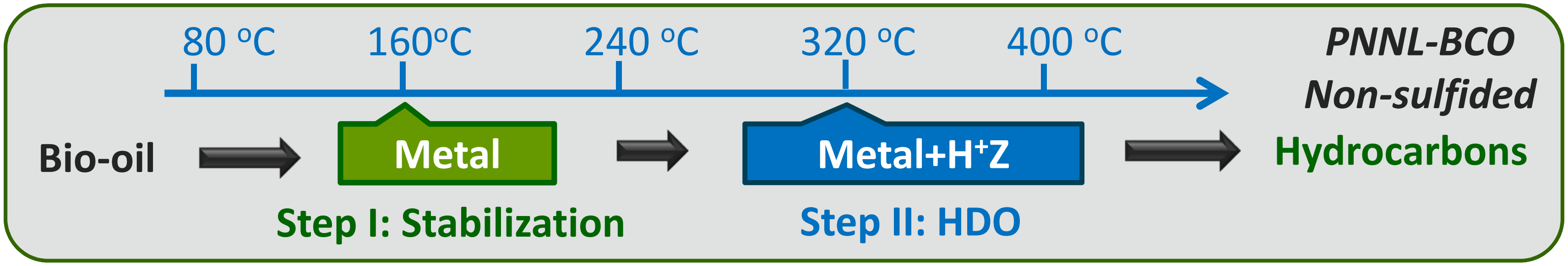
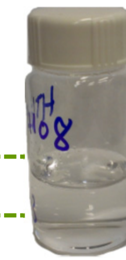


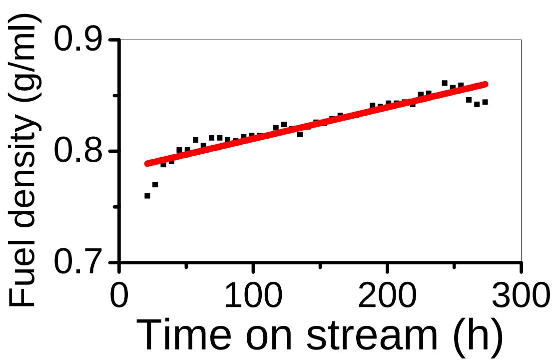
- PNNL's two-step process using non-sulfided bi-functional catalysts demonstrated promising performance.


→ **Metal** →

→ **Metal+H^+Z** →


	Bio-oil	After Stage 1	Final product
Density:	~1.2 g/ml	~1.14 g/ml	0.80-0.86 g/ml
H/C (dry):	~1.4	~1.7-1.8	~1.8-1.9
O% (dry):	~35	~32	<1~2

- 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

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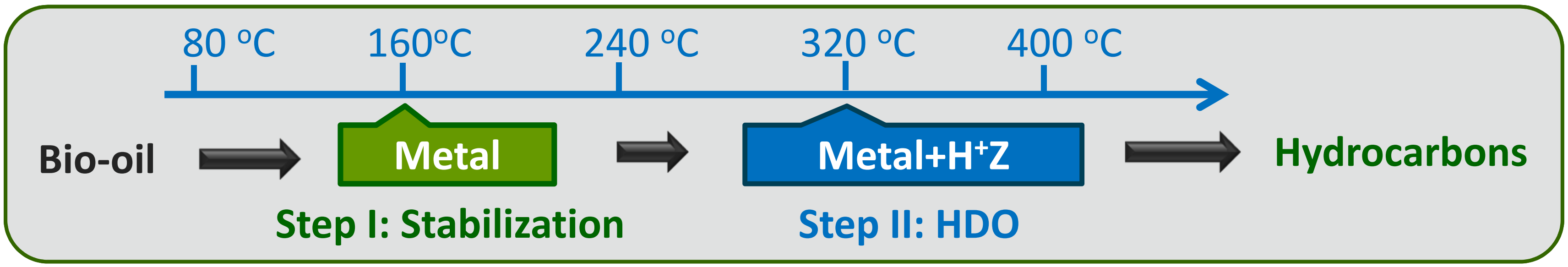
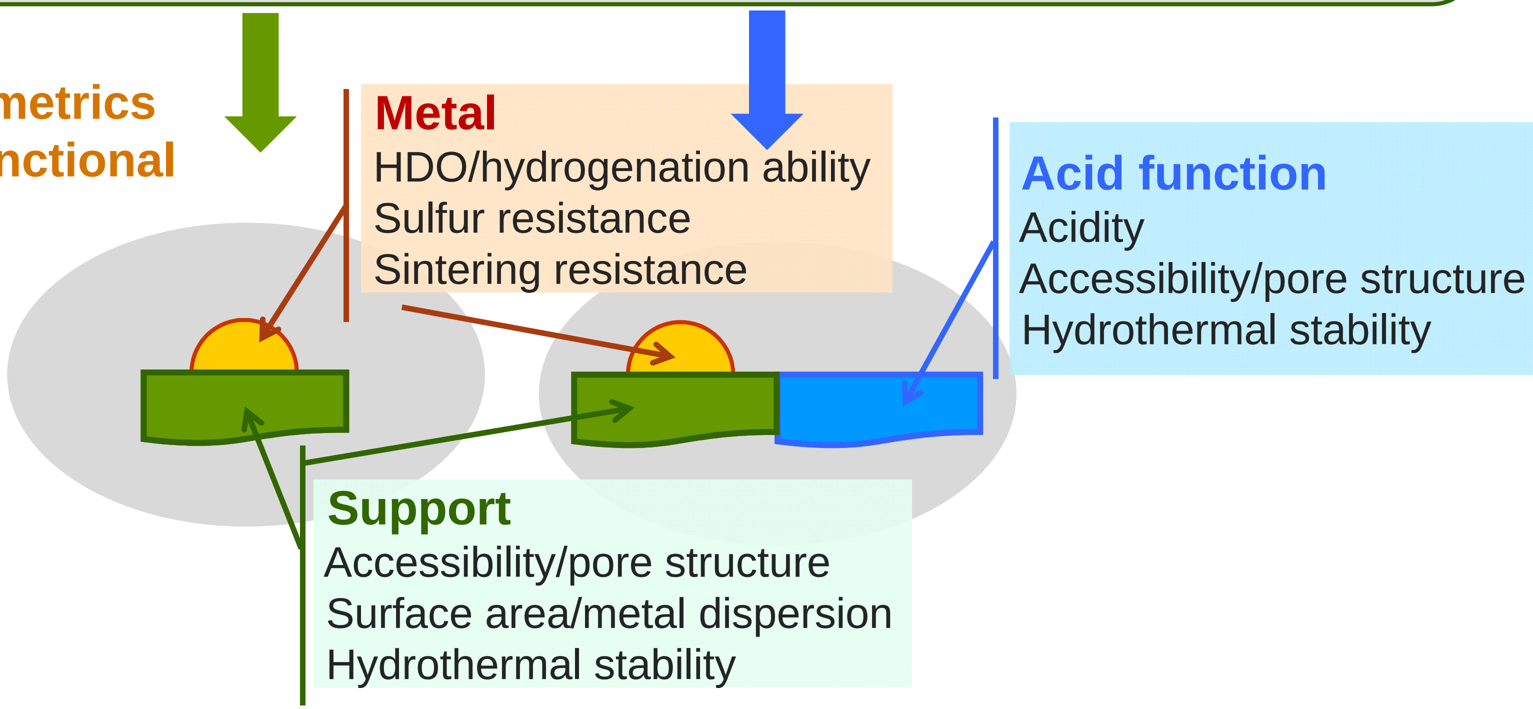
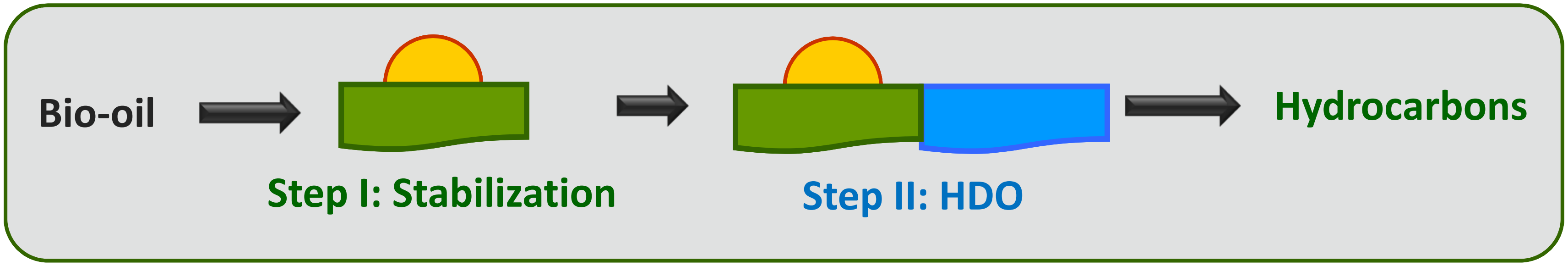


- **Property metrics for the bi-functional catalysts:**



- **Other novel catalysts** have also been considered and tested with a focus on inexpensive base metal catalysts.

3 – Technical Progress
Catalyst synthesis and analysis - accomplished



- **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.

3 – Technical Progress
Catalyst synthesis and analysis - accomplished

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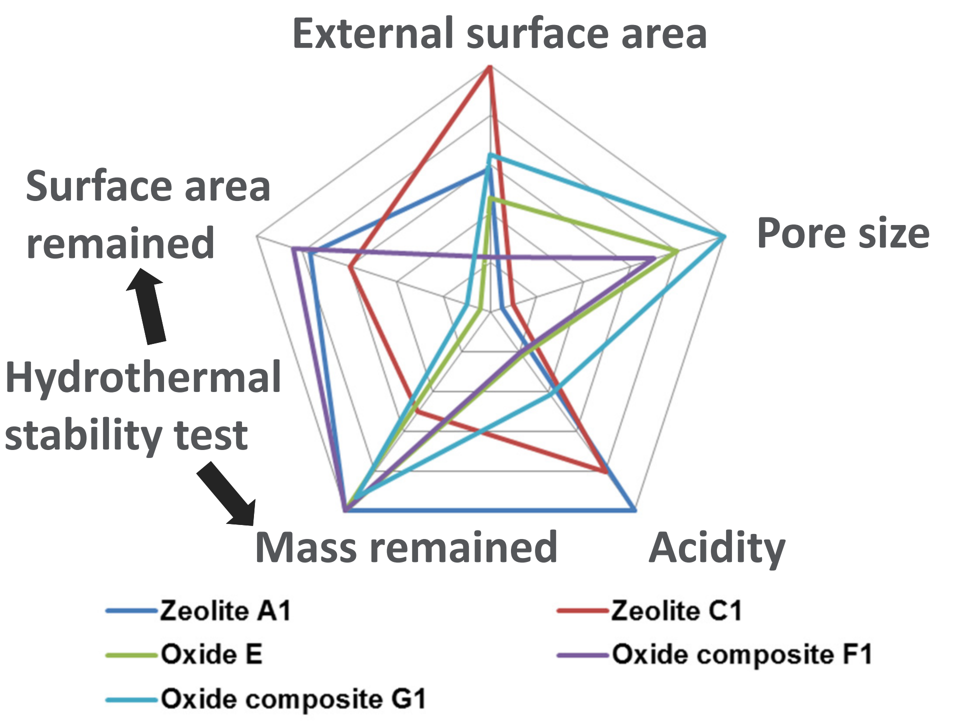
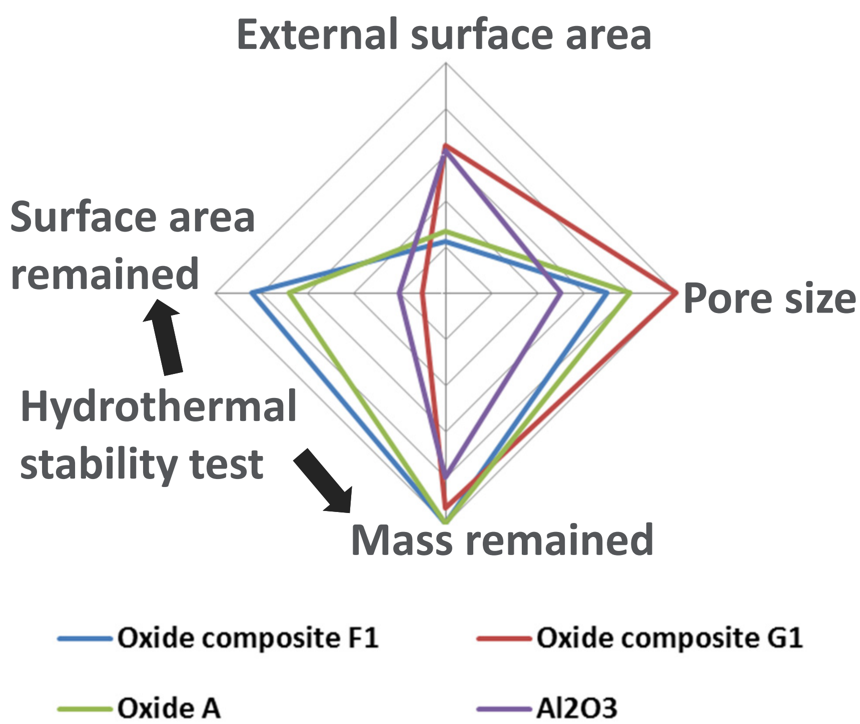
Representative characterization results (normalized) of selected solid acids and supports

Solid acids



Supports



- 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

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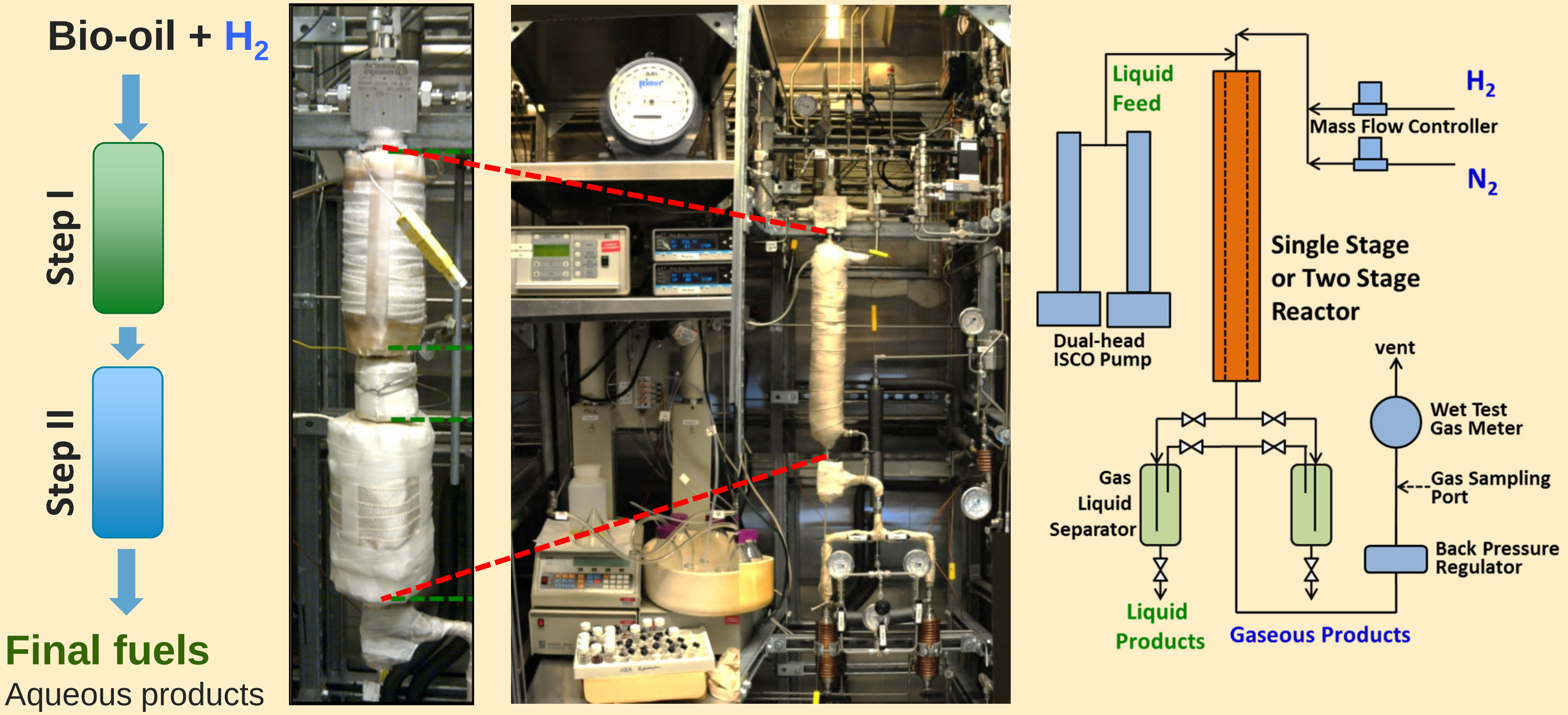


30 ml x 2 capacity, 2000 psig, 450 ^oC, unattended operation approved.

- **Condition matrix:** pressure of 1500-1800 psig, temperature of 160-170 ^oC for step I and 320-340 ^oC 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.

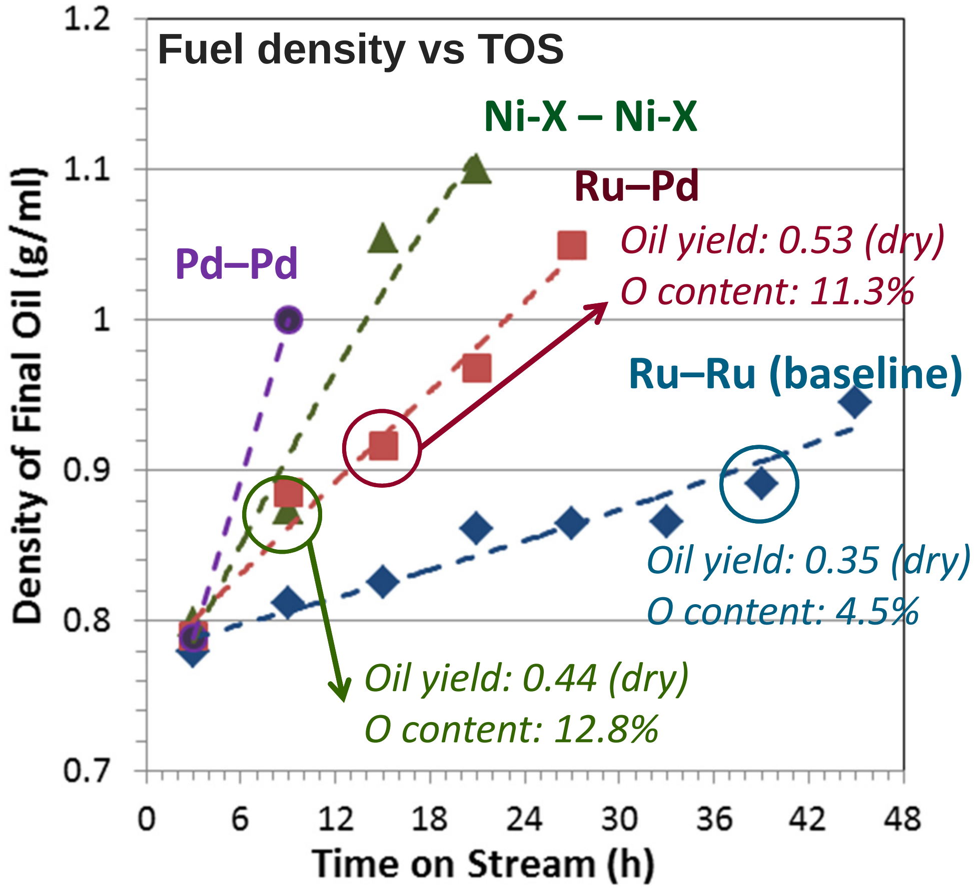
3 – Technical Progress
Effect of metal identity - accomplished

- 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.

M1-M2

Metal used in **step I** - **step II** catalyst

Baseline oxide support and zeolite as solid acid



T step I: 160 °C, T step II: 320 °C,

H_2 pressure: 1500 psig, H_2/bio-oil: 2700 L/L

LHSV: 0.40 L/L h for each step

3 – Technical Progress
Effect of solid acid - accomplished

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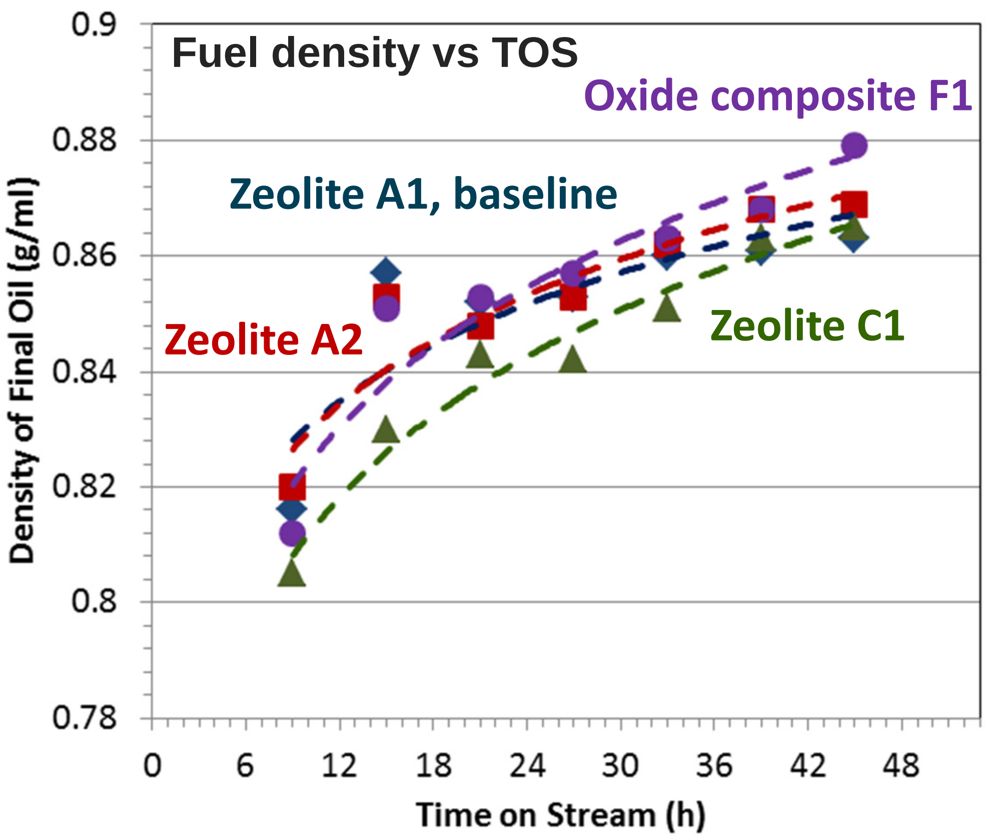
- The step II HDO catalysts with different solid acid function showed minimal difference regarding stability and product yields.
- The pore structure, which related to the accessibility of the active site in zeolite, played a more important role than the acidity of the zeolite as the solid acid component 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, H_2 pressure: 1500 psig, H_2/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.

3 – Technical Progress
Effect of metal to solid acid ratio - accomplished

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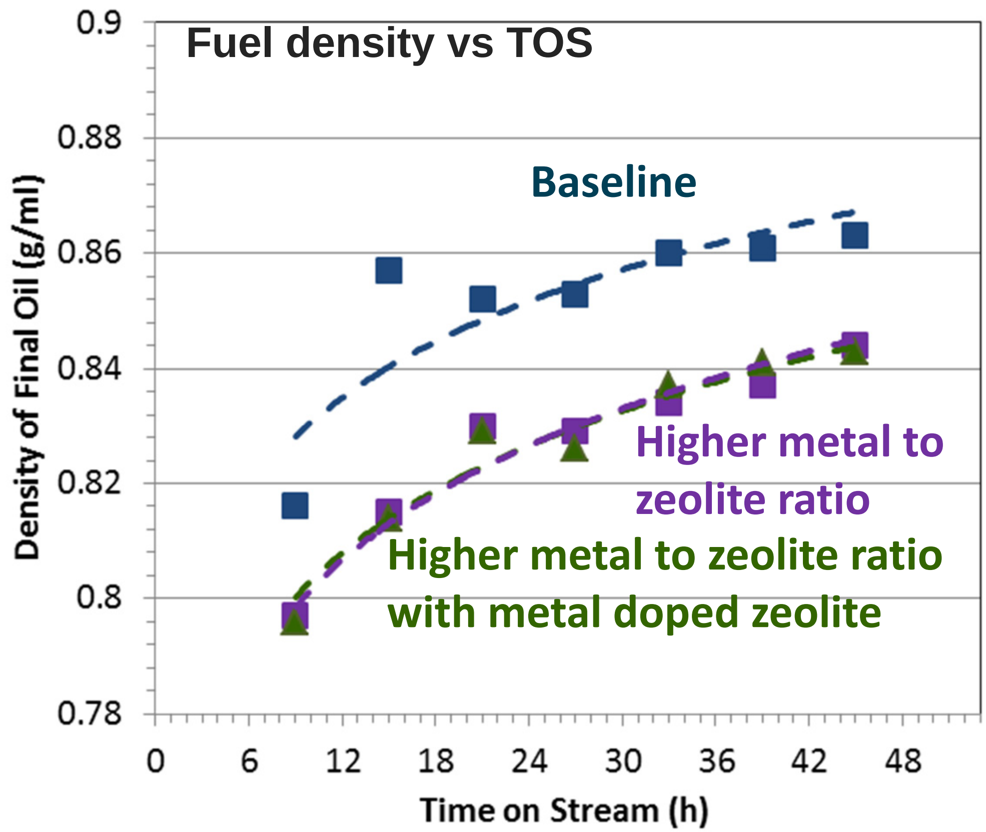
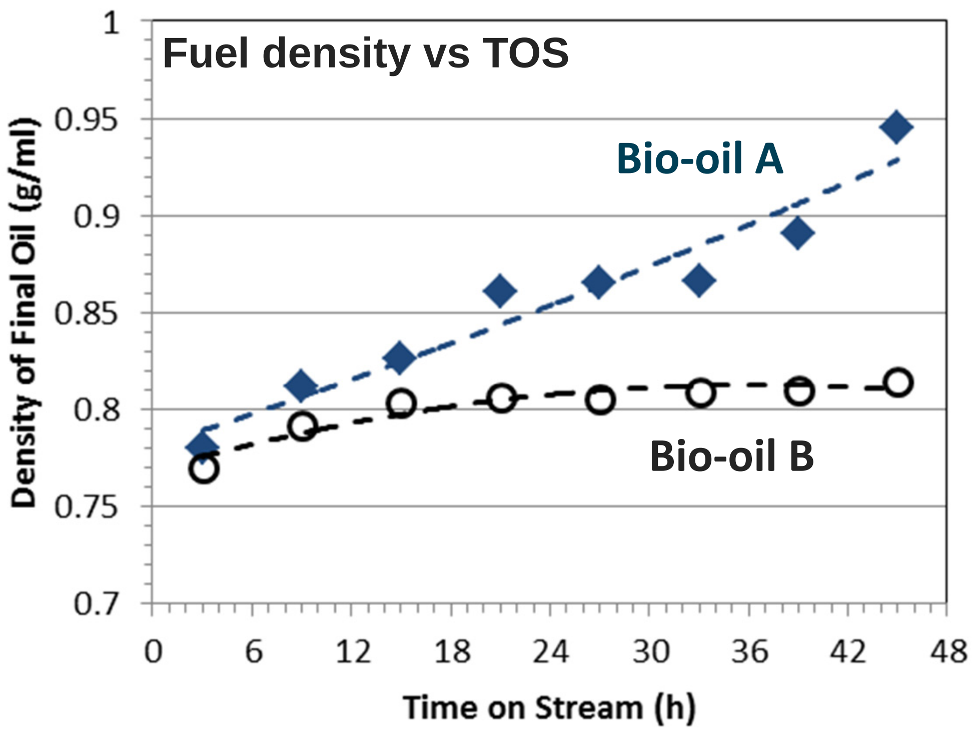
- Increase metal to solid acid ratio resulted in a significant increase of catalyst activity and minimal change in stability.
- Doping zeolite with metal to eliminate coke formation on zeolite did not result in a difference in performance.
- Metal poisoning by contaminants in bio-oil, such as sulfur, 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,
H_2 pressure: 1500 psig, H_2/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.

3 – Technical Progress
Impact of bio-oil properties - initialized



	Sulfur content	Inorganic content (Ca, K, Mg, P)	Carbonyl (% mol C, by NMR)
Bio-oil A	60 ppm	~80 ppm	7.1 %
Bio-oil B	10 ppm	~40 ppm	6.1%

Baseline catalysts, T step 1: 160 °C, T step 2: 320 °C, H_2 pressure: 1500-1750 psig, H_2/bio-oil: 2700 L/L LHSV: 0.40 L/L h for each step

- Bio-oil properties, such as contents of potential contaminates 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

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- 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

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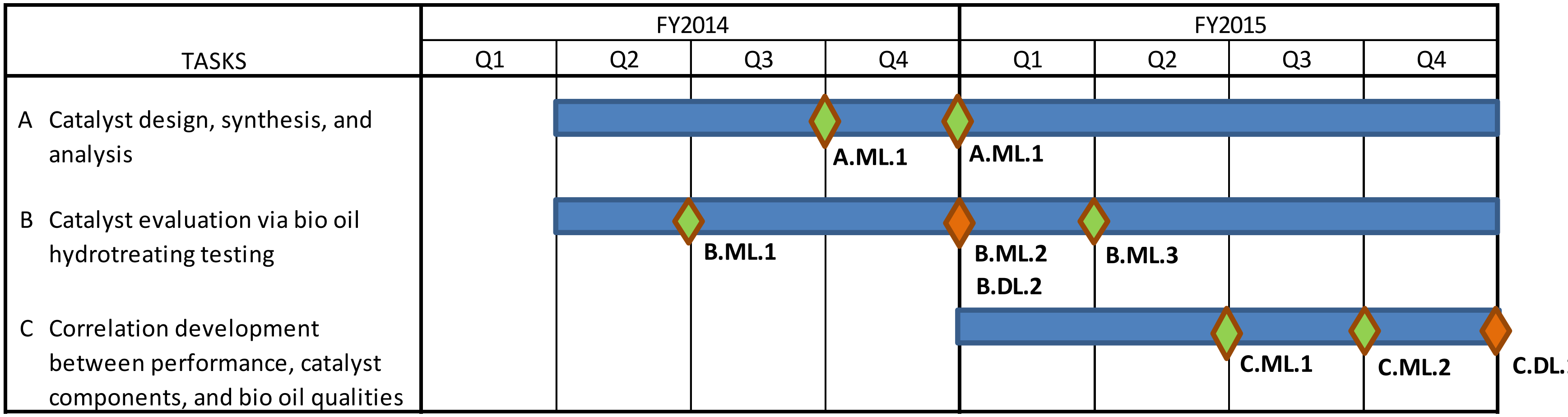

	Milestone	Planned Completion Date
B.ML.3	Complete hydrotreating testing of catalysts developed in FY14.	31-Dec-14
C.ML.1	Identify the most likely principle correlations between bio oil properties and hydrotreating performance.	31-Mar-15
C.ML.2	Complete testing of principle correlations identified in Q2.	30-Jun-15
C.DL.1	Establish/define principle corollary relationships and deliver annual report.	30-Sep-15

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

5 – Future Work

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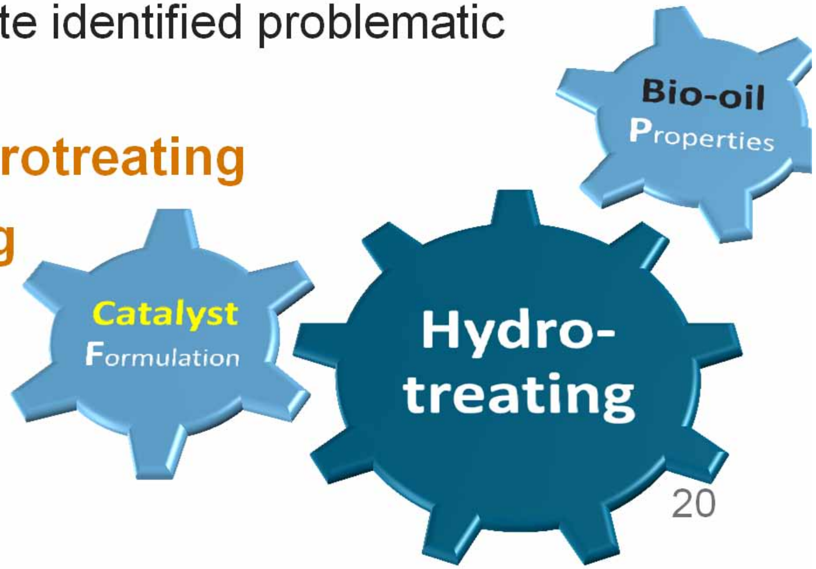
- **Catalyst development**
  - Further develop and evaluate new catalytic materials by characterization and bio-oil hydrotreating.
  - Transition to inexpensive base metal catalysts.
  - Evaluate advanced zeolite with enhanced stability and accessibility.
- **Understand the correlations**
  - Further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

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- **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

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Responses to Previous Reviewers' Comments

- The project presented herein is a new project in FY2014 and were not peer reviewed in 2013.

Publications, Patents, Presentations, Awards, and Commercialization

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- Huamin Wang, et al., “Reduced metal catalysts for bio-oil hydrotreating in a two-step process”, to be presented (oral) at the 24th North American Meeting (NAM) of the Catalysis Society, June 2015, Pittsburgh, PA.