DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review
Upgrading of Biomass Fast Pyrolysis Oil (Bio-oil)

March 22, 2015
Bio-Oil Technology Area Review
Principal Investigator : Zia Abdullah
Organization: Battelle Memorial Institute

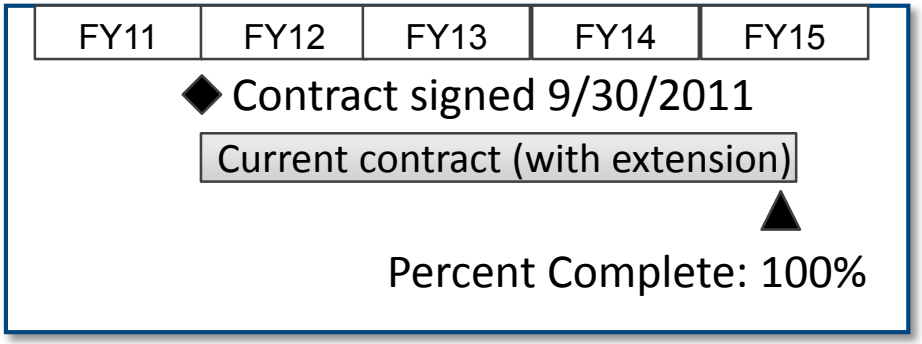
Goal Statement

To develop a hydroprocessing system & catalysts to achieve commercially relevant Time On Stream (TOS) and to produce blendable hydrocarbon fuel product

Addresses all FOA-0000342 Objectives	Supports BETO Pathways #1 and #3	Supports Industry Needs
• 1,000 hrs. TOS • H/C product 30% blendable with ASTM petroleum fuels • Compatibility with petroleum refining unit operations	• Fast Pyrolysis • In-situ catalytic fast pyrolysis • Ex-situ catalytic fast pyrolysis • Hydropyrolysis • Hydrothermal liquefaction • Solvent liquefaction	• Drop-in fuel • Competitive at market price • Low capital requirement • Scalable • Feedstock flexible • Environmentally sustainable • Near-Mid Term ROI

Quad Chart Overview

Timeline



Barriers

T t - E, T t - G:

- *Development of new methods to limit catalyst deactivation*
- *Increase product yield and quality*

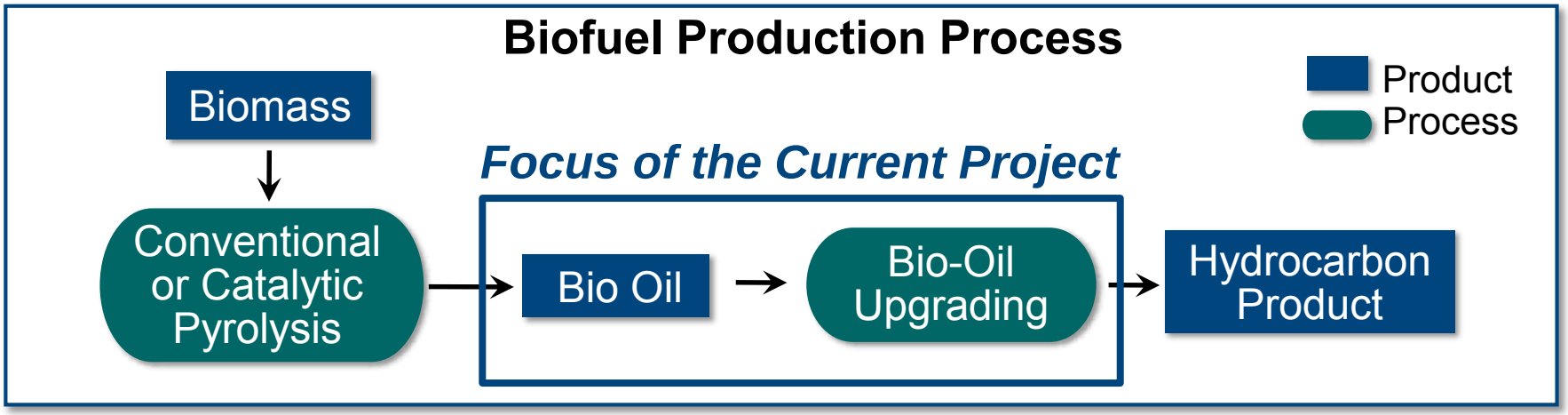
Budget

	FY10 - FY12	FY13	FY14	Total Planned (FY15-End)
DOE (Battelle)	$872,140	$593,220	$325,883	$821,528
DOE FFRDC (PNNL)	$720,914	$252,080	$159,237	$194,979
Cost Share	$607,384	$193,036	$160,751	$39,955

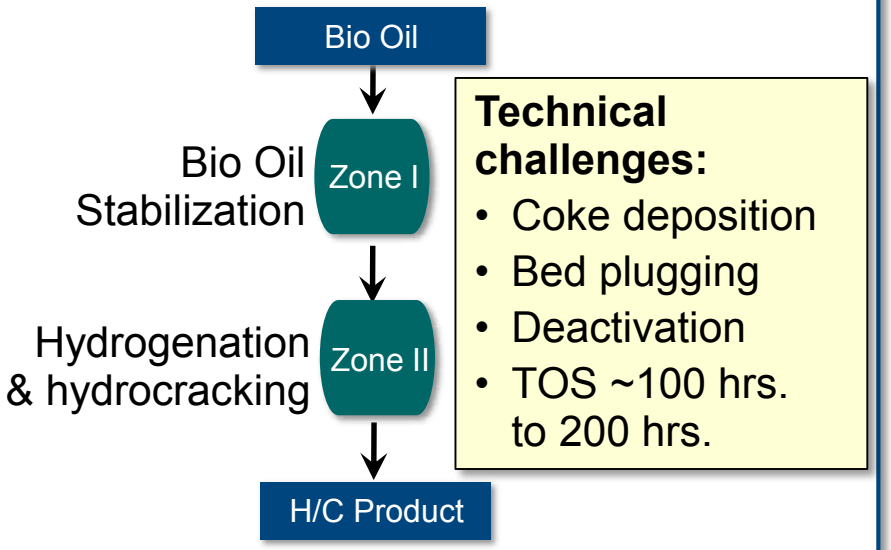
Partners

Organization	Role(s)
Battelle (66% Funds)	- PI, PM - Cat. Dev., Cat testing - Hydrotreatment - TEA
PNNL (34% Funds)	- Cat. Dev. - TEA
Marathon	Fuel assessment
Domtar	Feedstock supply

1 - Project Overview



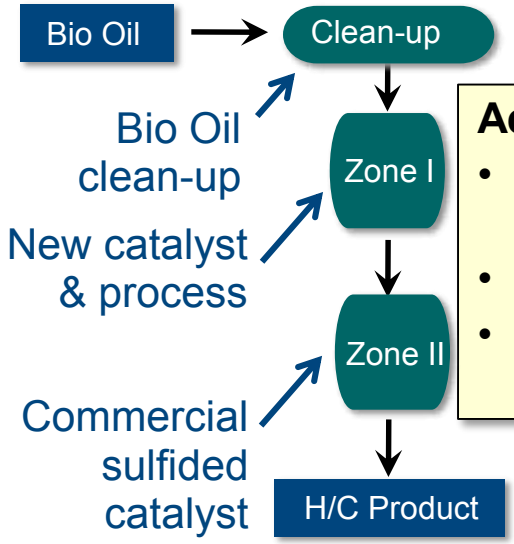
State of the Art of Bio Oil upgrading at the Beginning of the Project



Technical challenges:

- Coke deposition
- Bed plugging
- Deactivation
- TOS ~100 hrs. to 200 hrs.

Battelle – PNNL Bio Oil Upgrading Process Solves Technical Challenges



Accomplishments:

- Re-generable catalyst system
- TOS > 1,000hrs.
- Minimal plugging & deactivation

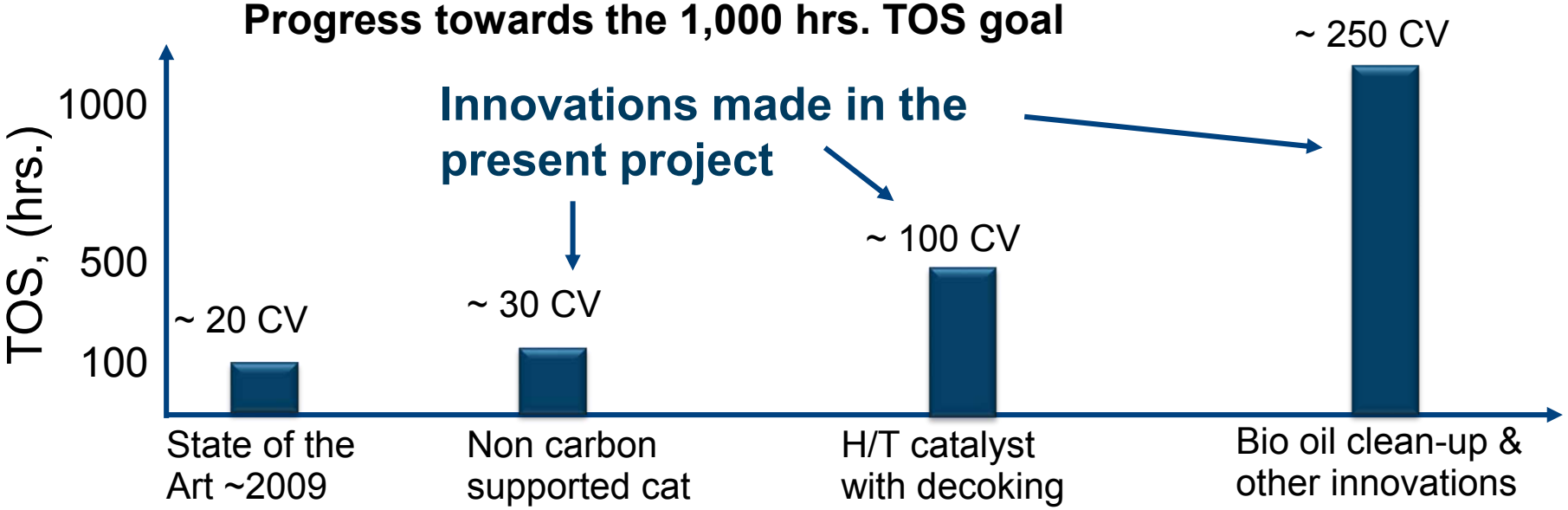
1 - Project Overview

Key Technical Barriers Addressed by This Project:

Technical Barrier	Project Focus to Address Technical Barrier
Hydrotreatment catalyst cost	Develop catalysts that can be regenerated
H/T catalyst coking	Develop regeneration capability
H/T catalyst poisoning	Develop methods to clean-up bio oil

Project History and Accomplishments:

Progress towards the 1,000 hrs. TOS goal



C.V.: Number of 'catalyst bed volumes' of bio oil processed

2 – Approach (Technical)

Novel & Essential Elements of The Technical Approach:

- Develop non carbon supported catalysts (PNNL)
- Develop catalyst regeneration processes (BMI)
- Conduct detailed root cause analyses of catalyst deactivation (BMI).
- Develop bio oil clean-up processes (BMI & PNNL)
- Conduct 1,000 hrs. TOS trials & TEA (BMI & PNNL)

Main Technical Challenges:

- Rapid coking of hydrotreatment catalyst
- Catalyst bed plugging during operation.
- Catalyst deactivation.

Success Factor	Achieved	Basis of Assumption
Regenerate catalyst at least 5 times while retaining 50% activity	☑	Long term operation
Demonstrate acceptable product quality	☑	Necessary for commercialization
Demonstrate 1,000 hrs. TOS on single catalyst charge	☑	Necessary for commercialization
Demonstrate 60 gal/ton yield	☑	Necessary for commercialization

2 – Approach (Management)

Management Approach:

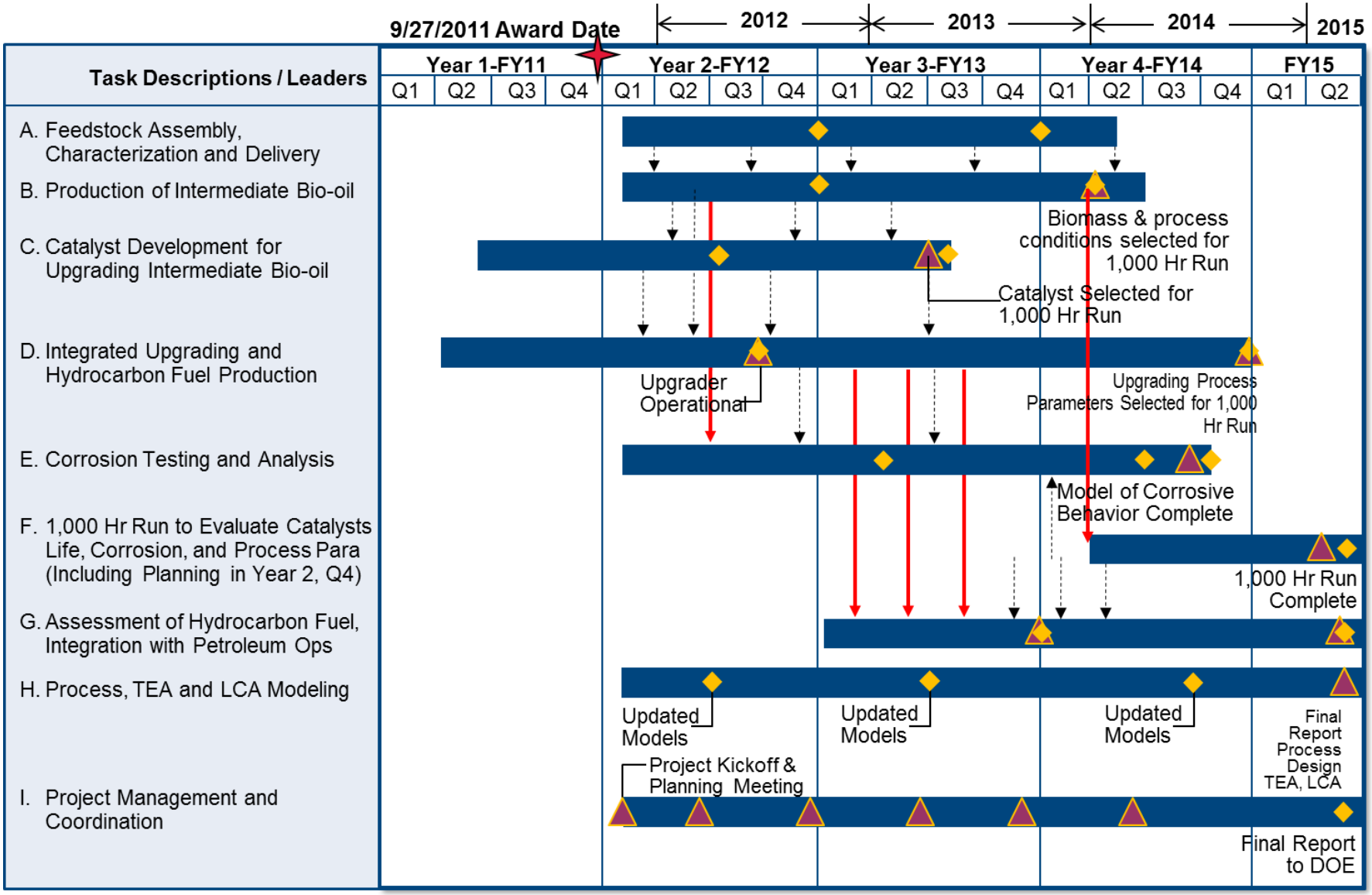
- Maintain safety as the #1 priority
- Use EVMS to evaluate progress & make decisions
- Leverage capabilities and research from outside the program to bring in additional value
- Modify scope & adjust effort as necessary to achieve milestones and deliverables
  - Update and receive frequent feedback and approval from DOE PM
  - Hold daily & weekly progress meetings

Main Non Technical Challenges:

- Availability of equipment
  - Schedule
- Availability of personnel
  - Train temporary staff
- Analytical capabilities
  - Use external labs if needed

Decision point	Adjust Scope
Did catalytic bio oil work?	If not, use conventional, non-catalytic bio oil
Catalyst regeneration necessary?	Develop cat. regeneration capability
Bio oil clean-up needed?	Develop bio oil clean-up capability
Use commercial catalyst in Zone II?	Leverage DOE core program work

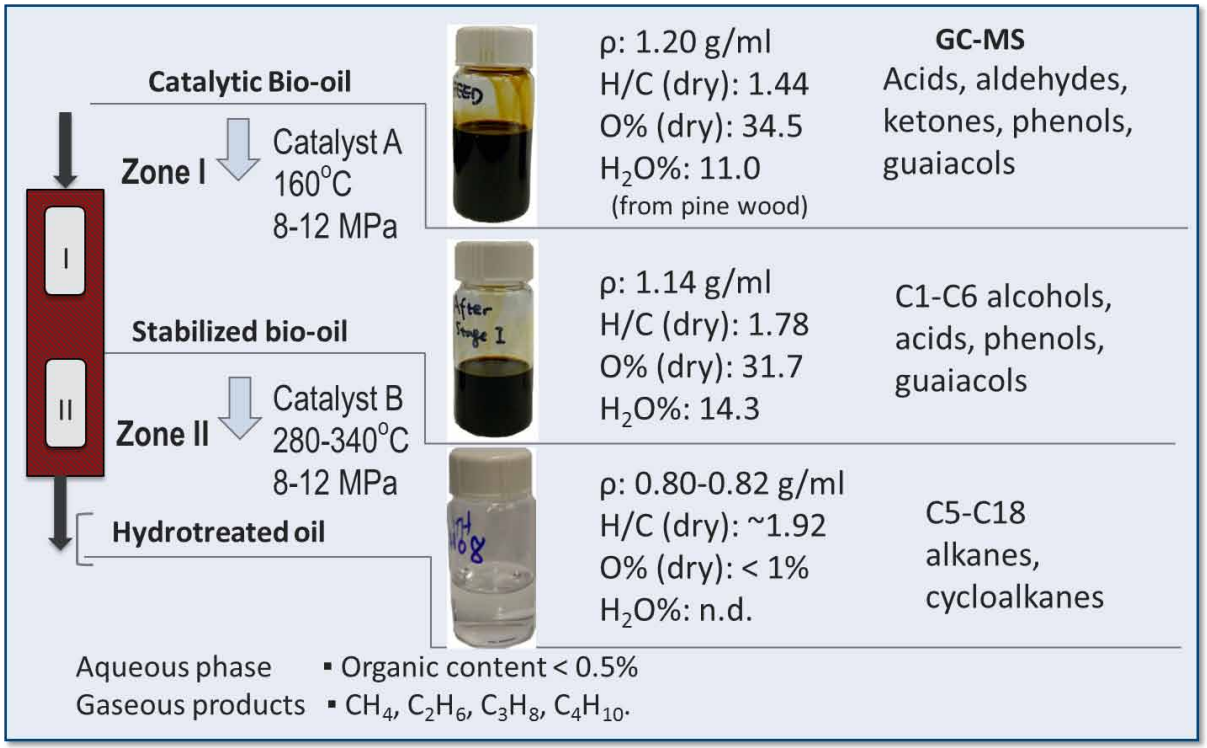
3 – Technical Accomplishments/Progress/Results



3 – Technical Accomplishments/Progress/Results

Task C:

- **Identified novel non-carbon supported metal catalysts with low coke formation rates**
- **These catalysts can be regenerated to remove coke and recover activity**
- **Achieved ~ 200 hrs. TOS while maintaining high activity**

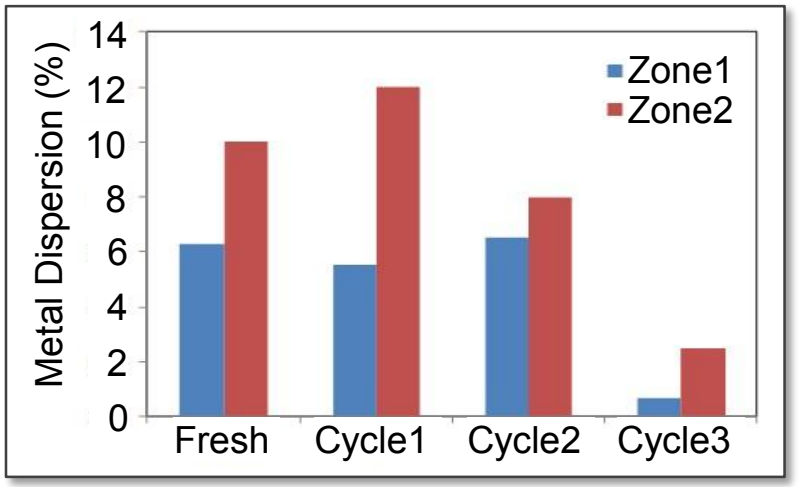


3 – Technical Accomplishments/Progress/Results

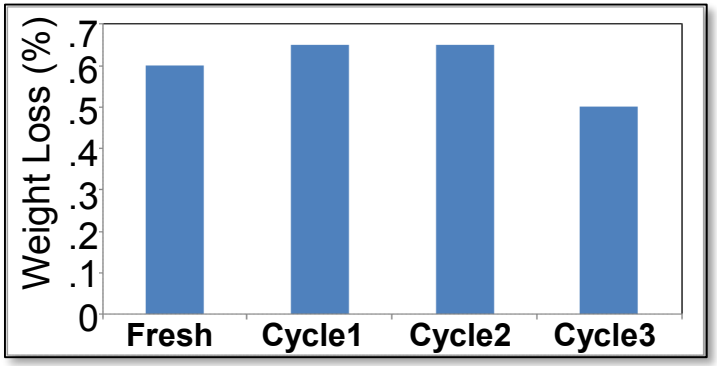
Task D : Developed a Method for Regenerating the Catalyst

Catalyst Regeneration Method:

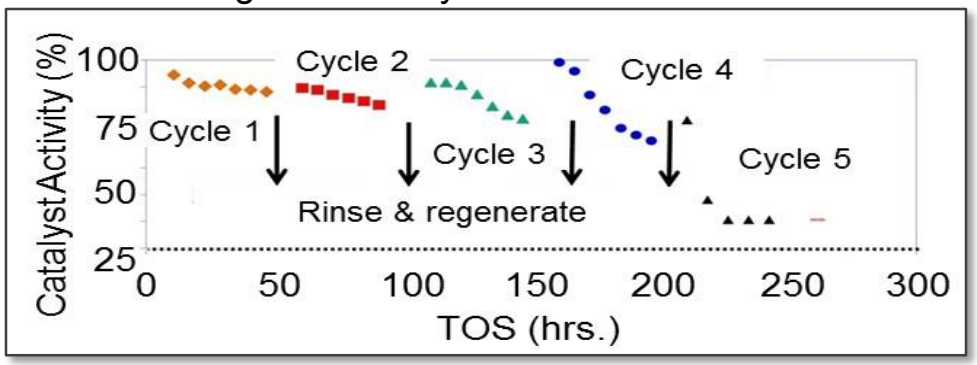
- Remove loosely bound carbon via rinsing with solvent
- Remove bound carbon (coke) via chemical reaction
- Reactivate catalyst via reduction with hydrogen



Metal dispersion lost after successive regeneration cycles



Weight loss of fresh and regenerated catalyst in oxidative furnace shows the efficacy of carbon removal



Activity lost after successive regeneration cycles

3 – Technical Accomplishments/Progress/Results

Task D :

- **Identified Heteroatom poisoning as root cause for catalyst deactivation**
- **Developed an Ion Exchange Process to Clean-up Bio oil**

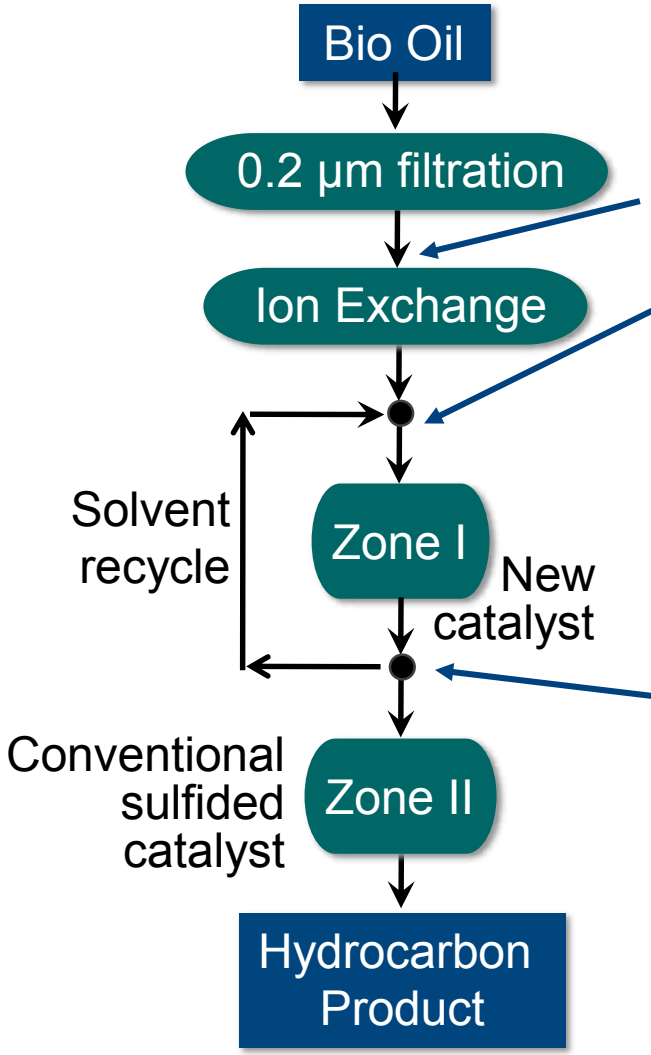
Deactivation cause	Justification
Poisoning	ICP data shows heteroatoms on catalyst
Metal leaching	ICP data does not show loss of active metal
Metal agglomeration	TEM data does not show active metal agglomeration
Support decomposition	XRD data does not show significant decomposition
Coke accumulation	TGA data shows almost complete coke removal
Loss of acidity	Not significant

Bio oil Clean-up Method:

- Low temperature slurry reaction
- Use of low cost ion exchange media
- Filtration of bio oil through 0.2 µm pressure filter to remove solid particulate

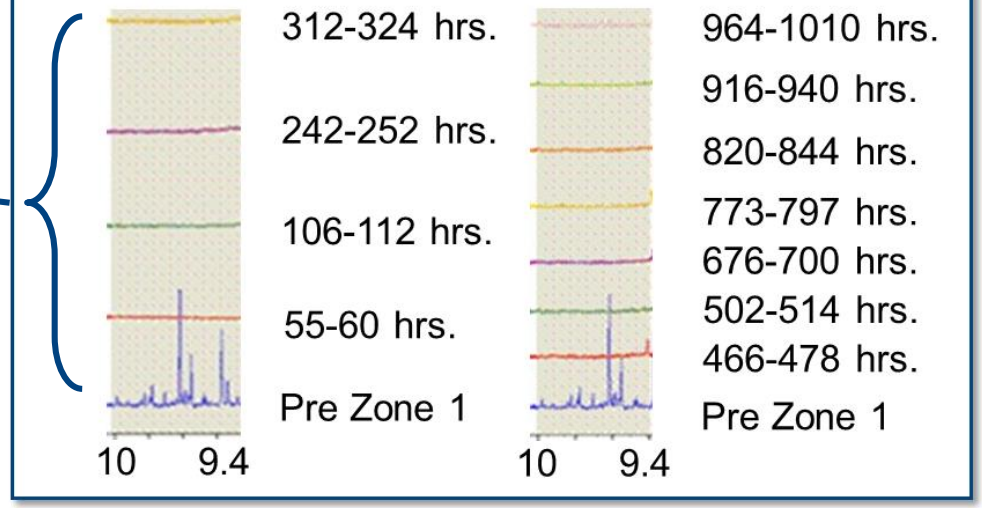
3 – Technical Accomplishments/Progress/Results

Task D : Developed a New Process For Bio oil Hydrotreatment



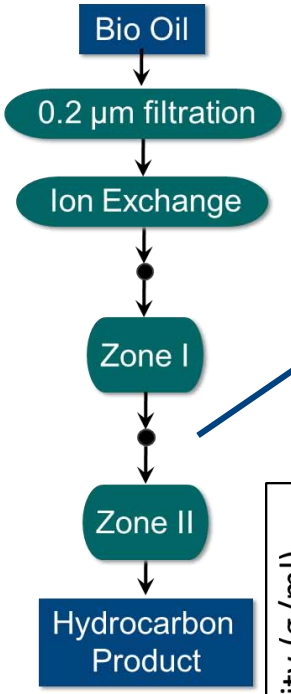
(ppm)	Al	Ca	Fe	K	Mg	Na	Si	S
Bio oil	5.1	18	15.8	57.2	5.1	3.8	10.6	10.1
Cleaned up Bio oil	<3	<3	<3	6	<3	2.8	.8	8.9

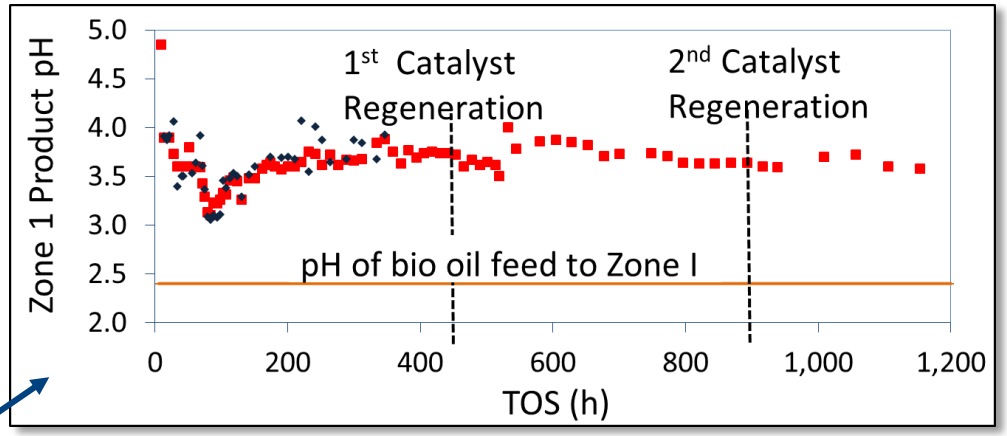
^{1}H NMR spectra between 9.4 to 10 ppm showing aldehyde conversion in Zone I



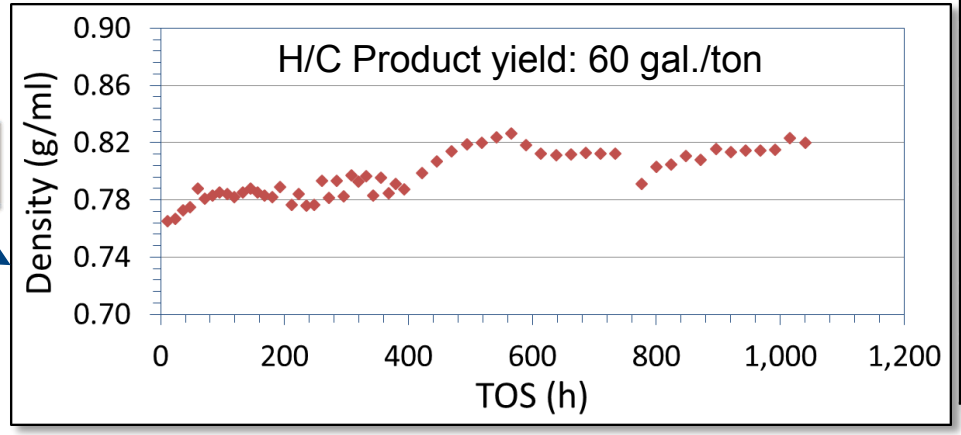
3 – Technical Accomplishments/Progress/Results

Task F, G : Approximately 1,200 hrs. TOS Achieved in Zone I, and as of March 17, 2015, 1,060 hrs. Achieved in Zone II





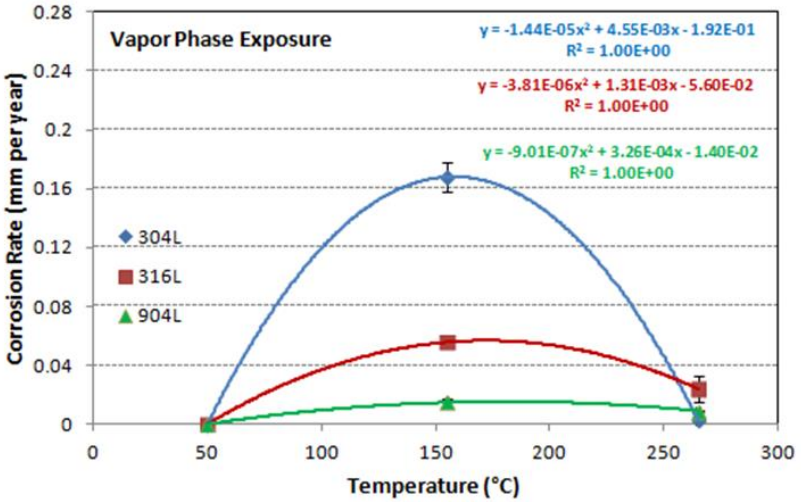
	%Wt
Paraffins	24.1
Total aromatic	5.6
Napththelenes	67.9
Olefins	2.4
Total	100

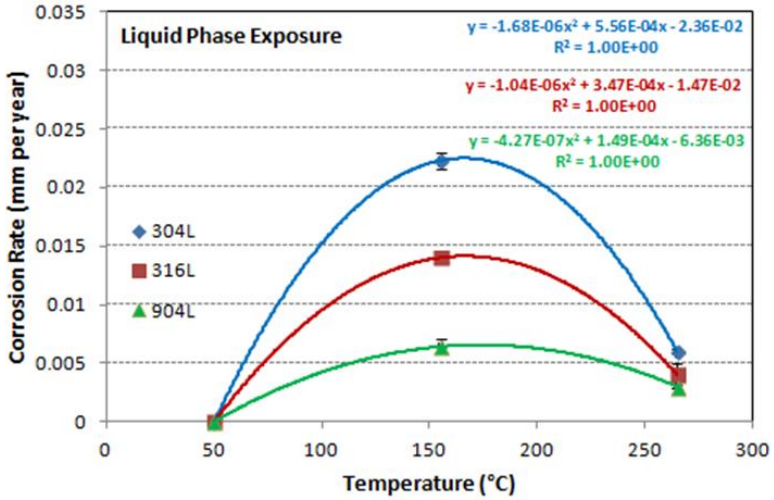


	Refinery example	Battelle Results
Density (kg/m3)	0.8-0.9	0.81-0.85
BSW (wt%)	0.5	NA (<0.5)
Total S (wt%)	0.082	<0.005
Total N2 (wt%)	0.015	<0.05
TAN (mg KOH/g)	0.5	<0.5
Pour Point (°C)	21-36	NA(<<20)
Viscosity (cPs)	3-236	<2

3 – Technical Accomplishments/Progress/Results

Task E : Predictive models were developed for general corrosion and show that higher corrosion may occur at the lower temperature, entrance region to the hydrotreatment reactor





The models are based on:

- 1,000 hrs. “low temperature” test at 50°C.
- 1,000 hrs. “intermediate temperature” test at 155°C.
- 1,000 hrs. “high temperature” test at 265°C.

Some assumptions include:

- Temp. range of 50°C - 265°C..
- Max. corrosion at 155°C.
- Model is only for general corrosion, not SSC or H_2 embrittlement.
- Autoclave tests are representative of hydrotreater

4 – Relevance

BETO's Strategic goal of thermochemical conversion R&D:

To develop commercially viable technologies for converting biomass into energy-dense, fungible, finished liquid fuels, such as renewable gasoline, jet, and diesel, as well as biochemicals and biopower. **[Section 2.2.2.1, BETO MYPP Nov 2014]**

This project has, to the best of our knowledge, for the first time enabled a commercially viable bio oil hydro-treatment process to produce renewable blend stock for transportation fuels.

- ✓ Novel, low cost bio oil cleanup process to enable long-term operation of a bio oil stabilization catalyst
- ✓ A non carbon supported catalyst and successful regeneration, allowing long-term hydrotreater operation
- ✓ New process to use this stabilization catalyst and over 1,200 hrs. of operation
- ✓ Hydro processing of the stabilized bio oil using a commercial sulfided catalyst for extended periods (~1,060 hrs. as of 3/17/15 – hydrotreater operation continuing)

4 – Relevance

Application of Project Outcomes

The technology developed under this project can be scaled up and commercialized in the near future:

- Battelle is developing small scale (~100 tons/day) biorefineries using fast pyrolysis bio oil as a platform intermediate product to produce fuels and chemicals.
- Distributed deployment of a large number of these systems will contribute significantly toward meeting goals & objectives of the DOE Biomass Program.
- A biochemicals company is already being spun off in FY2015. This company will scale up the 'front end' (pyrolysis) process.
- Hydrotreatment catalysts and processes developed under this project can be licensed to the spin-off company for the production of biofuels, using the already proven pyrolysis process.

Summary

We have completed our project and met the 1,000 hrs. TOS goal on DOE Approved Schedule and Budget

- **Relevance**
  - ✓ Aligned with BETO MYPP goals and relevant to bioenergy industry to enable production of biofuels by small systems, allowing incremental scale up in a capital constrained financial environment.
- **Approach**
  - ✓ Using a platform pyrolysis process with new hydrotreatment process which has been demonstrated for ~1,000 hrs. TOS, and with a biochemical will allow commercialization of this technology.
- **Technical accomplishments**
  - ✓ Successfully demonstrated long term (~1,000 hrs.) hydrotreatment and hydrocarbon production for the first time in a DOE contracted project.
- **Technology transfer**
  - ✓ Planning to scale up and further develop this technology and license it for commercial use.