U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Fast Pyrolysis and Upgrading

WBS: 2.3.1.301/302

U.S. Department of Energy (DOE)
Bioenergy Technologies Office (BETO)
2017 Project Peer Review

Thermochemical Conversion

March 7th, 2017

Project Leads:

Alan Zacher – PNNL

Jae-Soon Choi – ORNL

ChemCatBio Structure

Core Catalysis Projects

Catalytic Upgrading of Biochemical Intermediates
(NREL, PNNL, ORNL, LANL)

Liquid Fuels via Upgrading of Indirect Liquefaction Intermediates
(NREL, PNNL)

Fast Pyrolysis and Upgrading
(PNNL, ORNL)

Catalytic Fast Pyrolysis
(NREL, PNNL)

Recovering and Upgrading Biogenic Carbon in Aqueous Waste Streams
(PNNL, NREL)

Zeolites and Metal Oxide Catalysts

Supported Metal Catalysts

Cross-cutting Discussion Groups

Enabling Projects

Advanced Catalyst Synthesis and Characterization
(NREL, ANL, ORNL)

Catalyst Cost Model Development
(NREL, PNNL)

Consortium for Computational Physics and Chemistry
(ORNL, NREL, PNNL, ANL, NETL)

Consortium Integration

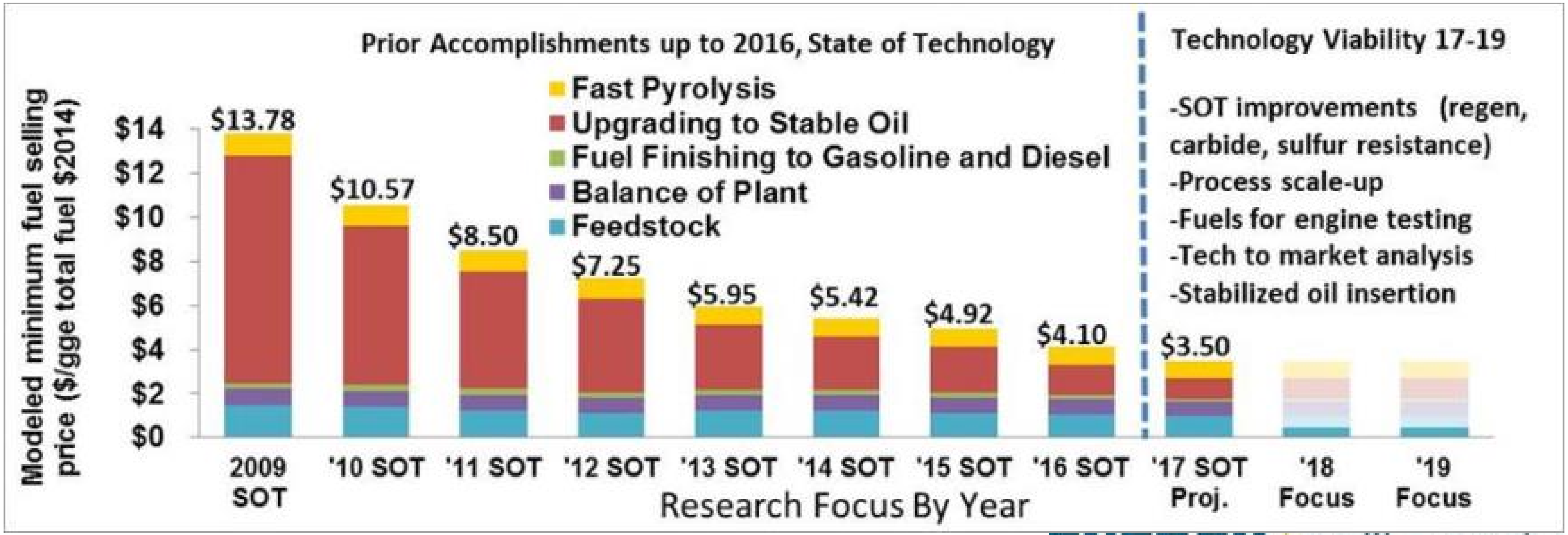
- Core catalysis projects focused on specific *applications*
- *Collaborative* projects leveraging core capabilities across DOE laboratories
- *Cross-fertilization* through discussion groups

Goal Statement

Goal: To develop cost competitive biofuels through catalytic stabilization and deoxygenation of Fast Pyrolysis Bio-oil (FPBO)

Outcome: Advancement of the State of Technology for upgrading FPBO by demonstration of gasoline and diesel blend stocks at a mature modeled price of \$3.50/GGE by

- Advancing stabilization catalyst lifetime
- Leveraging catalyst and process efficiencies
- Targeting modelled conversion cost of less than \$2.53/GGE, nth plant



Quad Chart Overview

Timeline

- Project start date: 10/1/2016
- Project end date: 9/30/2019
- Percent complete: 17%

Budget

	FY15 Costs	FY16 Costs	Total Planned Funding (FY17-Project End Date)
DOE Funded	$2.3M	$3.5M	$5.5M

*FY17 operating budget reduced to $1.95M

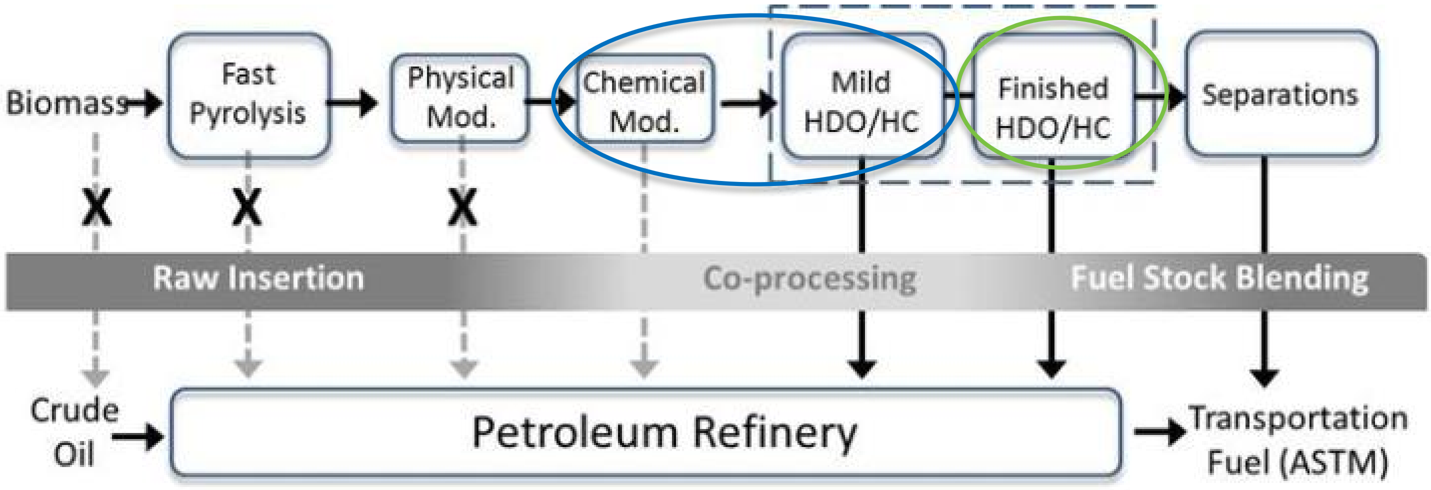
Barriers addressed & Actions

- Ct-G. Efficient Intermediate Cleanup and Conditioning: *Developing stabilization of bio-oils for upgrading and insertion*
- Ct-H. Efficient Catalytic Upgrading of Bio-oil Intermediates to fuels: *TEA guided development of processes and catalysts for hydrocarbon fuel production from bio-oil*
- MYPP Target: Validate pathway for hydrocarbon biofuel production at a mature modeled price of $3/GGE: *On schedule to complete FY17Q4*

Partners

- **National Labs**
  - PNNL (80%)
  - ORNL (20%)
- **Industry**
  - VTT Finland, CanmetENERGY, WR Grace, PFI Norway, IEA Task 34
- **Other Collaborations**
  - NREL

1. Project Overview: Context of FP&U

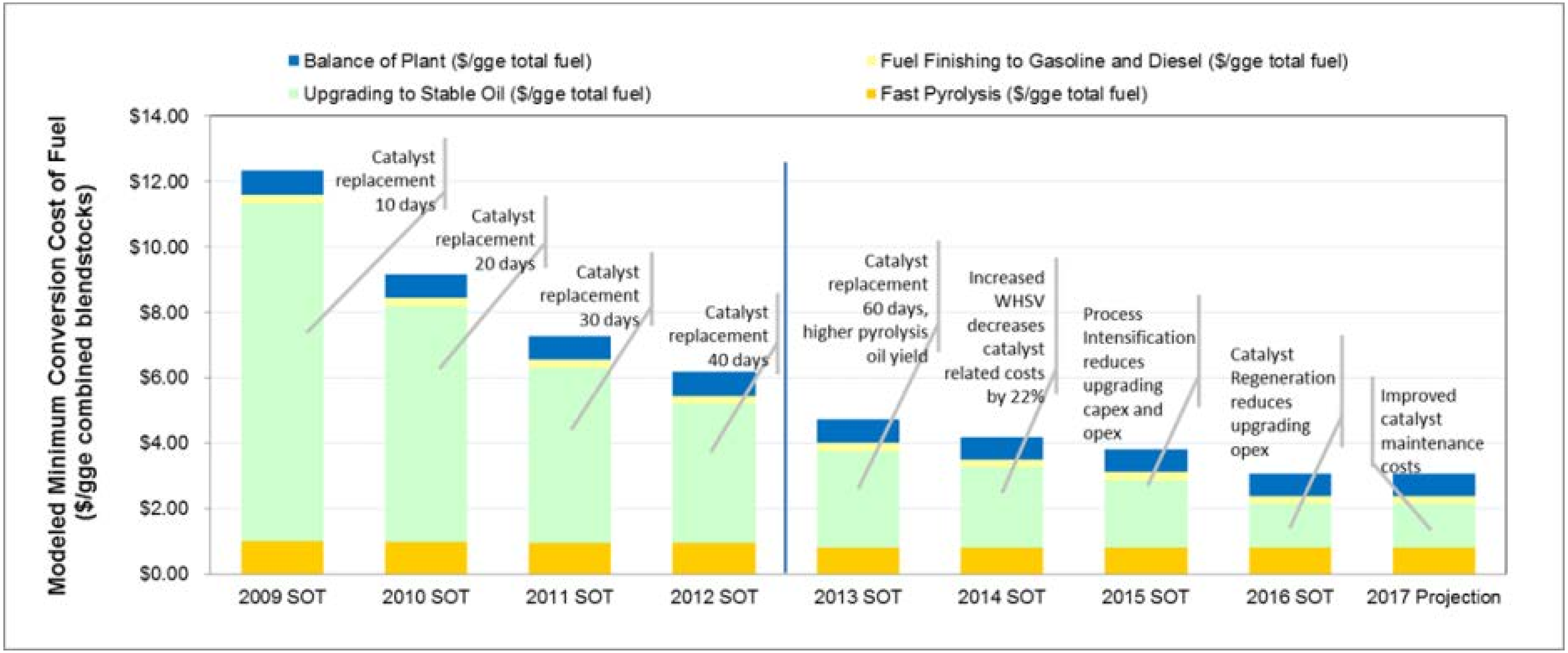


Green Chem., 2014, 16, 492.

Goal: Produce infrastructure compatible fuels and/or intermediates from FPBO and reduce processing costs by:

- Increasing bio-oil processing stability and catalyst lifetime through **hydrogenation and managing contaminants**
- Improving fuel quality and compatibility by **catalytic removal of oxygen**
- Identifying and solving catalyst and process efficiency barriers to improve conversion cost as guided by iterative technoeconomic (TEA) modelling

1. Project Overview: Progress History



Technoeconomic analysis used to guide research priorities and measure progress against the SOT

2. Technical Approach: Challenges and Success Factors

Primary Challenges

- **<u>Bio-oil thermal instability:</u>** Stabilization process must cost-effectively reduce oil carbonyl content to avg of 1.5mmol/g to enable HDO catalysis
  - May also enable refinery integration of a stabilized intermediate
- **<u>Sulfur in bio-oil:</u>** Interferes with stabilization. Reducing the sulfur content from 50ppm to 25ppm would result in low temp catalyst life improvement
- **<u>Polymer and sulfur fouling of catalyst:</u>** Regeneration is required
  - Increasing time between regenerations from 200 to 250h
  - Reducing initial and subsequent activity regenerations loss below 19% and 2.5% respectively

Critical Success Factors

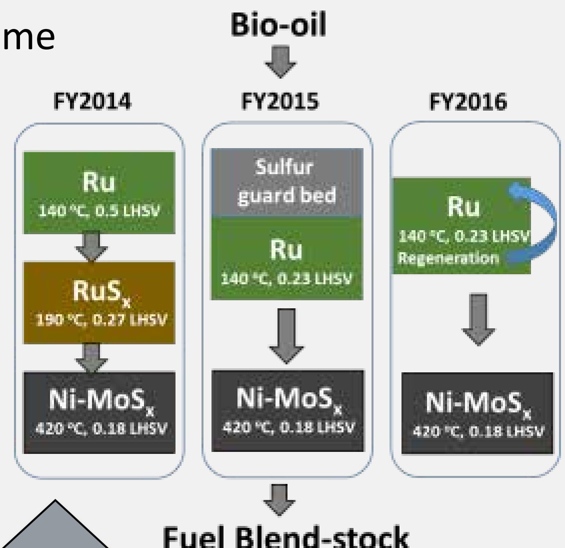
- Achieve modelled conversion cost target of $2.53/GGE
- Demonstrate fuel product suitability for blending for engine use
- Establish modeled performance at scale

2. Technical Approach: SOT and Technology Viability

Advancement of SOT

Develop bio-oil stabilization technique (*Task B*)

- Deep understanding of the chemistry
- Catalyst and process development
  - Elimination of unit ops
  - Increase in catalyst lifetime



Technology Viability

- Demonstration at larger scale, using other biomass sources (*Task A*)
- Develop reactor models for scale-up (*Task D*)

Technoeconomic analysis

FY15 and 16 cost goal achieved

Tech to Market

Roadmap (Task C)

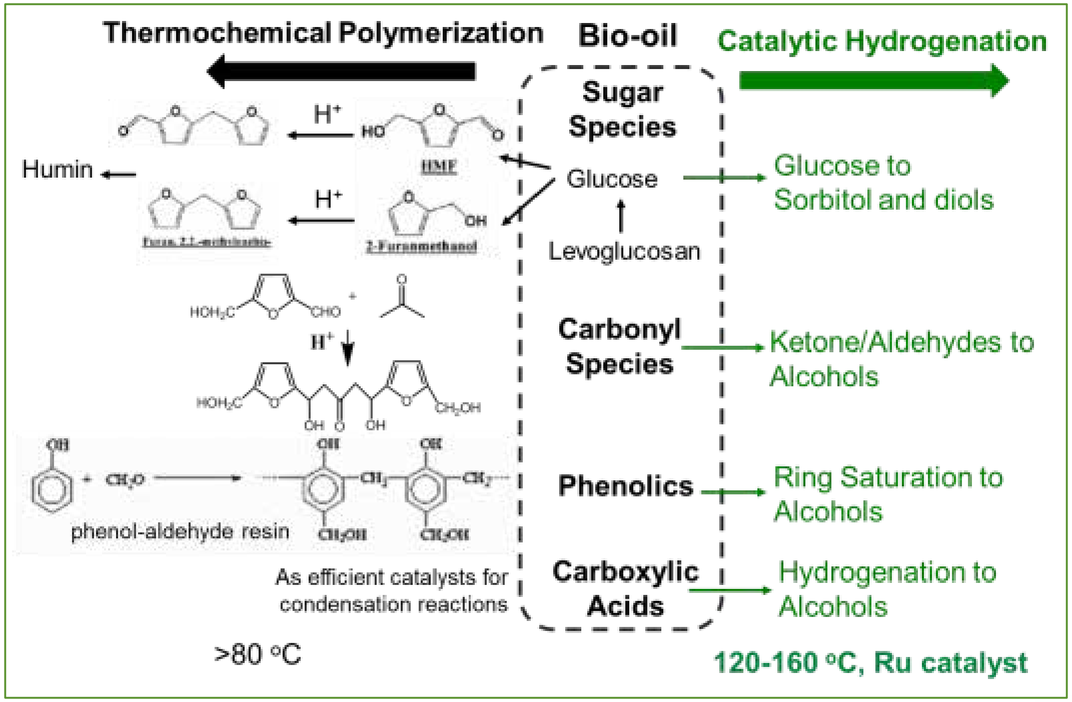
2. Management Approach

Management
Alan Zacher, PNNL (reporting)
Jae-Soon Choi, ORNL
Huamin Wang, PNNL Deputy

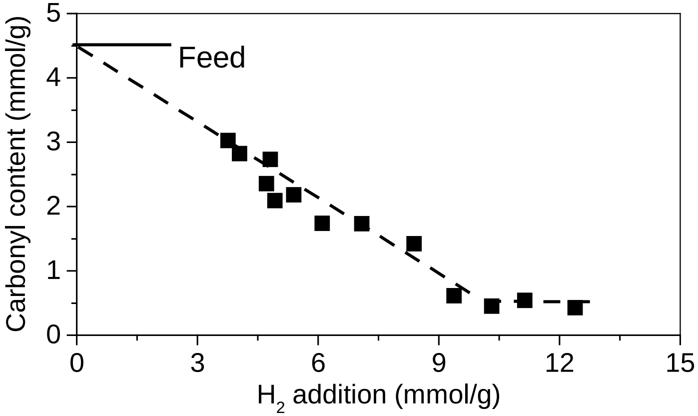
- **A. Pilot and Demo Plant Hydrotreating**
  M.V. Olarte
  - G. Neuenschwander
  - LJ. Rotness
  - M. Grey
  - T. Hart
  - A. Zacher
  - B. Gruel
  - R. Thornhill
  - L. Middleton
- **B. Advanced Stabilization and Hydrotreating**
  H. Wang, J.-S. Choi
  - J. Frye, jr.
  - M. Santosa
  - S-J. Lee
  - M. Olarte
  - G. Neuenschwander
  - B. Roberts
  - I. Kutnyakov

  - Z. Li
  - M. Connatser,
  - S. Lewis
  - B. Armstrong
  - M. Lance
  - H. Meyer
  - Z. Wu
- **C. Tech to Market**
  A. Zacher, J-S. Choi
  - M. Santosa
  - A. Meyer
  - S. Jones
- **D. Reactor Model Development**
  D.M. Santosa
  - M. Swita
  - H. Wang
  - M. Olarte
  - B. Weber

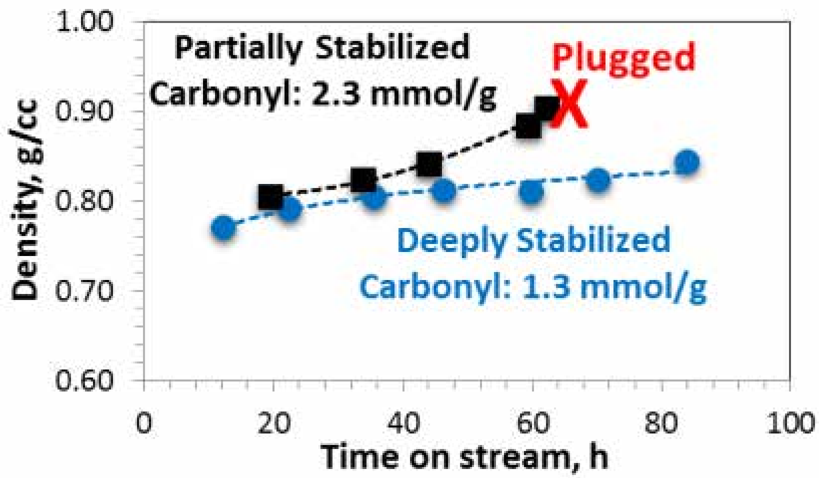
3. Research Progress: Deep Stabilization



Carbonyl content vs H_2 addition



Partially vs deeply stabilized bio-oil



- Hydrogenation of bio-oil stabilizes bio-oil to enable deoxygenation chemistry
- Ru catalyst is identified as an efficient catalyst for bio-oil hydrogenation
- For fast pyrolysis oil, carbonyl content correlates with suitability for 400 °C hydrotreating

H Wang et al. ACS Sustainable Chem. Eng., 2016, 4, 5533

3. Research Progress: Deep Stabilization

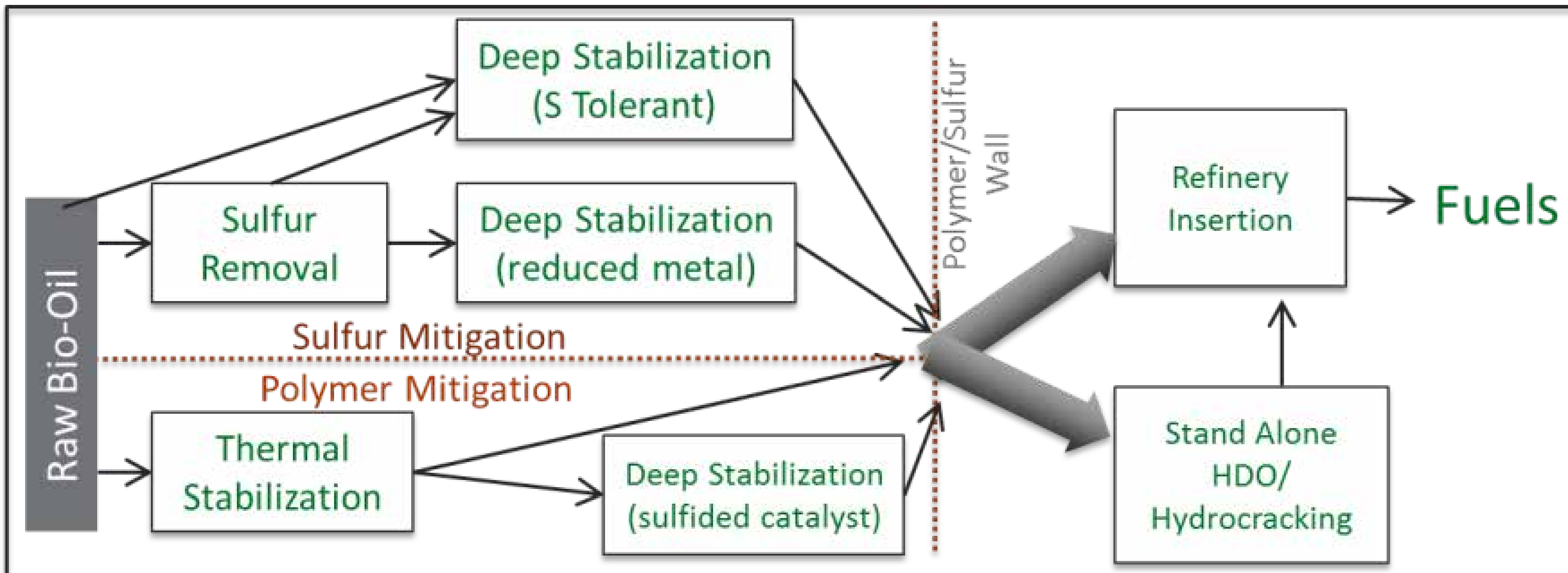
Improve catalyst life by mitigating poisoning

Catalyst life can be improved by:

- Removing sulfur from bio-oil
- Improving sulfur tolerance
- Catalyst/method to stabilize bio-oil without low T hydrogenation

Success is achieved by:

- Hydrogenation to improve thermal stability to enable upgrading catalysis
- Reducing the impact of sulfur on the stabilization catalyst
- Regeneration of deactivated catalyst



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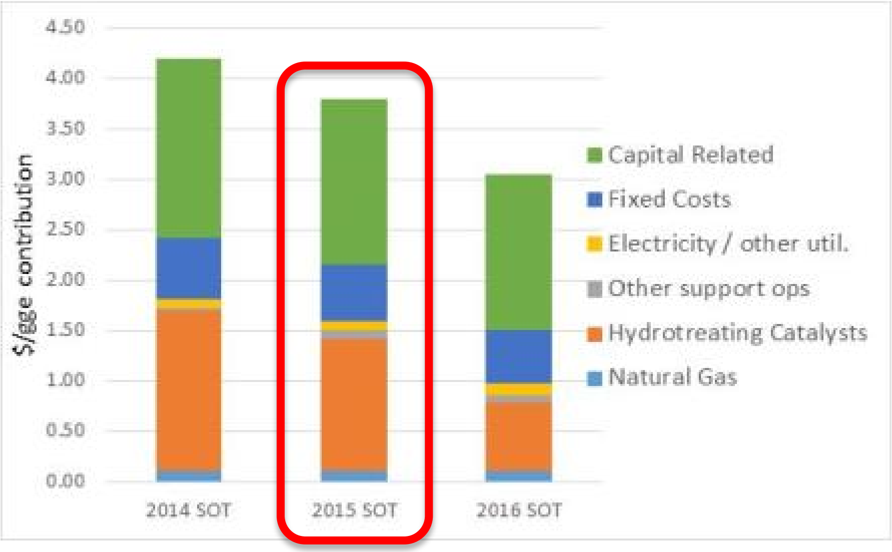
3. Research Progress: FY15 SOT Achieved

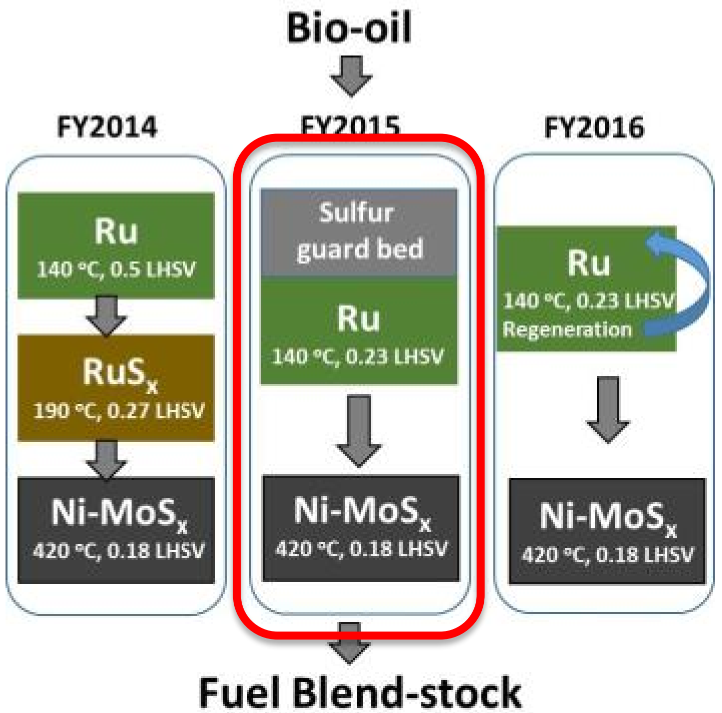


FY15 SOT Research

2015 SOT and cost goal achieved by

- Deep stabilization eliminating one hydrotreating stage
- Sulfur removal from bio-oil enabling longer life of catalyst

Reactor	2014	2015	2016
Stabilizer	LHSV: 0.5 T: 140°C P: 1200 psig Catalyst: Ru-based	*Sulfur guard bed* + *Stabilizer bed* LHSV: 0.23 T: 140 °C P: 1200 psig Catalyst: Ru based	*Stabilizer bed* LHSV = 0.23 T= 140 °C P=1800 psig Catalyst: Ru based with catalyst regeneration
Upgrading Bed #1	LHSV: 0.27 T:180-200°C P: 2000 psig Catalyst: Ru-based		
Upgrading Bed #2	LHSV = 0.18 T = 420°C P = 2000 psig Catalyst: Mo-based	LHSV: 0.22 T: 420 °C P: 1800 psig Catalyst: Mo-based	LHSV: 0.22 T: 420 °C P: 1800 psig Catalyst: Mo-based



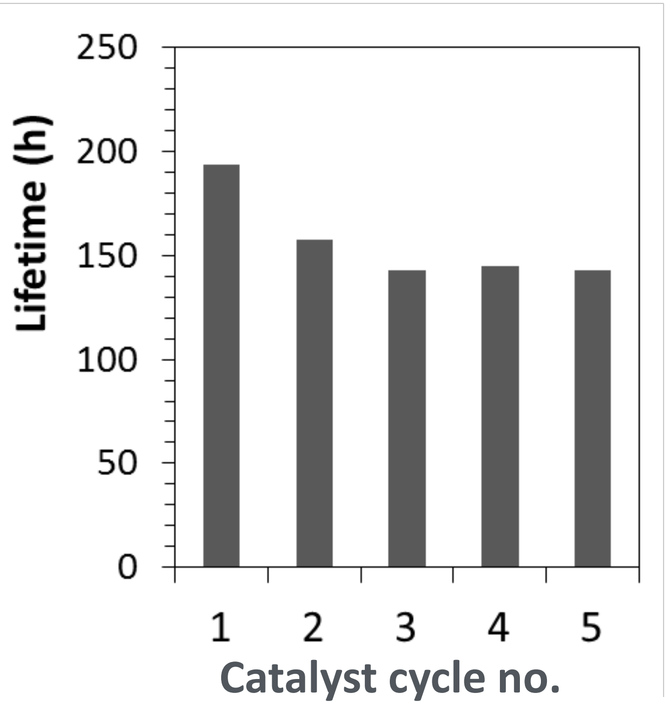
3. Research Progress: **Catalyst and Process Development**

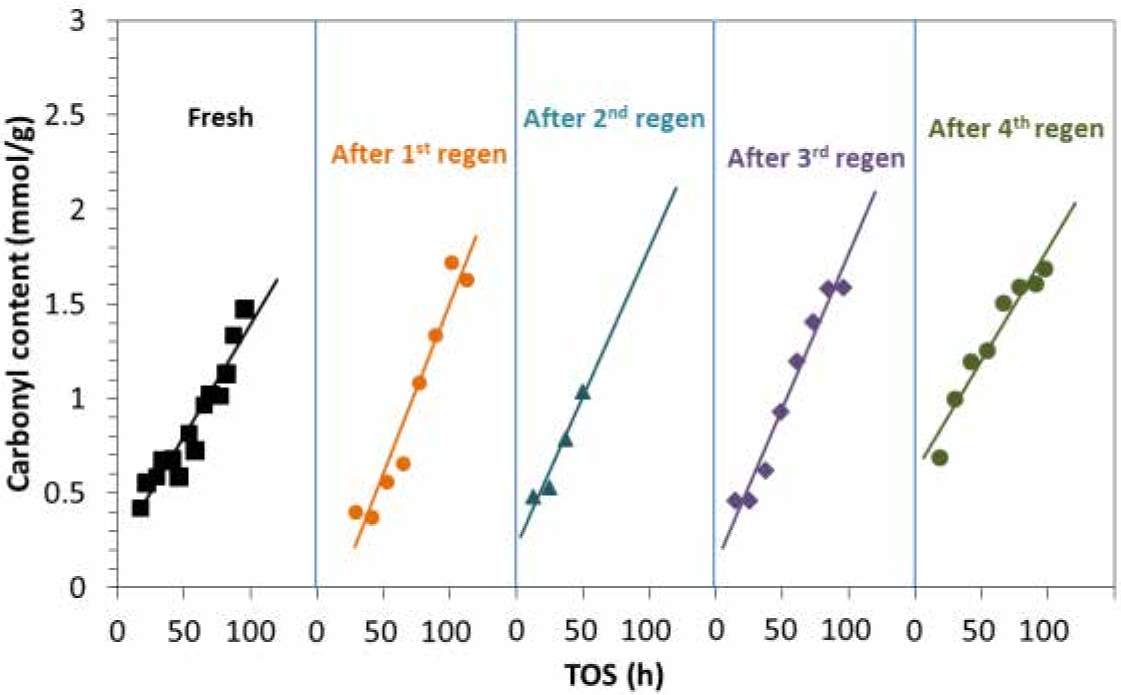
FY16 SOT Research

Catalyst life can be improved by:

- Improving sulfur tolerance
  - Catalyst regeneration
  - Sulfur tolerant catalyst

- Regeneration by low temperature extraction to remove sulfur species and polymers from catalyst surface
- Regeneration frequency dictated by feed sulfur content and uptake
- Activity of catalyst measured by hydrogenation of carbonyl content





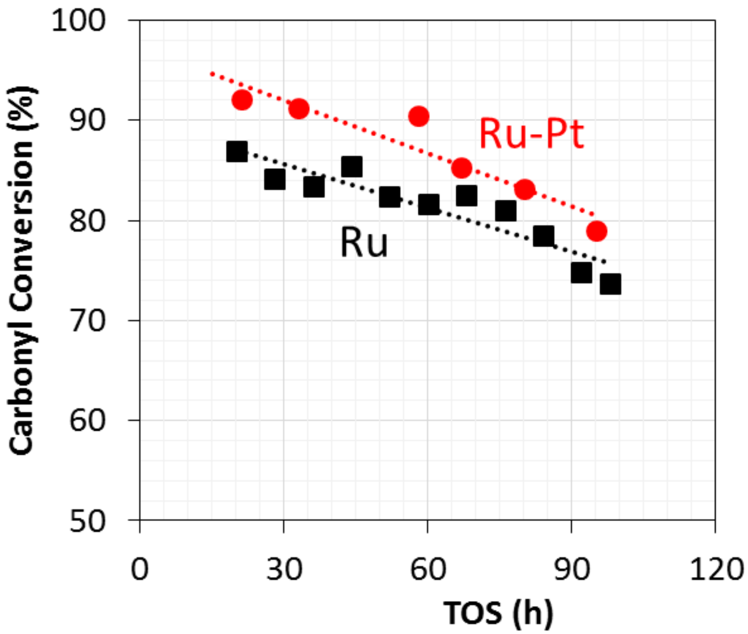
3. Research Progress: **Catalyst and Process Development**

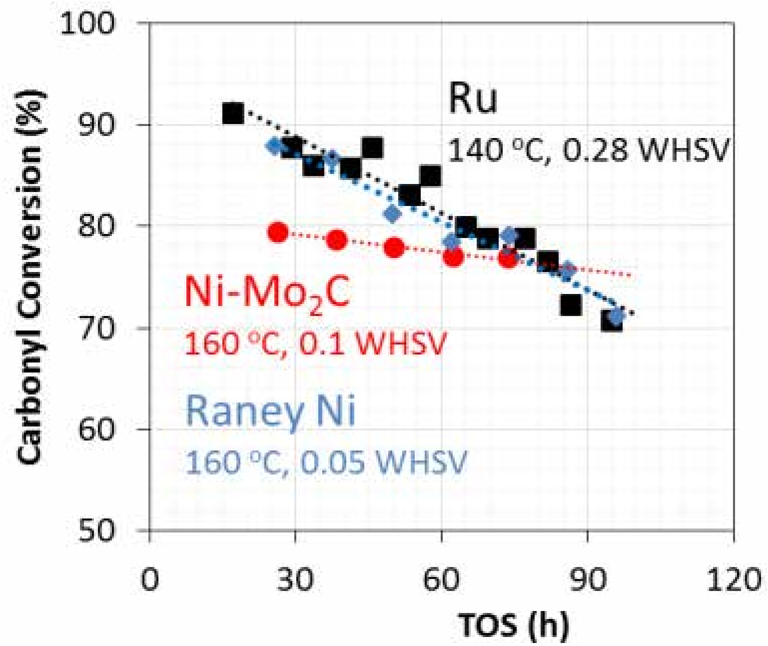
FY16 SOT Research

Catalyst life can be improved by:

- Improving sulfur tolerance
  - Catalyst regeneration
  - Sulfur tolerant catalyst

- Developing alternative catalysts in parallel with SOT (Ru) optimization
  - Bimetallic and base metal : PNNL
  - Mo carbides: ORNL





- Ru-based bimetallic catalysts (eg. Ru-Pt) can be more active than Ru but are not cost-effective

- Base metals (eg. Ni) and Mo carbides are lower cost, but require enhanced activity for economic competitiveness

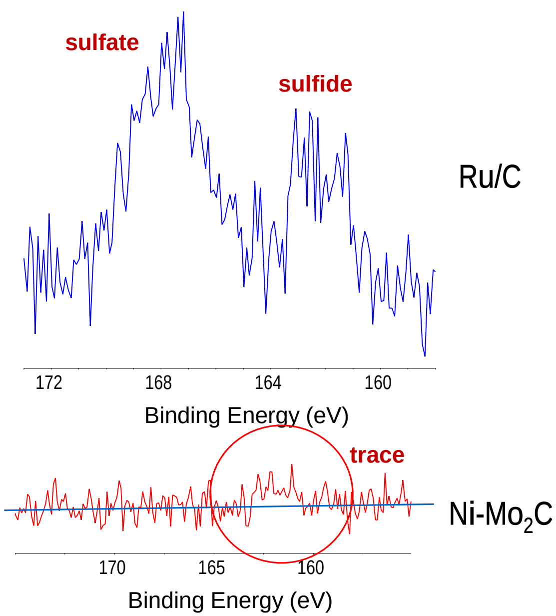
3. Research Progress: **Catalyst and Process Development**

FY16 SOT Research

Catalyst life can be improved by:

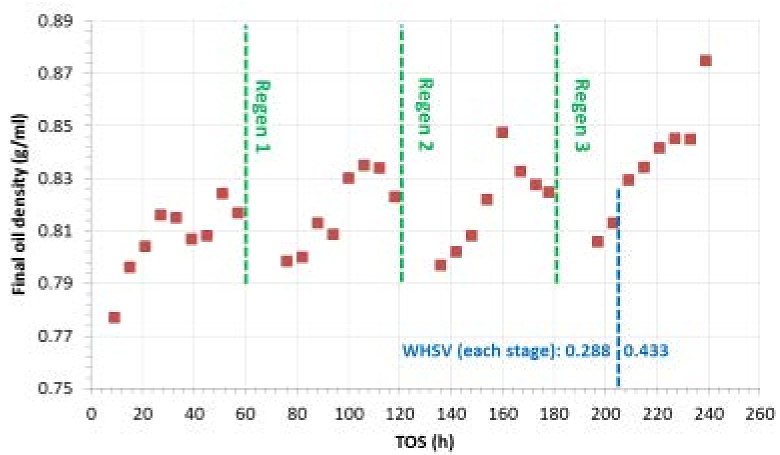
- Improving sulfur tolerance
  - Catalyst regeneration
  - Sulfur tolerant catalyst

Surface sulfur content after furfural HDO (150 °C)



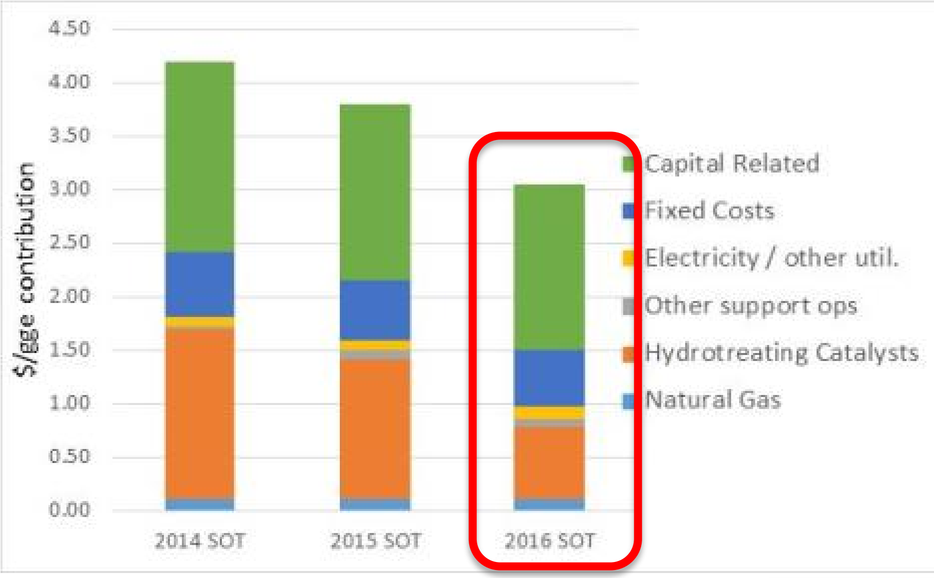
- Ni-Mo$_2$C intrinsically less sensitive to sulfur
  - Confirmed by XPS after testing with furfural (ORNL) and real bio-oil (PNNL)

- Promising properties of Mo carbides confirmed and being optimized
  - 2015 Peer Review: feasibility of applying Mo carbides to real bio-oil hydrotreating proven
  - 2017 Peer Review: sulfur tolerance & *in situ* regenerability (decoking) demonstrated
  - In progress: maximize activity (via promoter chemistry: Ni) and catalyst engineering
  - Synthesis (ORNL), reactor & TEA (PNNL), engineered catalyst (ORNL, PNNL)



- Carbides are *in situ* regenerable

3. Research Progress: FY16 SOT Achieved



FY16 SOT Research

2016 SOT and cost goal achieved by

- Catalyst regeneration enabling extended lifetime of Ru catalyst

Reactor	2014	2015	2016
Stabilizer	LHSV: 0.5 T: 140°C P: 1200 psig Catalyst: Ru-based	*Sulfur guard bed* + *Stabilizer bed* LHSV: 0.23 T: 140 ºC P: 1200 psig Catalyst: Ru based	*Stabilizer bed* LHSV = 0.23 T= 140 ºC P=1800 psig Catalyst: Ru based with catalyst regeneration
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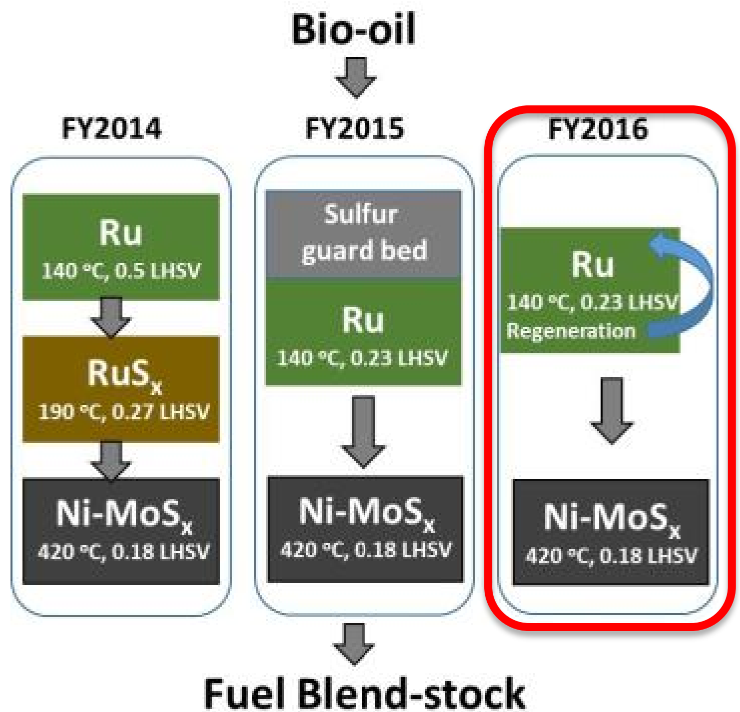


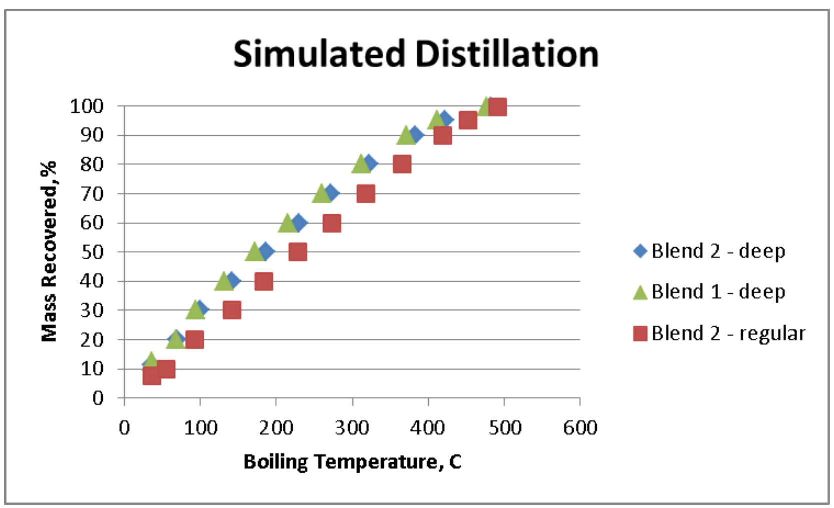
3. Research Progress: Technology Viability

FY16 Technology Viability

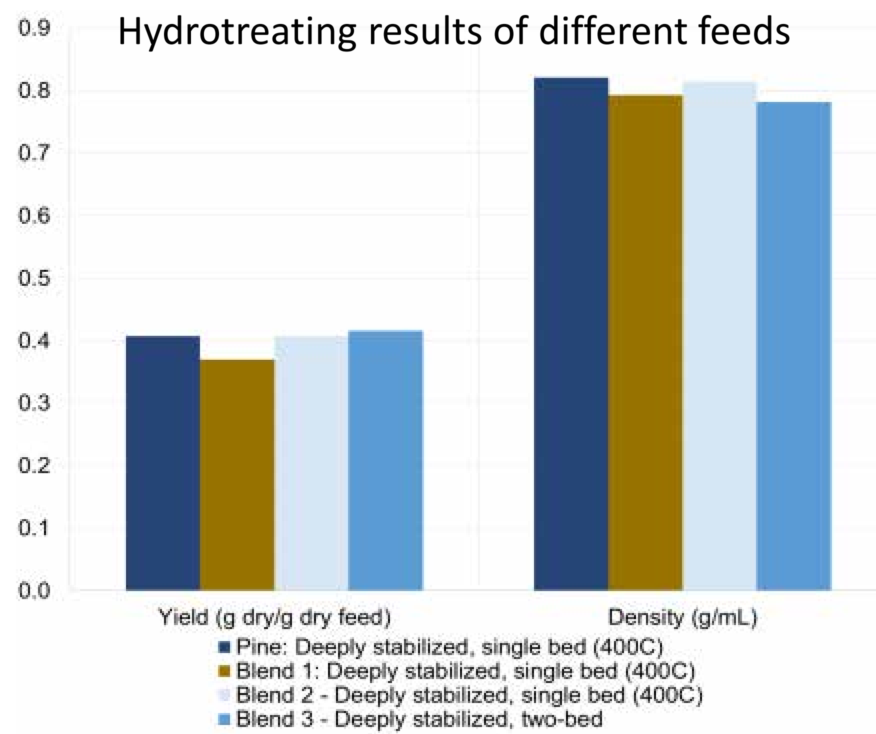
Technology viability can be improved by:

- Expanding biomass sources
- Demonstrate at larger scale

Evaluation on hydrotreating of pyrolysis oils produced at different pyrolyzer scales and types (NREL's 2-FBR vs. TCPDU) currently on-going



- Feedstock costs more than 20% of the MFSP
- Different types of lignocellulosic tested: results not much different in yield and product densities



3. Research Progress: Technology Viability

FY17 Technology Viability

Technology viability can be improved by:

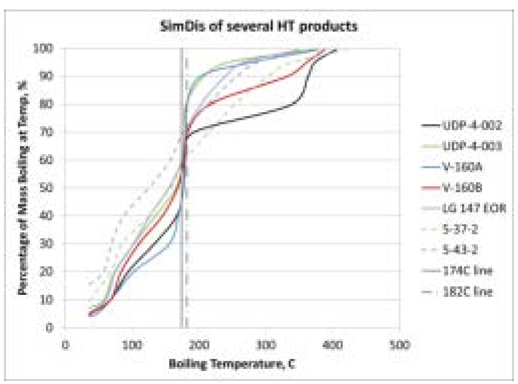
- Expanding biomass sources
- Demonstrate at larger scale

- FY17Q1 milestone achieved: Commissioning Demo-scale (20 L catalyst capacity) hydrotreater
- Hydrocarbon fuels produced from biomass derived bio-oil with low oxygen content

Analysis (wet basis, as received) of feed and product of scaled-up reactor

	C	H	O	N	S	Moisture	TAN
Feed	45.1	7.1	43.4	<0.05	<0.03	19	117
Product*	85.7	14.7	0.6	<0.05	<0.03	<0.3	<0.1

*collected product from receiver contains approximately 12% decane from initial sulfurizing step in process start-up.



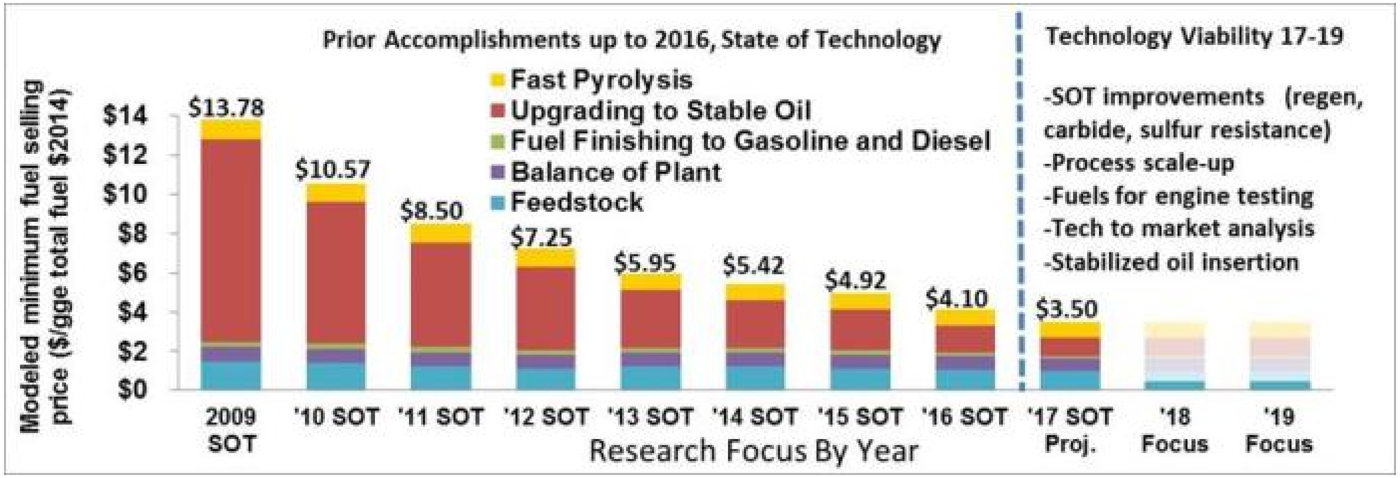
Demo Scale Outcomes:

- Future engine testing of fuels from pyrolysis/upgrading of woody biomass
- Identify scale-up challenges

4. Relevance

Goal: To develop cost competitive biofuels through catalytic stabilization and deoxygenation of Pyrolysis Bio-oil (FPBO)

- Project has made continuous improvements to meet BETO's targets for the FP state of technology every year since 2009, targeted and measured by TEA.



- On schedule to meet BETO's 2017 target for FP of $3.50/GGE
- Results from this project will be leveraged by other BETO funded efforts
  - Upgrading processes and catalysts: HTL, CFP, other thermochemical liquefied biomass
  - Capabilities: Catalytic hydrotreaters, separations, and know-how developed for systems from demonstration plant to microscale that are used for biomass hydrogenation to produce fuels and chemicals for existing and future BETO funded efforts

4. Relevance: Advancing BETO Know-How

- Reactor know-how and systems will be leveraged by other BETO projects
- Capabilities and know-how developed at 5-scales to support projects for hydrogenation of biomass fuels or chemicals
- Continuous improvement operation strategies and systems
  - Production of samples at all scales to support related research

Nominal temperature: Up to 450C
Nominal pressure: Up to 2000psi

8 x 1.4ml beds

40ml bed (3 systems, +2 in FY17)

400/800ml bed

1 liter hydrotreater

20 liter bed + distillation

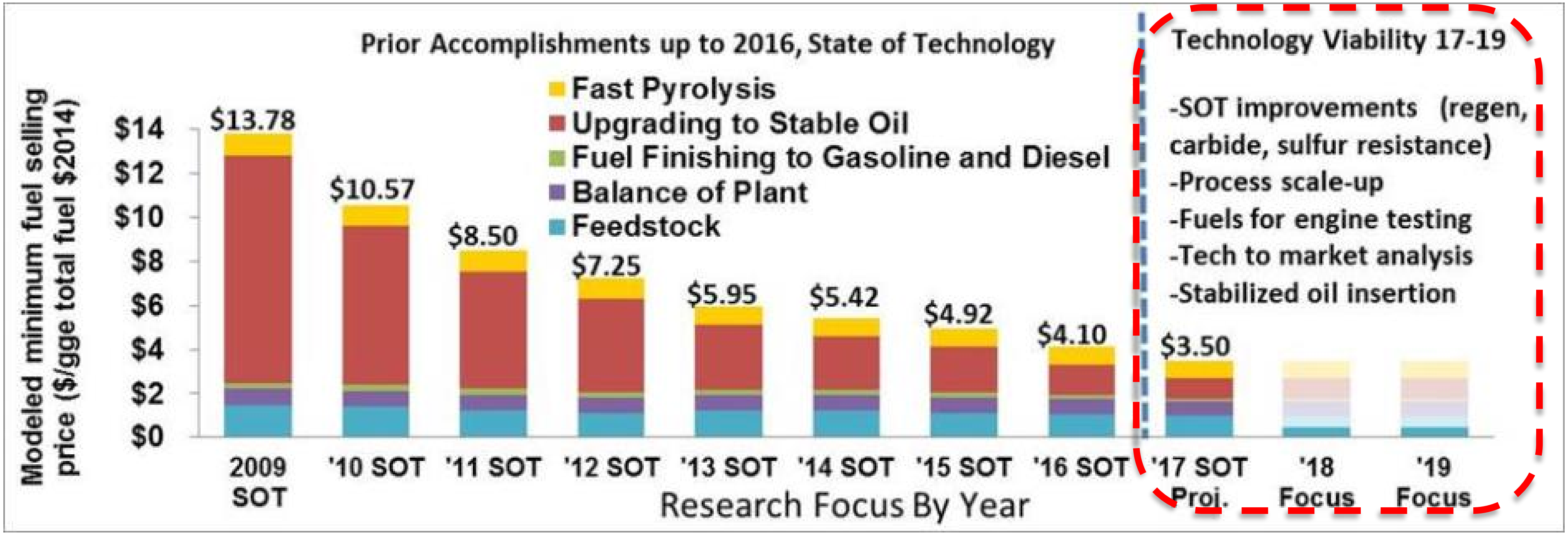
Catalyst Screening

Catalyst Evaluation

Process Development

Fuel or products for large scale evaluation and testing

5. Future Work: FY17 Cost Goal and Technology Viability



Advancement of SOT

Catalyst and Process Development

- FY17 cost goal
- Further improvement of quality of bio-oils and products

Technology Viability

- Process Scale-up
- Fuels for Engine Testing
- Reactor Model
- Stabilized Oil Insertion

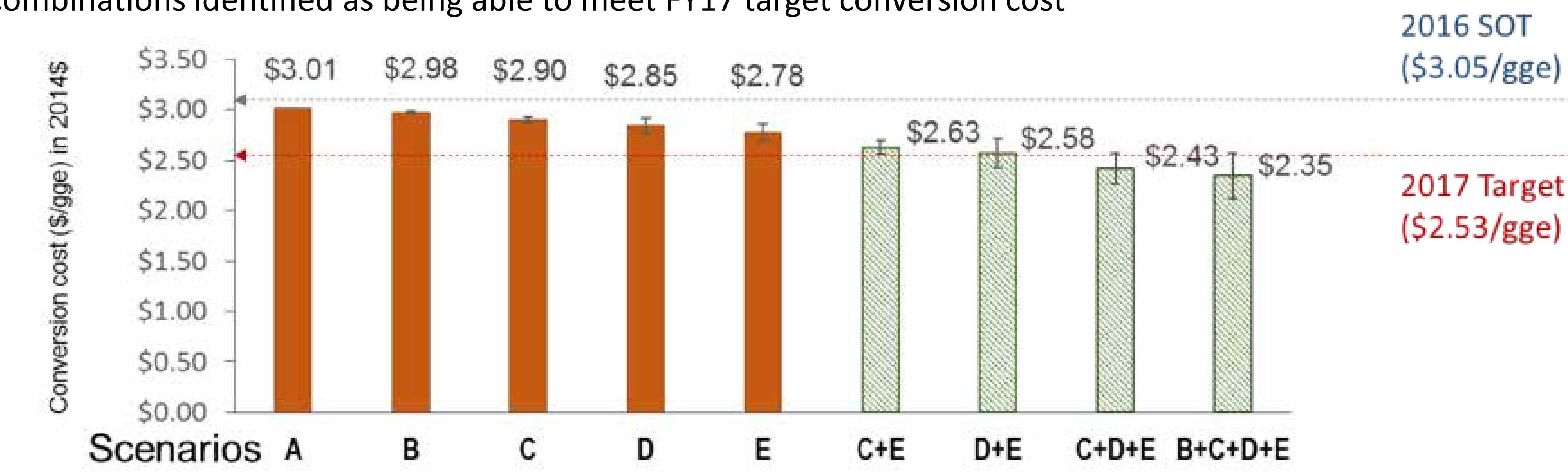
Technoeconomic analysis

Tech to Market Analysis

5. Future Work: Catalyst/Process Development for SOT Targets

12 proposed improvements to SOT identified for FY17

Of these, TEA identified 5 (A to E) as largest cost reduction to SOT, established target metrics for each combinations identified as being able to meet FY17 target conversion cost



A Increased 2nd HDO bed lifetime

B 7-15% reduction of stabilization catalyst cost
- Less Ru loading or other low cost catalyst

C Eliminated hydrocracking bed
- Co-feeding residues to the 2nd HDO bed

D Low cost sulfur guard bed
- Spent Ru catalyst as guard bed

E Using Ru catalyst with improved activity
- Project developed Ru/TiO_2 showed better activity than commercial Ru catalyst
- Synthesize engineered form and demonstrate regeneration
- Improve the regeneration protocol

5. Future Work: Quality Improvement of Bio-oils and Products

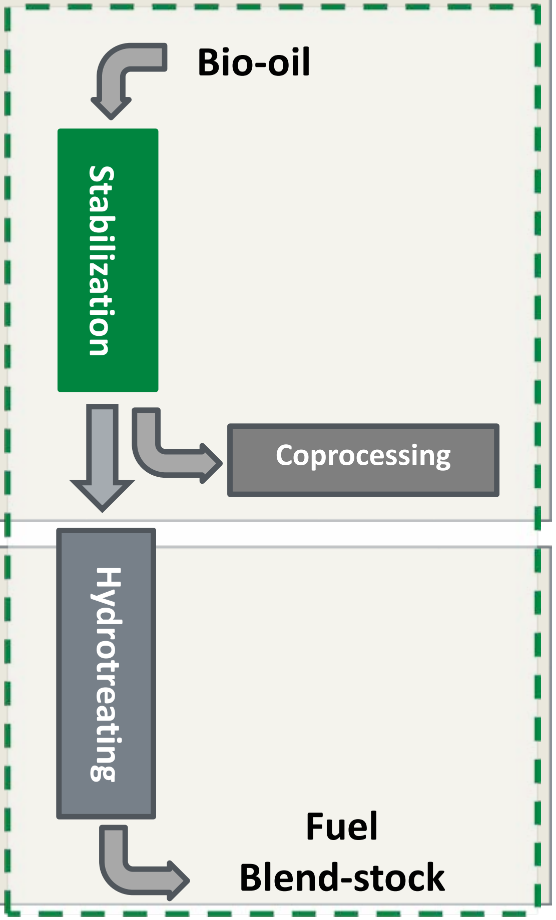
Advanced stabilization for bio-oil quality improvement:

exploiting fundamental insights gained through ChemCatBio: ACSC (2.5.4.303-305) & CPCC (2.5.1.305)

- Optimize catalyst and process enabling high-performance, long-term operation of catalytic bio-oil stabilization processes
  - Improve regeneration methods
  - Enhance low-temperature activity (higher SV)
  - Maximize hydrogen efficiency (hydrogen selectivity)
  - Develop cost-effective catalysts (carbide catalysts)
  - Explore novel stabilization approaches
- Quality improvement enabling bio-oil coprocessing

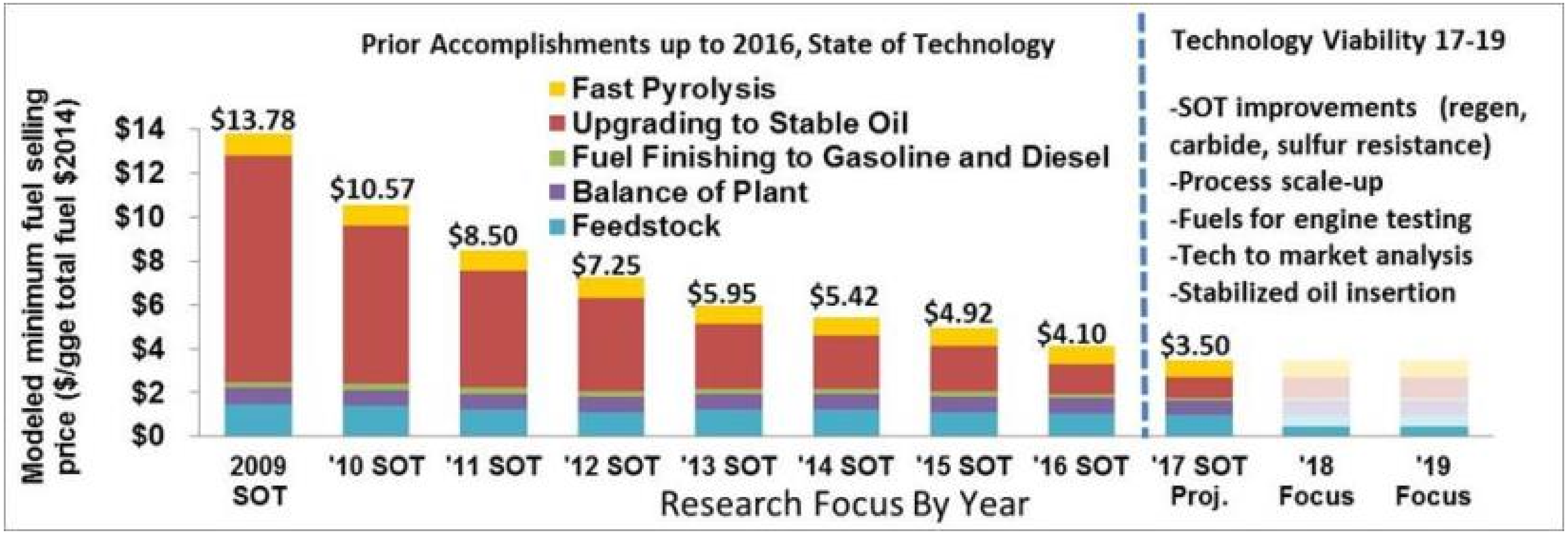
Catalyst and process optimization for hydrotreating:

- Improve product quality (fuel performance testing)
- Improve carbon efficiency (yield)



Summary

- TEA guided and measured research
- Continuous improvement to the FP SOT
- Working towards BETO's goal for FP&U pathway verification
- Successes from this project will be leveraged by existing and future research in biomass to fuels and chemicals
- Advances in stabilization may also enable bio-oil co-processing



Acknowledgements

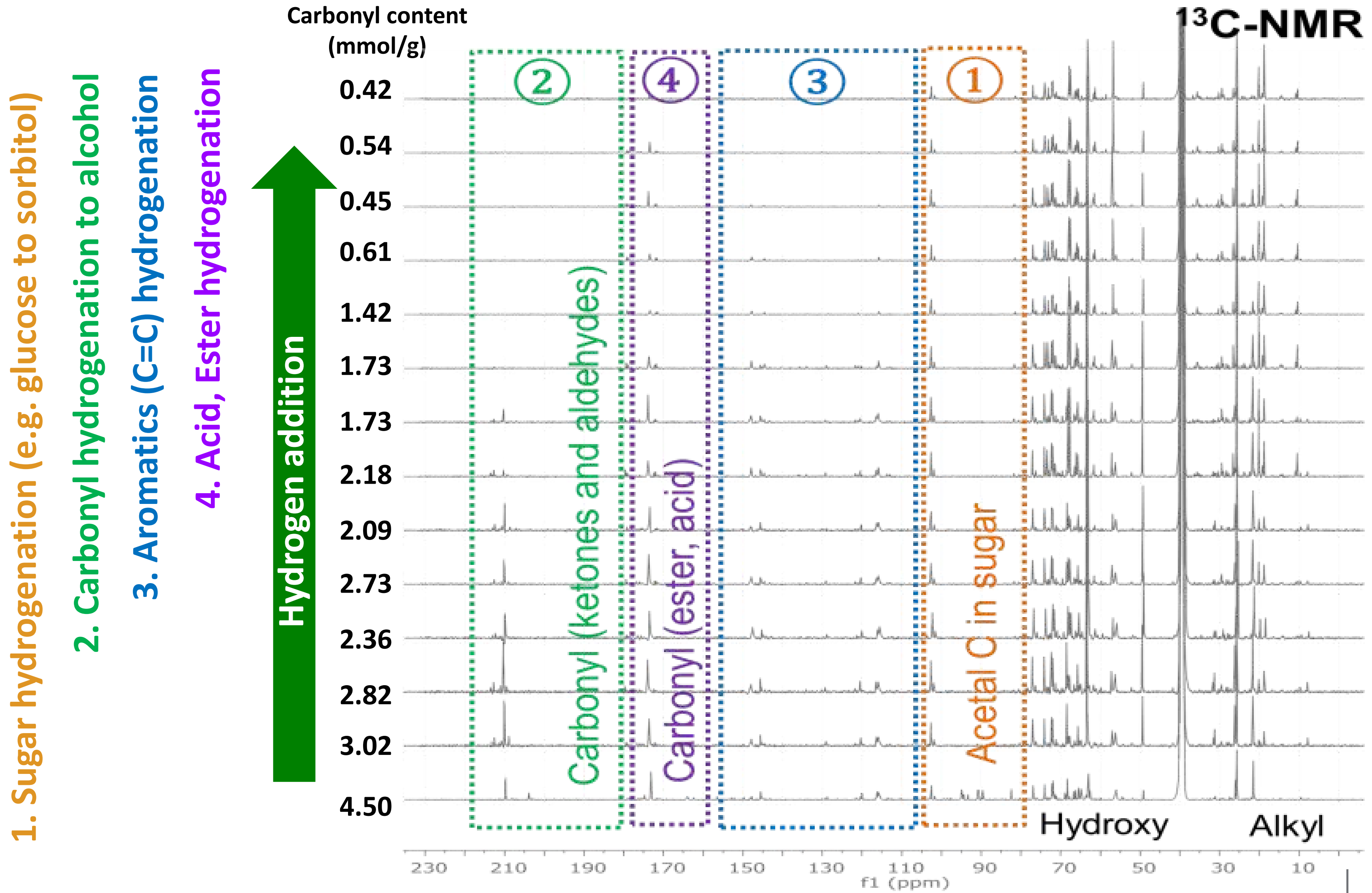
- **Funding: U.S. DOE Bioenergy Technologies Office**

- **Access to Characterization Capabilities**
  - DOE SC, Center for Nanophase Materials Sciences
  - DOE NE, Fuel Cycle R&D Program and the Nuclear Science User Facilities
- **ANL collaboration (DFT via CWG-CPCC)**
  - Mingxia Zhou, Lei Cheng, Rajeev Assary, Larry Curtiss
- **INL collaboration**
  - Magdalena Ramirez-Corredores, Tyler Westover
- **NREL collaboration**
  - Esther Wilcox, Katie Gaston, Conner Nash, Josh Schaidle, Danny Carpenter
- **PNNL project team**
  - Huamin Wang, Mariefel Olarte, Daniel Santosa, John G. Frye, Susanne Jones, Aye Meyer, Suh-Jane Lee, Dan Howe, Gary Neuenschwander, LJ Rotness, Bob Gruel, Randy Thornhill
- **ORNL project team**
  - Jae-Soon Choi, Zhenglong Li, Maggie Connatser, Samuel Lewis, Beth Armstrong, Michael Lance, Harry Meyer, Zili Wu

Additional Slides

Hydrogenation reactivity scale of species in bio-oil

Ru catalyst, 160/120 °C, 0.4 LHSV, 1500 psig, H_2/bio-oil: 2500 L/L

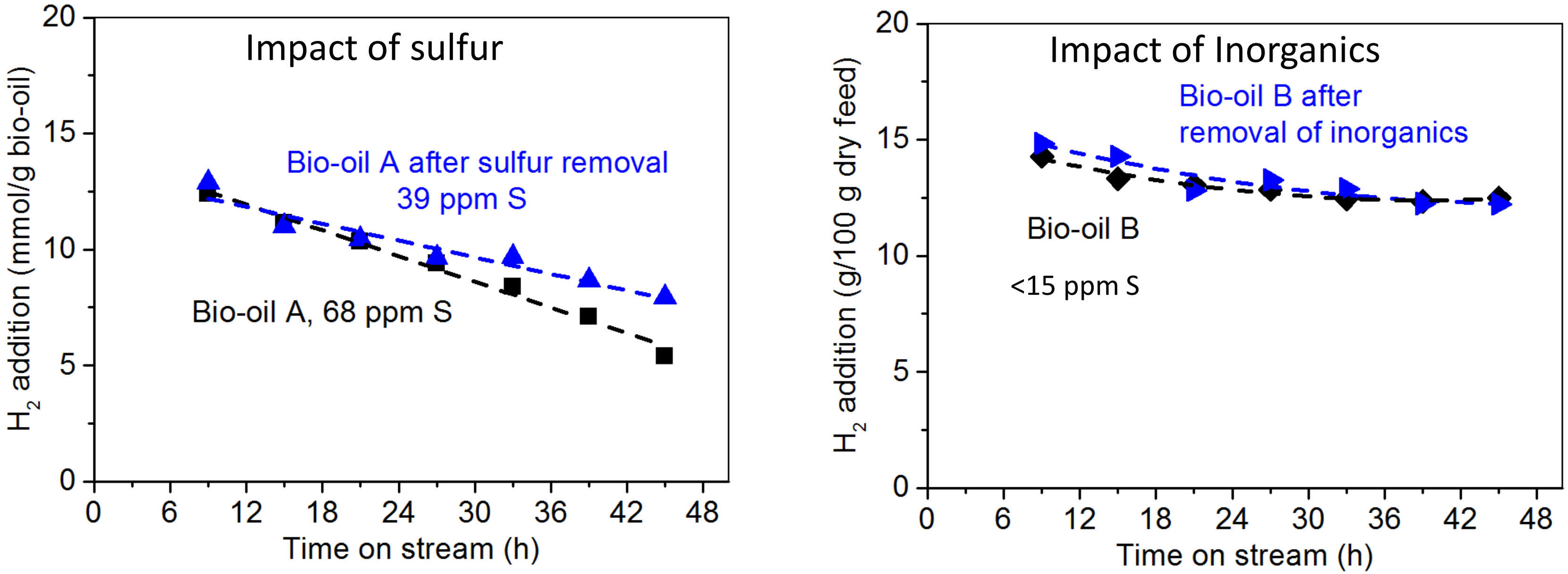


H Wang et al. ACS Sustainable Chem. Eng., 2016, 4, 5533

Deep Stabilization

FY15 SOT Research

Catalyst deactivation by sulfur poisoning



	Fresh	68 ppm S oil	39 ppm S oil
S_{BET} (m^2/g)	54	45	-
C (wt.%)	0	6.3	5.5
S (ppm)	<35	2169	1436

- Deactivation of Ru based catalyst for bio-oil stabilization
- Sulfur is the primary cause of deactivation
- Inorganics has negligible impact on catalyst stability compared to sulfur

H Wang et al. ACS Sustainable Chem. Eng., 2016, 4, 5533

Catalyst and Process Development

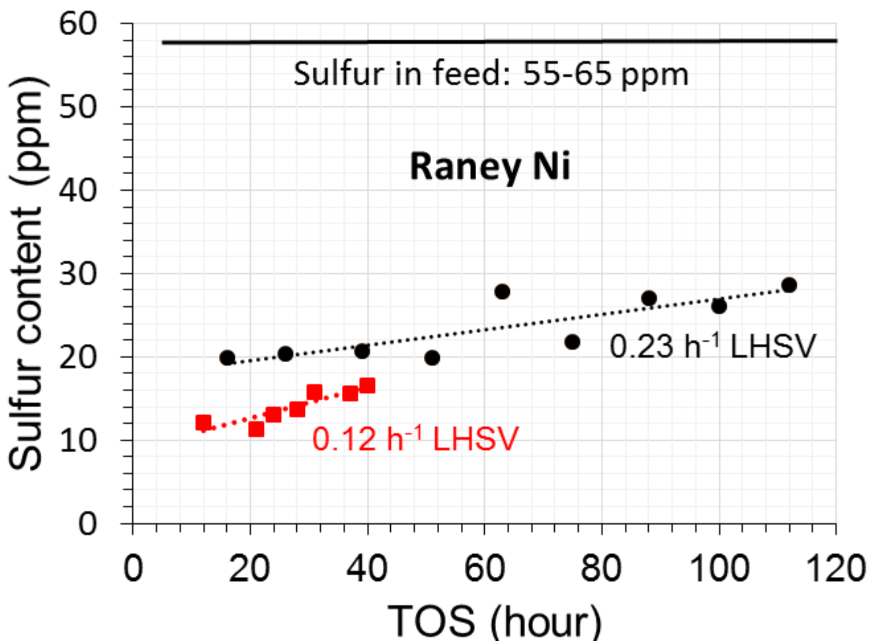
FY15 SOT Research

Catalyst life can be improved by:

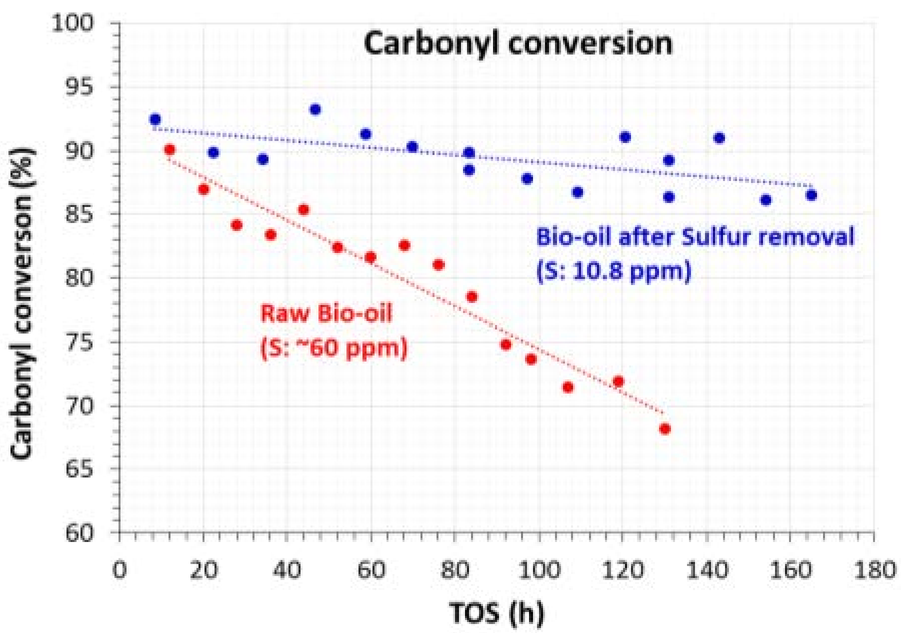
- Removing sulfur for bio-oil

- Sulfur removal from bio-oil by Ni guard bed, enable longer life Ru catalyst
- Further advance the sulfur removal bed will bring increase in the maintenance costs

Sulfur removal from bio-oil by Raney Ni



Impact of sulfur removal



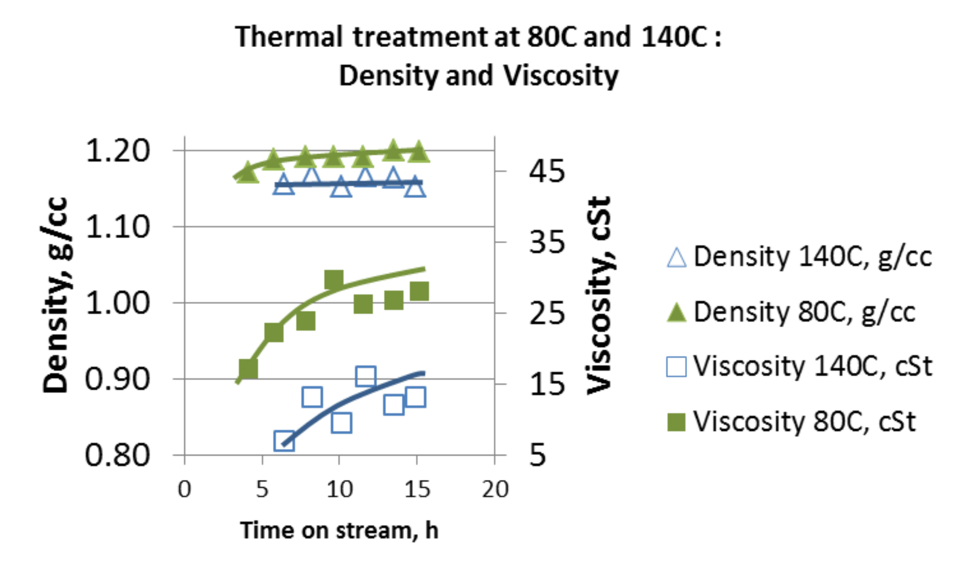
Non-hydrogenation method for bio-oil stabilization

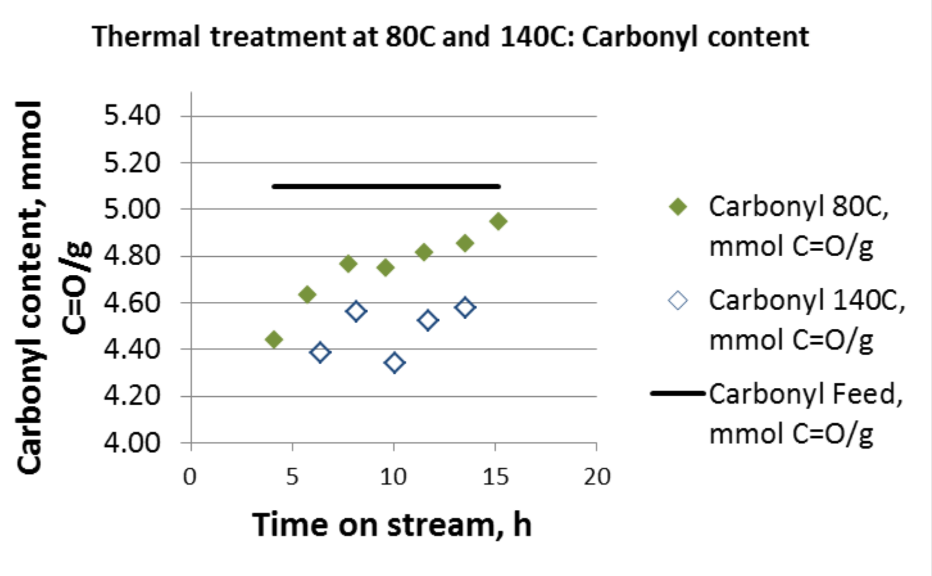
Catalyst life can be improved by:

- Removing sulfur for bio-oil
- Improving sulfur tolerance
- Catalyst/method to stabilize bio-oil without low T hydrogenation

Goal: use non-hydrogenation method to partially stabilize bio-oil to enable deep stabilization using sulfide catalyst at a higher temperature (>250 °C)

- Efforts are ongoing: thermal stabilization by controlled condensation (bio-crude like product)



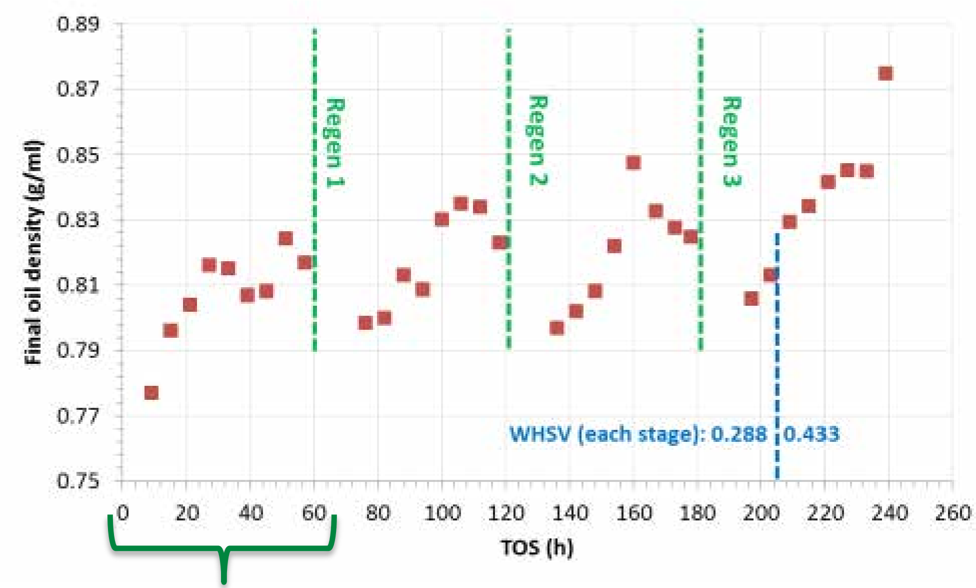


Carbide Catalyst Development

In situ regenerability of carbides confirmed

2-stage hydroprocessing

180 °C/400 °C Ni-Mo_2C/Ni-Mo_2C



cf. FY15 peer review: Ni identified as promoter & 60-h run without plugging demonstrated.

Cost impact (high-level TEA)

"-" sign indicates cost reduction

Catalyst type	Baseline RuS2/NiMoS	Mo2C/Mo2C
Minimum fuel selling price		
% change	-	18%
% change (with 1 regen)	-	-9%
Conversion costs		
% change	-	20%
% change (with 1 regen)	-	-9%
Catalyst-related op costs		
% change	-	53%
% change (with 1 regen)	-	-19%
Installed upgrading capex		
% change	-	-16%
% change (with 1 regen)	-	-34%

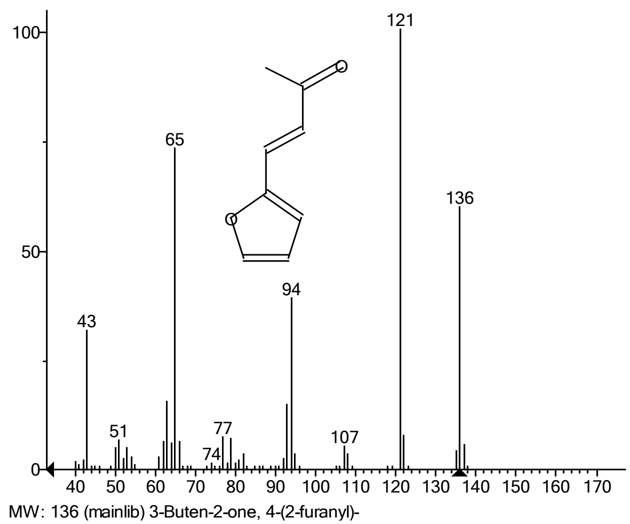
- Successful upgrading of raw (unstabilized) bio-oil demonstrated for 240 h
  - Conventional catalysts run ~60-100 h before bed plugging due to fouling
  - H_2 reduction removes surface coke from Mo_2C preventing bulk coking (fouling)
  - *In situ* regenerability can significantly reduce conversion cost

Carbide Catalyst Development

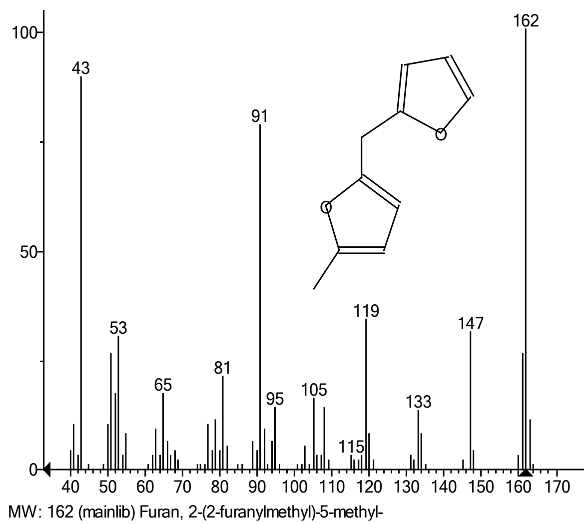
High affinity for C-O bonds => C and H atom efficiency

Furfural hydroprocessing liquid products
(150 °C, S as thiophene)

Ru/C



Ni-Mo_2C



- Ni-Mo_2C consumes less H_2 to achieve similar levels of C-O conversion
- Conversion products more stable when using Ni-Mo_2C than Ru/C
  - More amenable to high temperature hydrotreating/hydrocracking (less coking)

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Carbide Catalyst Development – Future Work

Focus: optimize catalyst functions, operating conditions, and regeneration procedures enabling high-performance, long-term operation of catalytic bio-oil stabilization processes

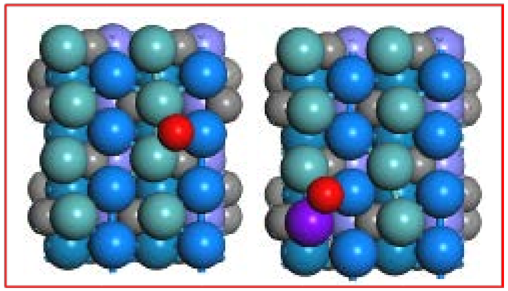
- Develop cost-effective regeneration methods (C, S)
- Enhance low-temperature activity (higher SV)
- Maximize C and H atom efficiency (higher liquid HC, lower H_2 consump.)

FY17
- **Develop “sulfur” regeneration methods**

FY18
- **Enhance low-temperature activity**
  - Ni doping optimization
- **Maximize C and H atom efficiency**
  - Metallic and acid property balance

FY19
- **Scale-up and large reactor implementation**

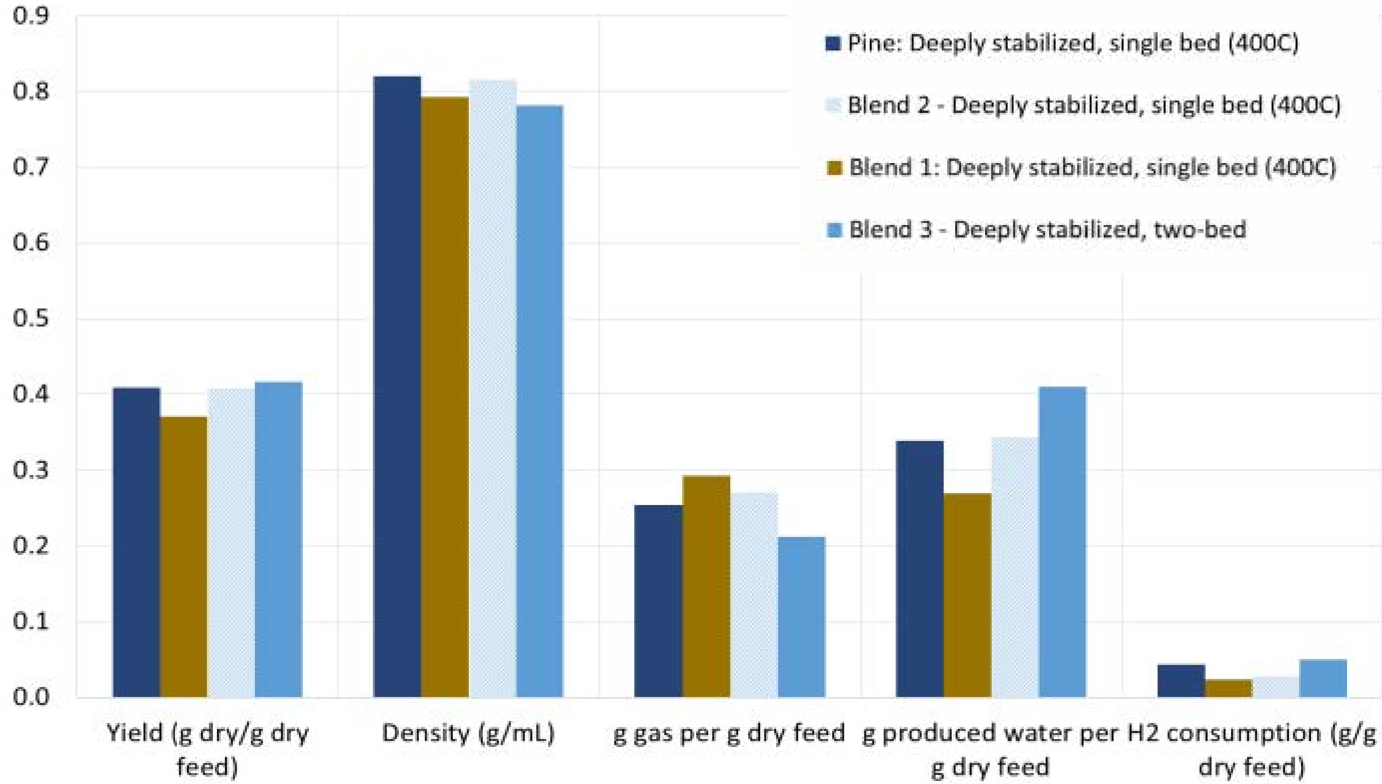
- **Elucidation of structure-function relationships** w/ ACSC (2.5.4.303-305) & CPCC (2.5.1.305)



ANL DFT study of Ni doping impact on Mo_2C reactivity

O: red Ni: dark purple

Hydrotreatment of different feedstocks

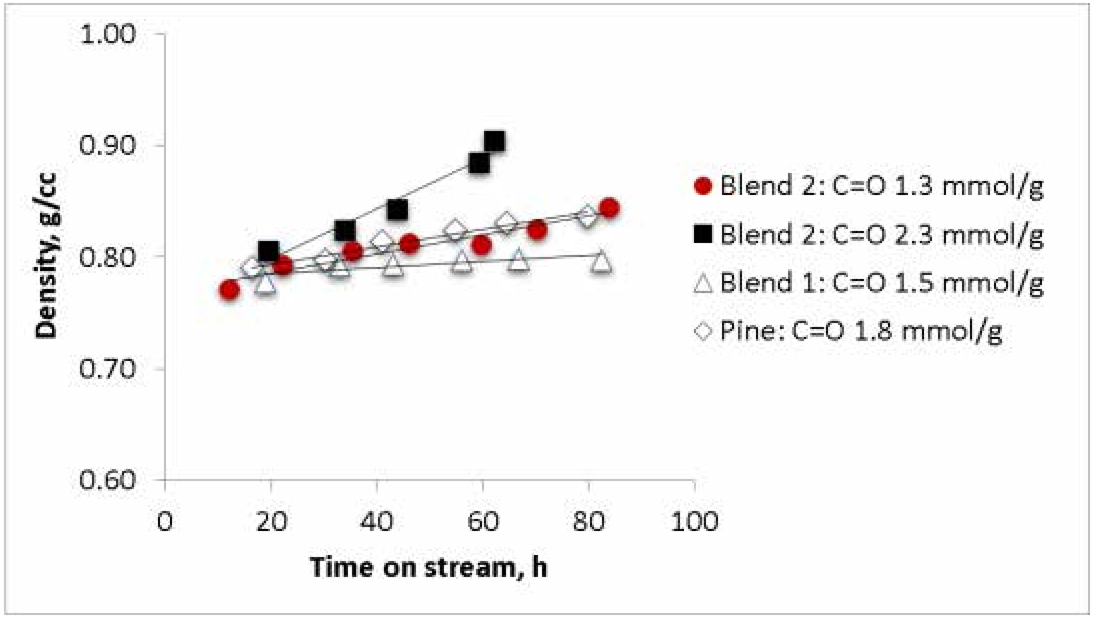


- Woody biomass blends upgrade similarly to Pine
  - Confidence in applicability of clean pine historical research
- Predicting FP bio-oil** upgrading success by carbonyl content confirmed
  - Confidence in metric for upgrading success broadened to other biomass sources

** different metric for CFP

Effect of Carbonyl Content of Stabilized Product (Bed 1) to Final Hydrotreating (Bed 2)

Feed/Stabilization Level	HT Observation	Feed Carbonyl content, mmol C=O/g
Blend 1 - Deep	Top Restriction	1.5
Blend 2 - Deep	No Fouling	1.3
Blend 2 - Regular	Plugged	2.3
Pine - Deep	Top Restriction	1.8



- Carbonyl content indicates potential processing issue with direct HT of FP
- Deeply stabilized pine has the lowest density products
- Blend 1 and Blend 2 deeply stabilized oils have similar products profile
- Blend 2 regularly stabilized had slightly heavier product

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Commissioning Demo-scale HTDC

Demonstrating scale-up for technology viability

Biofuels

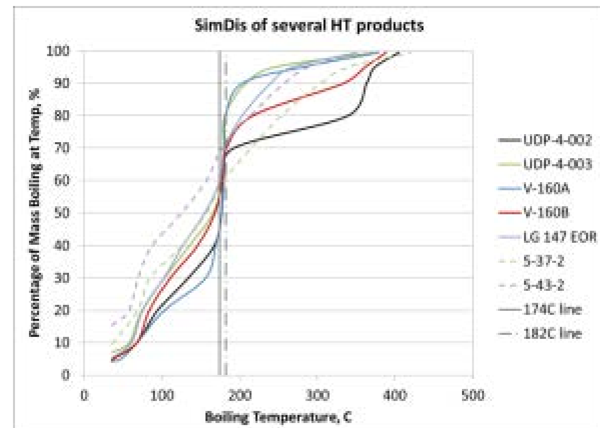
↓

Blending

↓

Engine Testing

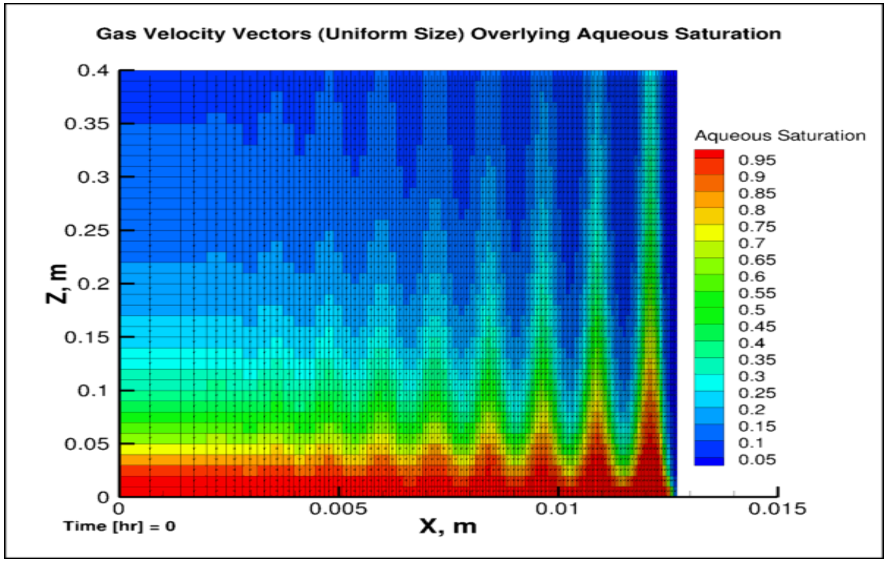
- Produce scale-quantity fuels for engine blend testing
  - Target: 16 gal gasoline, 16 gal diesel of one feedstock
  - In collaboration with NREL and INL



Outcomes:

- Engine testing of fuels from pyrolysis/upgrading of woody biomass
- Identify scale-up challenges

Future Work: Reactor Engineering



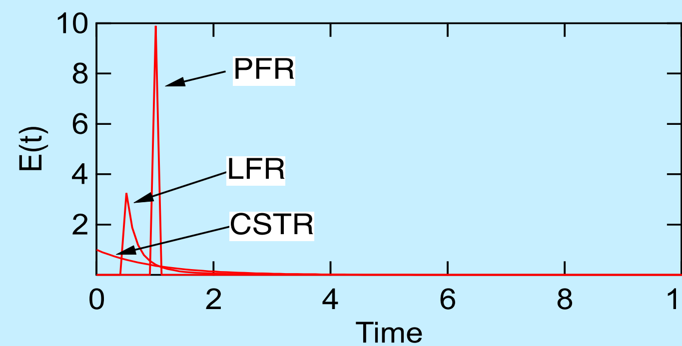
CCPC preliminary fluid dynamics model shows alternating rich-liquid and rich-gas concentration profile over reactor length (Z) and across reactor radius (X)

<u>RTD testing:</u>

- *In situ* hydrogenation conditions (T,P)-products forms a new mobile phase
- Identify mobile-phase(s) and their appropriate tracer(s). Criteria for tracer:
    - Sampling needs to be fast
    - Inert at hydrogenation conditions (Cat, T, P)
    - Quantifiable at low concentration

<u>Problem</u>

- Bio-oil exhibits multiple mobile-phases which constrain catalyst interaction
- Need correlation of performance versus scale, and predict scale barriers such as channeling and phase behavior which affect catalysis



<u>Outcome:</u>

- Characterize RTD of mobile-phase(s) of the liquid in the reactor (above)
- This will help correlate performance data between the bench, pilot, and demo scale reactors.

Responses to Previous Reviewers' Comments

Comment: The project overview is reasonable and states the problem to be solved qualitatively, but does not clearly show how much improvement is needed to make the process successful.

Answer: The project is directed by the Technoeconomic Analysis (TEA) to identify areas of research that can most impact cost of the current state of technology, and we can go into more detail in future reviews.

Comment: A generic technical approach was presented with a reasonable path forward. The international teaming is excellent and leverages the value of the work. The presentation included weak non-quantified critical success factors. With the high funding aimed at bringing bioblends into refinery, this project needs partners with expertise in refining. Technical approach, being a broad-scope project, is as comprehensive as can be possible, but must be at a high-level due to time constraints. Critical success factors are meaningful. Identified a challenge of suitable unit operations reflects the age old scale-up problem.

Answer: Indeed, the scope is quite broad as there is are many elements of upgrading where success can have a measurable impact on making the technology more viable. This also highlights the need for TEA to focus the research. The international involvement has been valuable, and we agree with the reviewers that we need to find industry partners to team with.

Comment: Work so far has been of top quality. I'm concerned with scale-up and a potential moving target for final "acceptable" product. Dealing with exothermic reactors is not particularly novel. There are many approaches to attack problem. Substantial technical progress has been made. Good to see the rapid screening capability has come on line. The ability to regularly produce multi-gallon quantities of HC product is a significant achievement for the Program.

Answer: There have been many findings, all contributing towards the success of the process. We agree and intend to first apply industry known solutions whenever we discover a problem or limitation. This also underscores the need for intermediate scale up and the focus on scalable solutions, as the reviewer rightly highlights that some laboratory solutions are not solutions at all at scale.

Responses to Previous Reviewers' Comments

Comment: Relevance is very high with respect to stable catalyst or reactor operation for hydrotreating, but not sure how improvements to catalyst life will be attempted with respect to catalyst design. It's not clear that the investigators have clearly defined the requirements for incorporation of feed streams into refineries. In this case, bio-oil integration to the petroleum HC infrastructure the comparison should be against those systems, unit operations, and market.

Answer: To better demonstrate the relevance, we will highlight the use of the TEA to guide research and measure success in future reviews. We agree that a new focus should be on defining quality of the products and how and where those products would be incorporated into a refinery. This is where refinery partners will be important: once bio-oil can be converted reasonably into a hydrocarbon, we need to leverage the industry that knows best how to use hydrocarbons.

Comment:. The deliverables and specifics in future work will determine acceptance for commercialization. Put lots of focus there! A question was raised in discussion what sort of feedback from petroleum refineries as to accepting end product - this is where you'll get blindsided. Commissioning the large reactor is likely to take at least one year, so that the investigators will need to work hard during the final years of the project to achieve results.

Answer: We agree with the reviewers that the research is at the point where we need to drive it by the potential hydrocarbon market, looking forward, rather than focusing solely on the conversion to the hydrocarbons. The relationship of historical progress and future work was obfuscated by the way this technology has matured from its inception. Indeed, the commissioning process has already been longer than a year, but our focus has been on getting it started safely.

Responses to Previous Reviewers' Comments

Comment: Another technology development that will be ready for tech-transfer in the next few years, showing good promise at this stage in the project life. The project is making very good progress in the area of catalytic upgrading of liquid bio-oils Need to address scale-up issues, mass transfer, heat transfer, and gas-liquid distribution. Also, need to get beyond pricing on a GGE basis by using heat values. Need to look at the fuel quality.

Answer: As reviewers advise, we have been focusing more with squaring our results with modeling to capture the issues of mass transfer, scale, and heat transfer to capture the process in a way that it can be both understood and scaled. We agree with the reviewers, product quality is now in focus, particularly as we are moving towards scale that can reliably generate the sample fuels needed for product specific analyses.

Comment *(carbide catalyst development):* This reviewer believes that the problems of metal sulfide catalysts has been overstated. Sulfides on steam-stable supports should be adequate for hydrotreating.

Answer: Even though carbides can compete favorably with sulfide catalysts in bio-oil hydrotreating (generally done at >300 °C), the project focus is on developing carbides as superior alternatives to ruthenium catalysts for use in lower temperature stabilization (<200 °C). Short lifetime of stabilization catalysts represents a major technical and economic challenge facing fast pyrolysis bio-oil upgrading technology development. While steam durability of oxide catalysts is well known, in bio-oil applications, catalysts have been shown to significantly degrade, often due to conversion of the alumina to boehmite forms as the exposure in liquid water is different than steam exposure. This is captured in "Historical Developments in Hydroprocessing Bio-oils" by Douglas C. Elliott, Energy & Fuels 21 (2007) 1792-1815 which also points to prior research from the 1990s in similar fields of high temperature liquid water exposure.

Responses to Previous Reviewers' Comments

Comment *(carbide catalyst development):* Clear explanation of the program and its aims, but no clear targets given for success.Future work really needs to focus on the 4th and 5th items - catalyst life and regeneration, and TEA. I'm concerned these are lower on the list and time will be spent on the first items, even though they are related. This project needs to get on track with addressing BETO 2017 objectives.

Answer: We made an effort to set clearer research targets and quantifiable measures of success based on TEA. As frequent catalyst replacement and maintenance related to the bio-oil stabilization step (140-200 °C) represent a major portion of the fast pyrolysis derived biofuel production cost, our effort has been focused on developing more durable (against hydrothermal aging, coking/fouling, sulfur poisoning) and easily regenerable catalysts. The impact of achieved performance enhancements on the state of technology has been assessed via TEA.

Comment *(carbide catalyst development):* Significant progress has been made in terms of catalyst selection, model compound testing, and testing with actual pyoil. In the end, however, there are few demonstrated improvements over the baseline catalysts. The presentation does not provide clear goals for the future improvements, so it is unclear if the work has significant potential for improvement.

Answer: Since the last review, we found three features of molybdenum carbides which when properly harnessed could lead to breakthrough next-generation catalysts: 1) in situ regenerability (decoking); 2) sulfur tolerance; 3) selectivity towards C-O bond cleavage (high C atom efficiency). Progress is being made in further understanding structure-function relationship as well as optimizing/evaluating at increasingly relevant conditions.

Responses to Previous Reviewers' Comments

Comment *(carbide catalyst development):* Bed plugging and fouling is a big issue. Carbon/char/polymerized mess. Still have a coking issue. Problem not solved with novel support. Project needs to identify the mechanism(s) for deactivation. Then solutions may become evident.

Answer: Chemistry and mechanisms responsible for catalyst fouling/plugging have been clarified through this and related BETO projects. The carbonaceous deposits leading to catalyst fouling can resemble coke; another type of foulant we have is more akin to a phenol formaldehyde resin chemistry, more of a homogenous chemistry issue. Very reactive carbonyls (e.g. sugars, ketones, aldehydes) undergo rapid thermal polymerization if exposed to high temperatures. Low-temperature stabilization of raw bio-oil is therefore critical to ensure long-term operation of hydrotreaters. Finding active and selective catalysts for carbonyl hydrogenation which are also durable in condensed phase bio-oil processing environments has been a key objective.

Publications, Patents, Presentations

Publications

- H. Wang, S.-J Lee, M.V. Olarte, A.H. Zacher, “Bio-oil Stabilization by Hydrogenation over Reduced Metal Catalysts at Low Temperatures”, *ACS Sustainable Chem. Eng*. **4** (2016) 5533-5546.
- J.-S. Choi, A.H. Zacher, H. Wang, M.V. Olarte, B.L. Armstrong, H.M. Meyer III, I.I. Soykal, V. Schwartz, “Molybdenum Carbides, Active and *In situ* Regenerable Catalysts in Hydroprocessing of Fast Pyrolysis Bio-oil”, *Energy & Fuels* **30** (2016) 5016−5026.
- M.V. Olarte, A.H. Zacher, A.B. Padmaperuma, S.D. Burton, H.M. Job, T.L. Lemmon, M.S. Swita, L.J. Rotness, G.G. Neuenschwander, J.G. Frye, D.C. Elliott, "Stabilization of Softwood-Derived Pyrolysis Oils for Continuous Bio-oil Hydroprocessing“, *Topics in Catalysis* **59** (2016) 55-64.
- H. Wang, D.C. Elliott, R.J. French, S. Deutch, K. Iisa, “Biomass Conversion to Produce Hydrocarbon Liquid Fuel Via Hot-vapor Filtered Fast Pyrolysis and Catalytic Hydrotreating” *J. Vis. Exp.* **118**, (2016) e54088.

Patent

- J.-S. Choi, B.L. Armstrong, V. Schwartz, “Method of Synthesizing Bulk Transition Metal Carbide, Nitride, and Phosphide Catalysts”, U.S. Patent No 9,012,349 (April 21, 2015).

Presentations

- A.H. Zacher, "Catalytic Hydroprocessing of Fast Pyrolysis Bio-oil to Hydrocarbon Fuels“, oral presentation at ABRN Science Symposium - International Biofuels Developments, Rotorua, New Zealand, on November 10, 2016.
- M.V. Olarte, A.H. Zacher, D.M. Santosa, H. Wang, C. Drennan, E. Wilcox, "Analysis and Catalytic Upgrading of Pyrolysis Oils from Various Biomass Feedstocks“, invited oral poster presentation at TCS2016, Chapel Hill, North Carolina, November 1-4, 2016.
- H. Wang, S.J. Lee, M.V. Olarte, D.M. Santosa, J.G. Frye, A.H. Zacher, "Bio-oil Stabilization by Hydrogenation: Chemistry, Catalyst Deactivation and Regeneration“, poster presentation at TCS2016, Chapel Hill, North Carolina, November 1-4, 2016.

Publications, Patents, Presentations

Presentations (Continued)

- Z. Li, A. Lepore, R. Connatser, J.-S. Choi, "Hydroprocessing of Biomass Derived Oxygenates Using Molybdenum Carbides", poster presentation at TCS2016, Chapel Hill, North Carolina, November 1-4, 2016.
- H. Wang, S.J. Lee, M.V. Olarte, A.H. Zacher, "Bio-oil Stabilization by Hydrogenation over Reduced Metal Catalysts", oral presentation at 252nd ACS National Meeting and Exposition, Philadelphia, PA, August 23, 2016.
- J.-S. Choi, H. Wang, A.H. Zacher, M.V. Olarte, Z. Wu, H.M. Meyer III, K.L. More, B.L. Armstrong, "Stability and *In situ* Regenerability of Molybdenum Carbides in Hydroprocessing Fast Pyrolysis Bio-oil", oral presentation at the 16th International Congress on Catalysis, Beijing, China, July 3-8, 2016.
- H. Wang, M.V. Olarte, S.J. Lee, D.M. Santosa, J.G. Frye, A.H. Zacher, "Catalytic Upgrading of Biomass Fast Pyrolysis Oil", poster presentation at Gordon Research Conference of Catalysis 2016, New London, NH, on June 13, 2016.
- J.-S. Choi, B.L. Armstrong, R.M. Connatser, I.I. Soykal, H.M. Meyer, V. Schwartz, A.H. Zacher, H. Wang, M.V. Olarte, S.B. Jones, "An Approach to Cost Reduction in Multi-stage Bio-oil Hydroprocessing: Applying Molybdenum Carbide Catalysts", oral presentation at tcbiomass 2015, Chicago, Illinois, November 2-5, 2015.
- H. Wang, S.J. Lee, M.V. Olarte, A. Zacher, "Bio-oil Stabilization by Hydrogenation on Reduced Metal Catalysts: Effect of Contaminants in Bio-oils", oral presentation at tcbiomass 2015, Chicago, Illinois, November 2-5, 2015.
- J.-S. Choi, A. Zacher, H. Wang, M. Olarte, V. Schwartz, I.I. Soykal, B. Armstrong, M.J. Lance, R. Connatser, S. Lewis "Performance of Molybdenum Carbide Catalysts in 2-Stage Hydroprocessing of Fast Pyrolysis Bio-oil", poster presentation at 24th North American Catalysis Society Meeting, Pittsburgh, PA, June 15, 2015.