2015 DOE Bioenergy Technologies Office (BETO) Project Peer Review

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

2.3.1.315- Biomass Deconstruction: Catalyst Development and Testing

March 24, 2015

Kim Magrini

Goal/Objectives

Program Mission: *Transform U.S. renewable biomass resources into commercially viable, high-performance biofuels, bioproducts, and biopower through targeted research, development, demonstration, and deployment supported through public and private partnerships.*

Task Goal: Seek/develop/evaluate and characterize ex-situ upgrading catalysts with biomass pyrolysis vapors at the DCR small pilot scale to produce **refinery compatible intermediates of**:

- **Oxygen content < 10%**
- **Coking < 10%**
- **Carbon efficiency > 43%**
- **2022 Cost Target : $3.31 (with feedstock)**

Task Objective: To design and test catalysts, understand their impact on catalytic biomass deconstruction and upgrading, and then tailor their activity to produce fungible hydrocarbon fuel intermediates at laboratory to small pilot scales (g-kg) using a coupled pyrolyzer/FCC reactor.

Project Quad Chart Overview

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

Timeline

- Project start date: 10/2012
- Project end date: 9/2022
- Percent complete: 24%

Barriers

- Tt-E. Liquefaction of Biomass and Bio-Oil Stabilization
- Tt-G. Fuel Synthesis and Upgrading
- Tt-E. and Tt-G. Conversion and Conversion Enabling Technologies

Budget

	Total Costs FY10 – FY12	FY13 Costs ($)	FY14 Costs ($)	Total Planned Funding (FY15-end) ($)
DOE Funded	0	1,728,910	2,058,441	2,377,649

Partners & Roles

- NREL: catalyst development, evaluation and characterization
- Johnson Matthey: VPU catalyst development
- NexCeris – modified catalyst preparation
- Equilibrium Catalysts – FCC ECAT and additives

1 – Project Overview

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

Catalytic Pyrolysis Sciences
WBS: 2.3.1.313

Catalyst Development/Testing *Deconstruction*
WBS: 2.3.1.315

Catalyst Development/Testing *Upgrading*
WBS: 2.3.1.314

Engineering Integration and Scale-up
WBS: 2.4.1.301

Work Flow

- Biomass pyrolysis
- Catalysts screening with model and raw pyrolysis vapors
- Catalyst CFD modeling

- Catalyst development (*existing*, *emerging*)
- Catalyst preparation, characterization, regeneration
- Conduct VPU experiments in DCR

- Pilot modifications
- Product fractionation
- Pilot scale runs

Thermochemical Platform Analysis
WBS: 2.1.0.302

Scale

mg-g | **g-kg** | **100's kg**

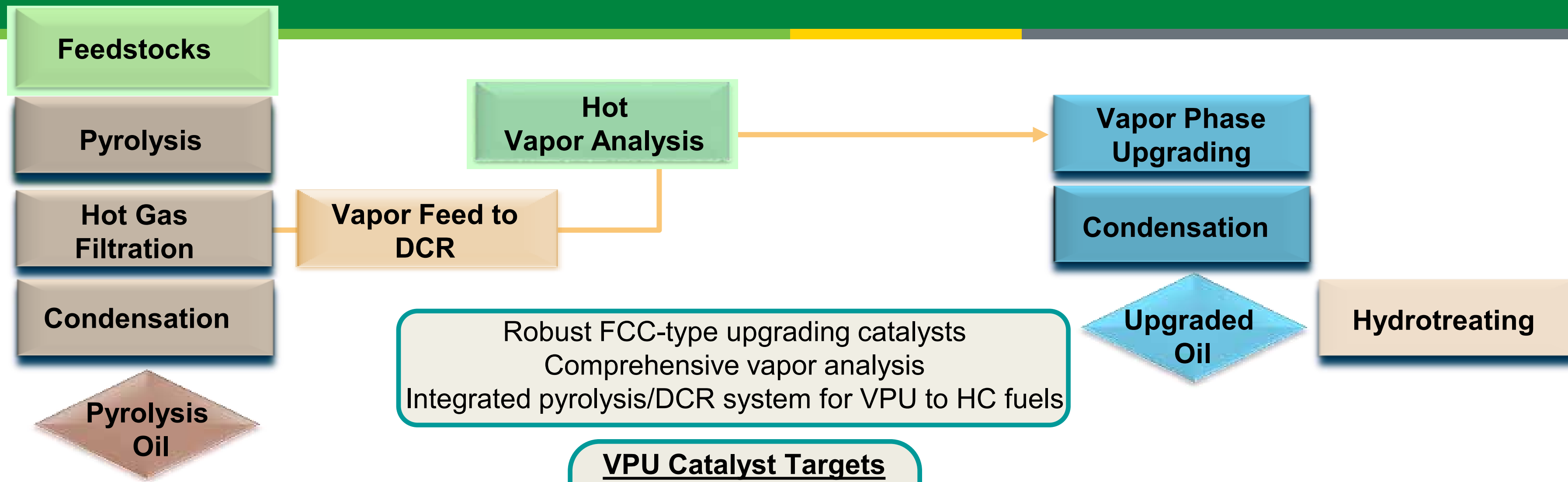
Synergistic Activities:

Hydrogen donor molecules
Hot gas filtration
Reaction kinetics

On line process gas analysis
Reactor design
Product characterization

1 – Project Overview

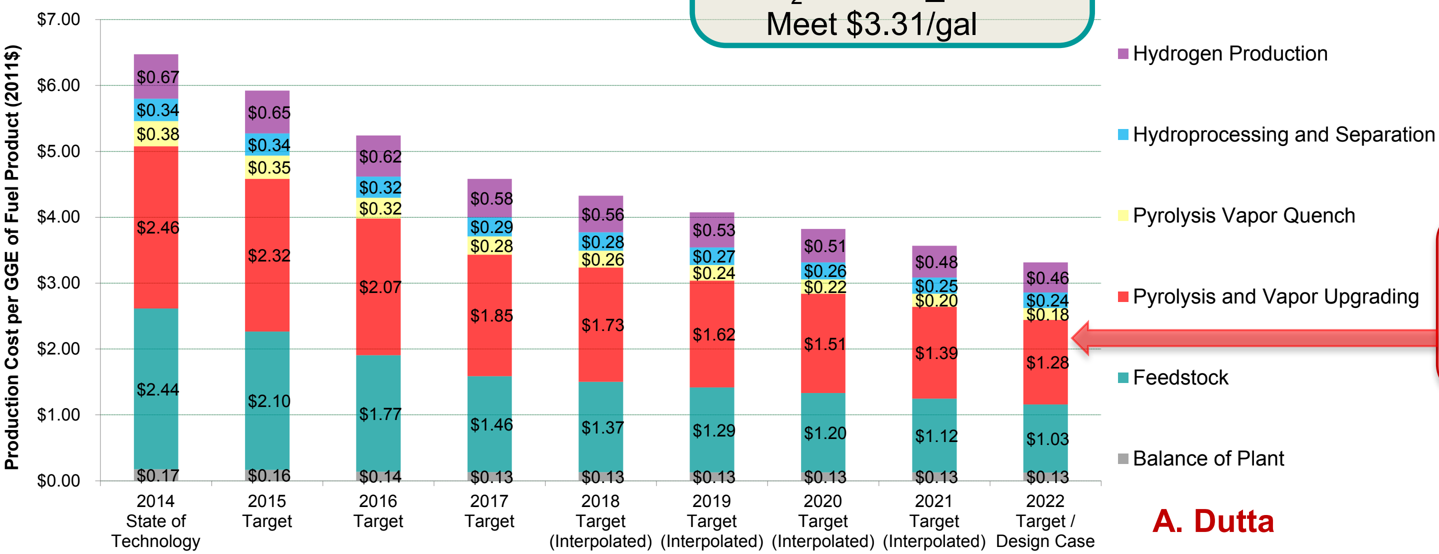
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy



Robust FCC-type upgrading catalysts
Comprehensive vapor analysis
Integrated pyrolysis/DCR system for VPU to HC fuels

VPU Catalyst Targets

- Coking ≤ 10%
- $\text{Carbon}_{eff} \geq 43\%$
- O_2 content ≤ 10%
- Meet $3.31/gal



Project rationale: Vapor phase upgrading a significant process cost component

A. Dutta

2 – Technical Approach

Task Structure

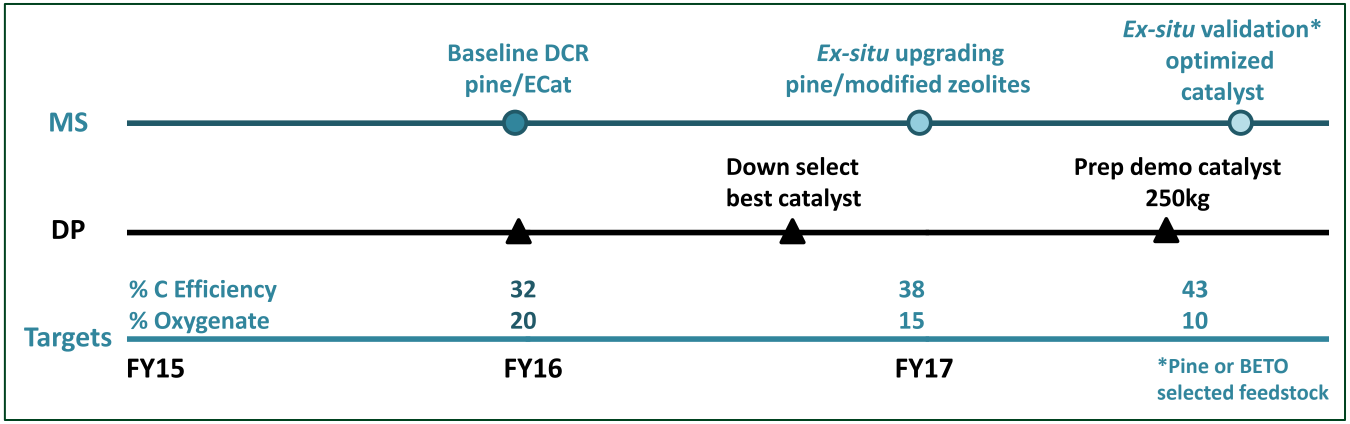
1) Pyrolysis vapor phase upgrading (VPU)
   - Coupled pyrolyzer/DCR operations to produce HC fuel intermediates
   - Process and CFD data to TEA, pilot plant, modeling tasks
   - Product analysis to assess fungibility, incorporation extent

2) Ex-situ catalyst development, testing, characterization
   - Deoxygenation
   - Carbon coupling
   - Hydrogenation

3) Condensed and vapor phase chemistry

   Liquids - GCTOFS, SIM DIS, GC, NMR, TAN, [Carbonyl]

   Gases - On line vapor analysis with mass spectrometry



2 – Technical Approach

- **Identify and benchmark** the state of the art in FCC conversion catalysts for biomass vapor phase upgrading (VPU) to hydrocarbon fuels or intermediates
- **Modify** candidate catalysts for improved performance (HC production, deoxygenation)
- **Provide performance information** for technoeconomic and CFD modeling of VPU processes
- **Validate** catalyst performance and product fungibility at the DCR small pilot scale
- **Down select/demonstrate optimized** VPU process for 2017 pilot scale HC fuel production

Project Start

2013
- Identify/procure/build VPU reactor system
- Develop deoxygenation and coupling catalysts
- Oil characterization: GC-TOFS
- DCR training at Zeton, WR Grace

2014
- Build out DCR laboratory
- Shakedown, benchmark pyrolyzer / DCR system
- Process data transfer to TEA, CFD tasks
- Oil characterization: NMR, PIANO

2015
- Upgrade biomass compounds in VGO
- Demonstrate vapor and oil production
- Test modified catalysts (acidity, deoxygenation, JM)

2016
- Upgrade pyrolysis vapors fcn temp, DCR conditions
- Catalyst down select for 2017
- Transfer optimized operating conditions to the TCPDU
- C^{14} product analysis (extent vapor incorporation)

2017
- Optimize catalyst regeneration in the DCR
- Prepare pilot scale catalysts (250 kg)
- Update optimized operating conditions to the TCPDU

2022
- Develop, optimize emerging catalysts for biomass products for other refinery insertion points, bioproducts, high energy fuel enhancers

2- Management Approach

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

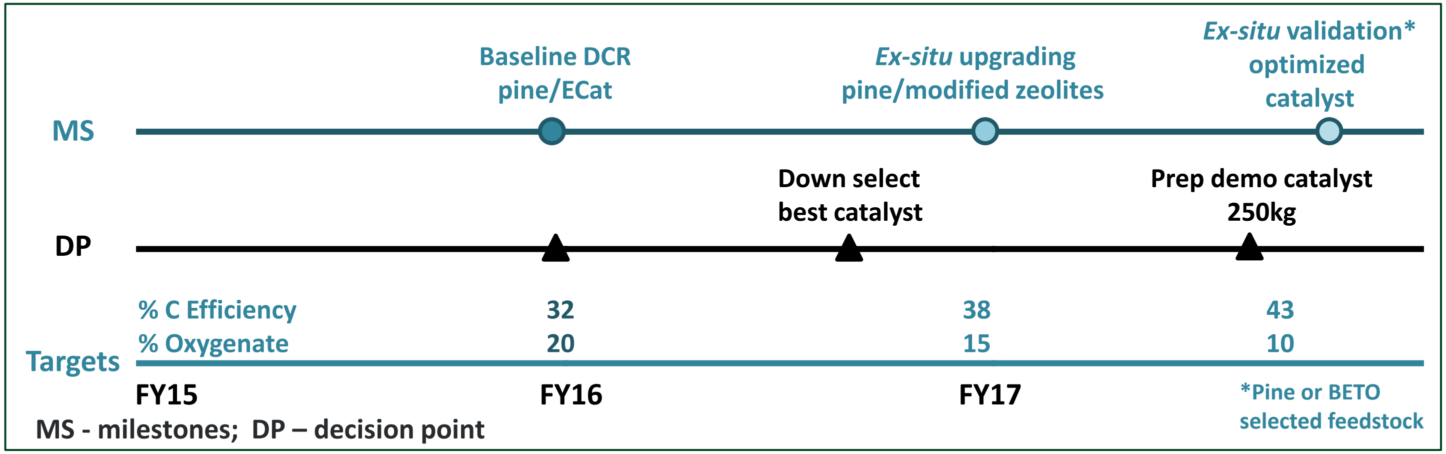
Critical Success Factors

Technical: Develop/identify/evaluate deconstruction and deoxygenation catalysts that are selective for fungible hydrocarbon intermediate production at (g-kg scale): **<10% oxygen, <10% coking, >43% C efficiency**

Market: Produce bio-oil or intermediates that can be processed in a conventional refinery with acceptable cost **($3.31/gal)**

Business: Technology that is technically and economically superior to other biomass conversion processes

Challenges: Develop efficient 1) catalysts and 2) biomass vapor conversion to products

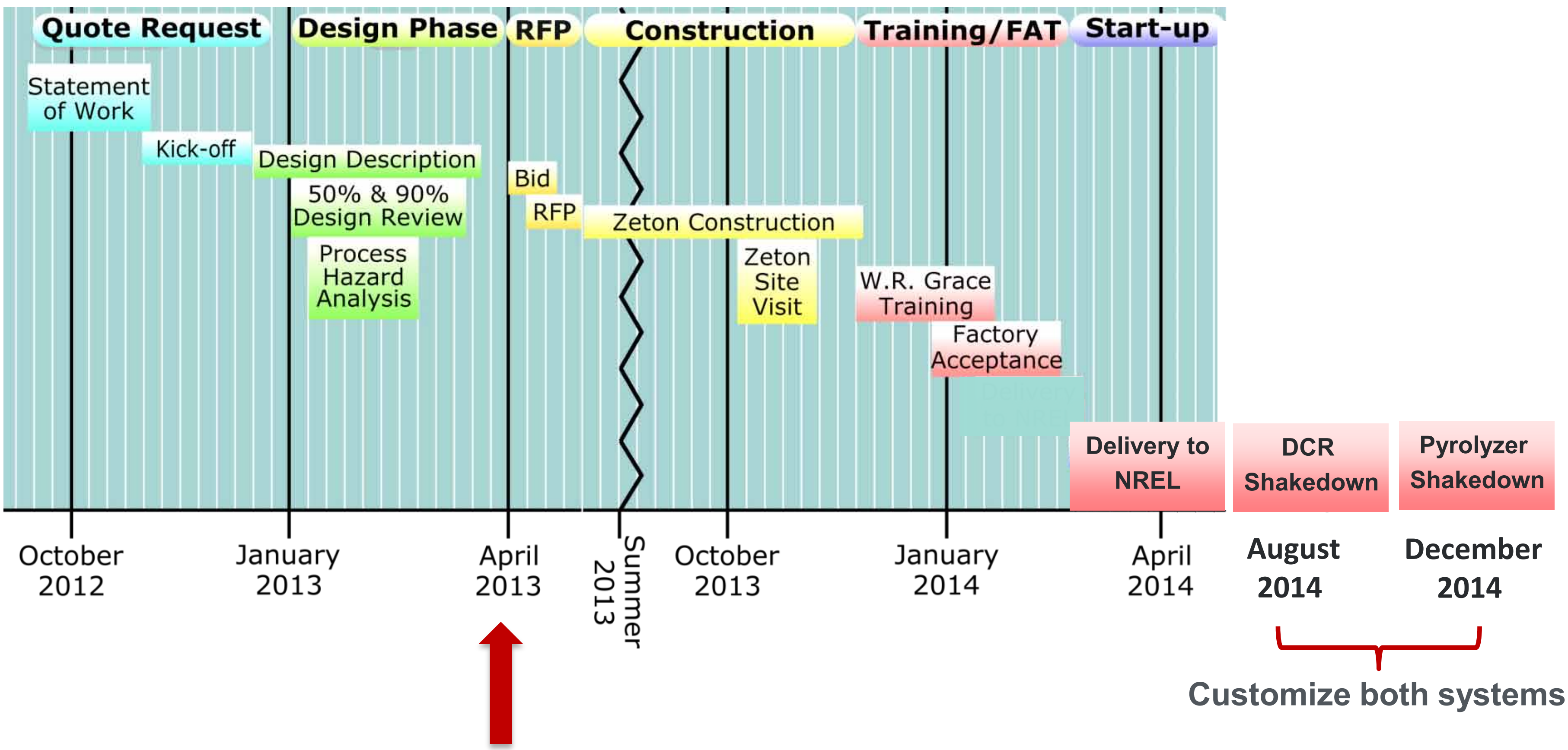


3 – Progress
Task 1: VPU System

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

Pyrolyzer-DCR Timeline

- DCR system ready for baseline operation June 2014
- Pyrolyzer system ready for vapor production February 2015



3 – Progress
Task 1: VPU System

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

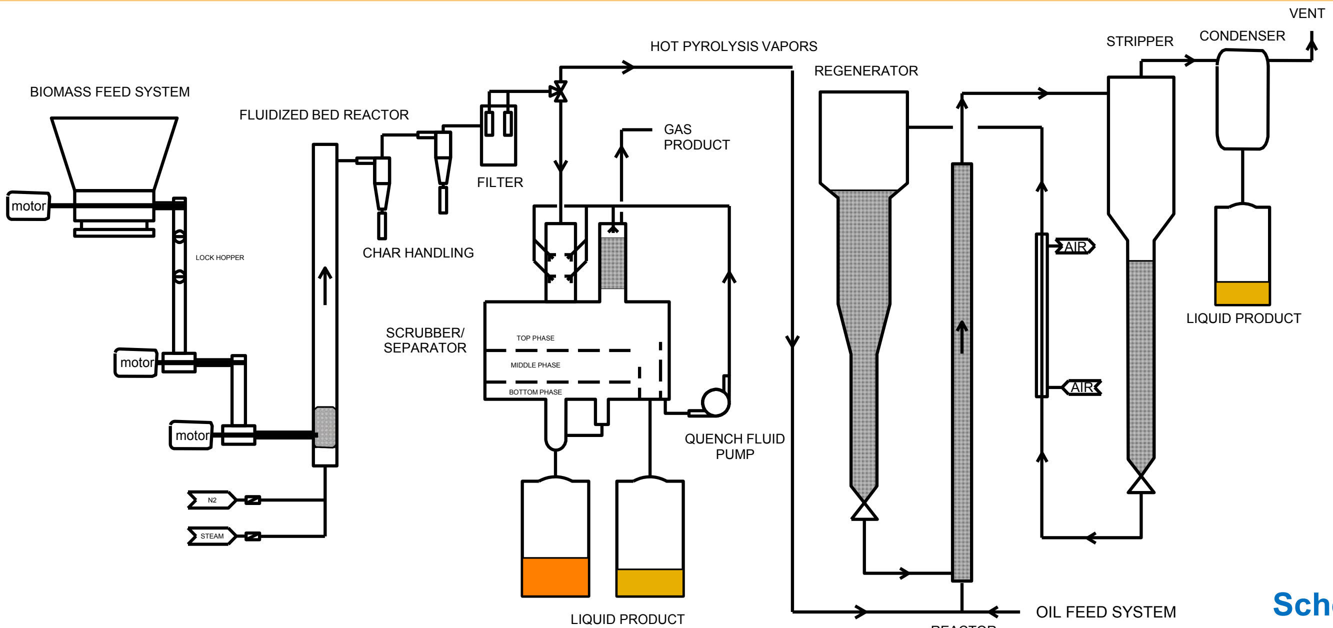
Feedstocks → Pyrolysis → Hot Gas Filtration → Condensation → Pyrolysis Oil

Hot Gas Filtration → Vapor Feed to DCR → Vapor Analysis MBMS → Vapor Phase Upgrading → Condensation → Upgraded Oil → Hydrotreating

Pyrolyzer
- 1-3 kg/ biomass feed
- 8 hr run time
- Pyrolysis oil: 1-2 gal
- Analytics: on line GC, MBMS

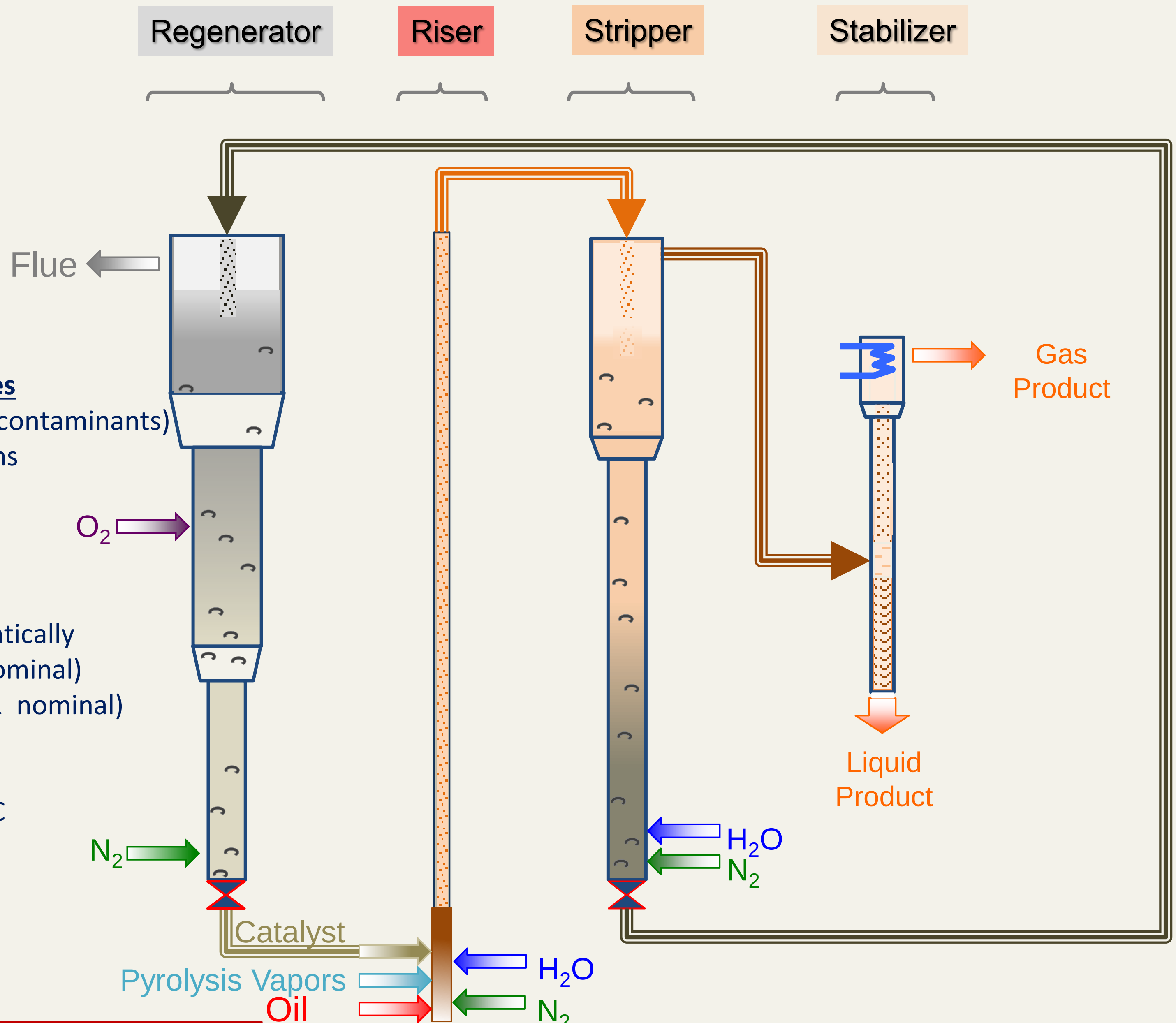
Oil, Product Analysis
- 2D GCTOFS, FID
- NMR, SIM DIS
- TAN, [carbonyl]

DCR
- Pyrolysis vapor feed (reduced contaminants)
- 2 kg catalyst
- 8 hr – 2 mass balance runs
- Upgraded oil: 2-4 liters
- Analytics: on line GC, NDIR, MBMS
- Continuous coke removal



Schematic: M. Jarvis

Davison Circulating Riser (DCR)



DCR Advantages

Pyrolysis vapor feed (less contaminants)
Provides mass balance runs
Upgraded oil: 2-4 liters
On-line hot vapor analysis
Continuous coke removal

System is operated adiabatically
Pressure 10-45 psig (25 nominal)
Riser Feed: 0.5-2.0 kg/h (1 nominal)
Riser Temp: 525 °C
Stripper Temp: 500 °C
Regenerator Temp: 700 °C

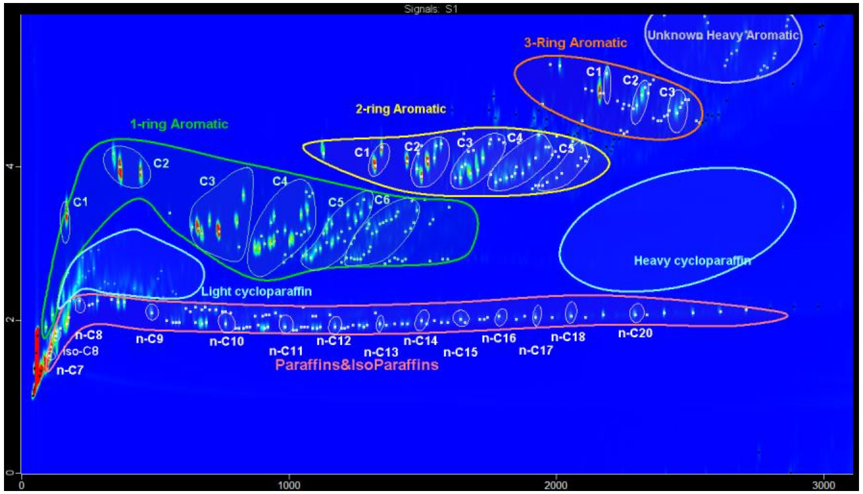
Results, products transferrable to industry

Y. Parent

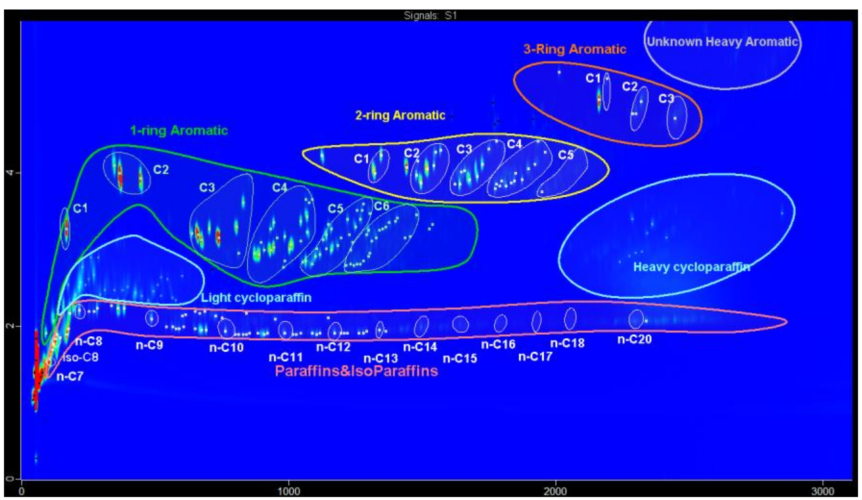
3 – Progress

Task 1: VPU - Baseline DCR

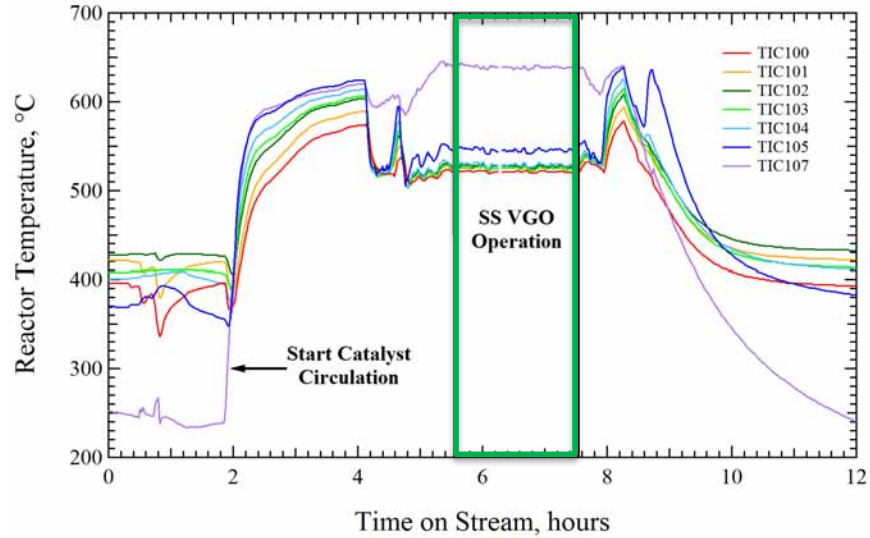
Ben, Olstad, Jablonski, Jarvis, Parent, Deutch



DCR product from VGO feed. Significant regions identified.



DCR product from mineral oil feed.



DCR riser temperature profile before, during, and after mass balance run with VGO. The mass balance experiment occurs during steady-state (SS) operation

Group	Mineral Oil	Mineral Oil	VGO	VGO	Gasoline
Paraffin	3.7	3.5	3.9	4.1	8.2
i-Paraffins	32.0	31.1	27.3	28.3	51.9
Aromatics	23.0	22.8	25.1	26.8	31.3
Naphthenes	10.8	10.7	7.5	7.2	5.0
Olefins	20.0	18.9	22.7	20.0	3.3
Unidentified	10.5	13.1	13.5	13.6	0.3

Compound class distributions (PIANO) reported in weight % of oil upgrading in the DCR:
Reproducible results with standard feeds.

3 – Progress
Task 1: VPU - Biomass Incorporation
Task 3: Oil /Vapor Phase Chemistry

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

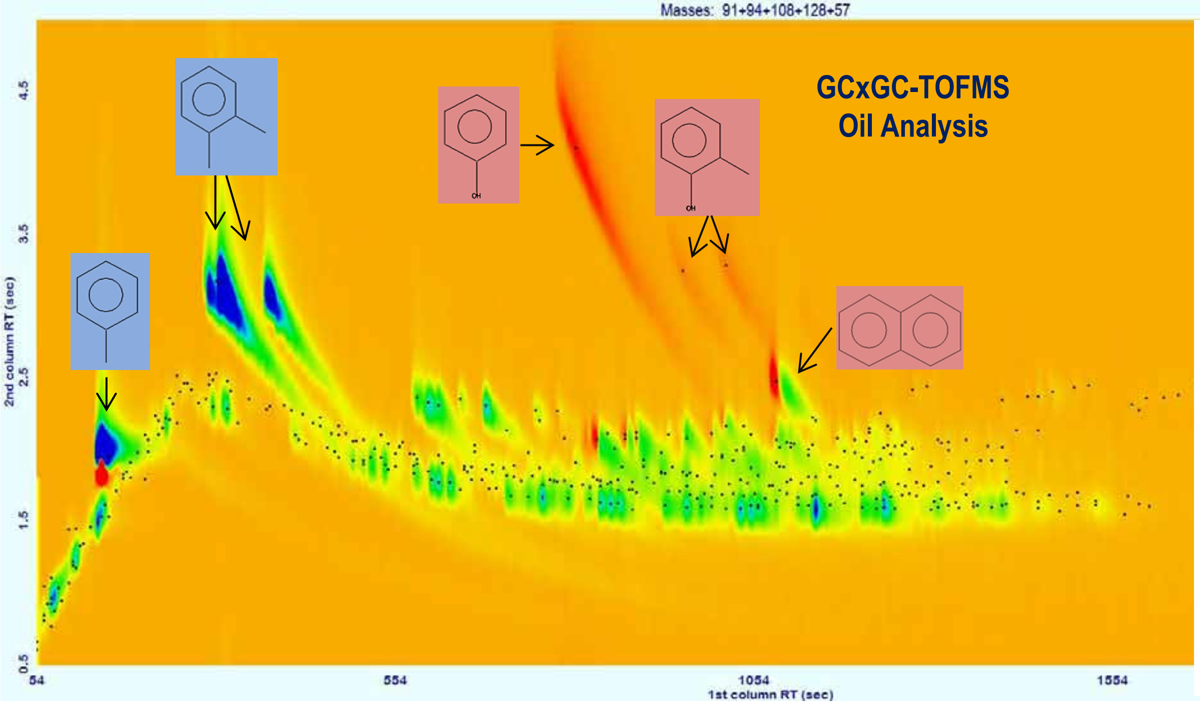
Olstad, Ben, Carpenter, Christiansen, Deutch

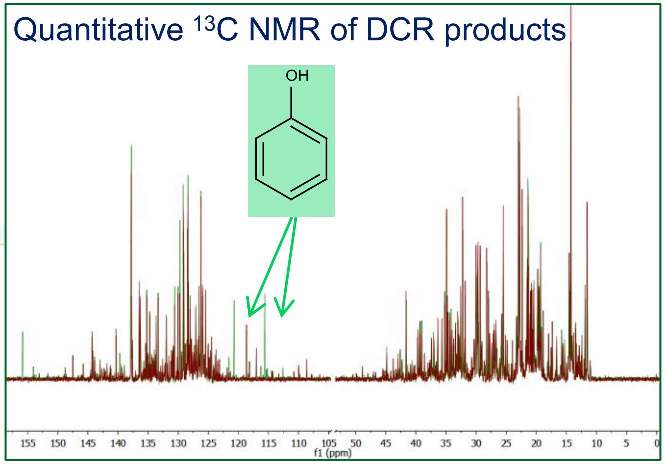
Model Compound	Wt % in Kerosene
Acetic Acid	14.1
Guaiacol	16.5
Sorbitan Monooleate	42.9
3 Compound Mix	84.7*

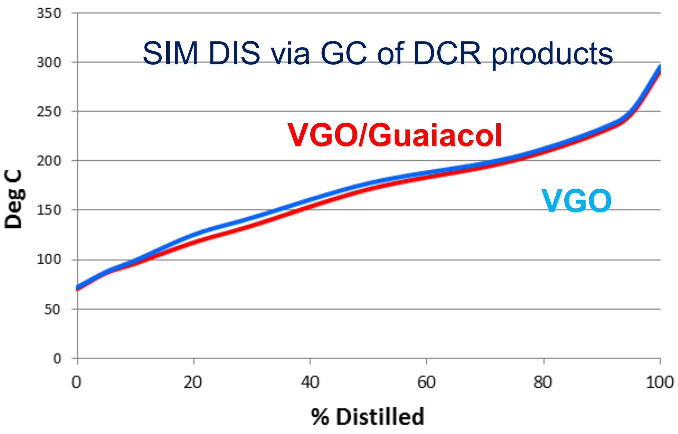
*Approximately 28 wt% of each compound

DCR - Guaiacol upgrading with Ecat and VGO:

- Validate biomass compound incorporation into upgraded product
- Guaiacol enhances naphthalene and phenol production; suppresses toluene
- NMR shows enhanced phenolics and complete guaiacol methoxy group decomposition
- SIM DIS is similar to VGO – fungible product

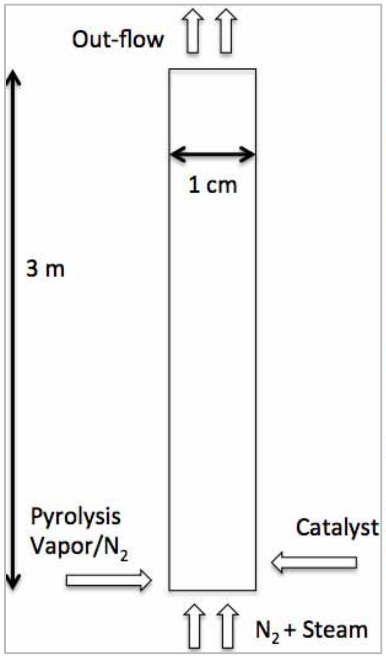


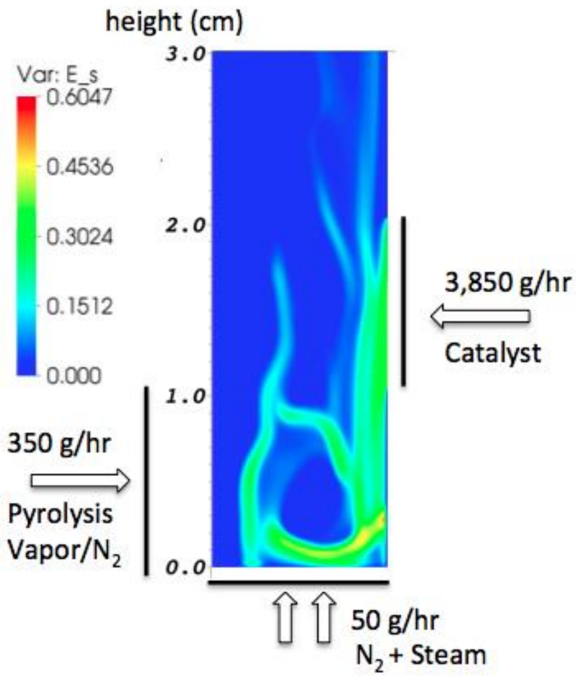




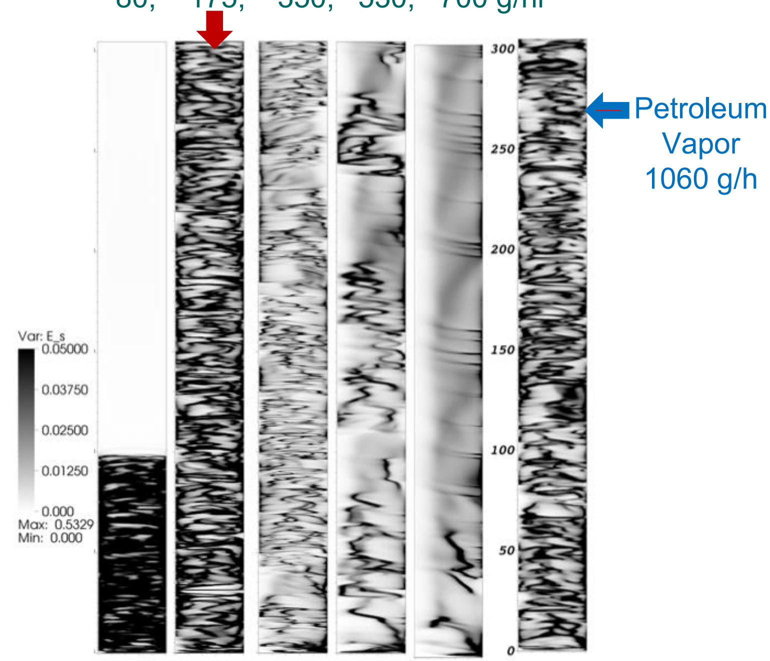
3 – Progress
Task 1: VPU - DCR CFD

Vapor mass flow rate (g/hr)	Mass & energy balance "Engr. Approx."	Mean	Std. Dev.	10-90% width	Mass Inv. (g)
700	2.1	2.09	1.74	0.43	13.0
530	2.7	4.19	2.49	3.26	12.8
350	3.8	6.88	4.59	3.36	13.8
175	6.3	16.9	13.6	35.1	28.3





DCR Pyrolysis Vapor
80, 175, 350, 530, 700 g/hr



Watch for asymmetries at high vapor flow rates

cpcbiomass.org

J. Ziegler

3 – Progress

Task 1: VPU - Biomass Incorporation
Task 3: Oil /Vapor Phase Chemistry

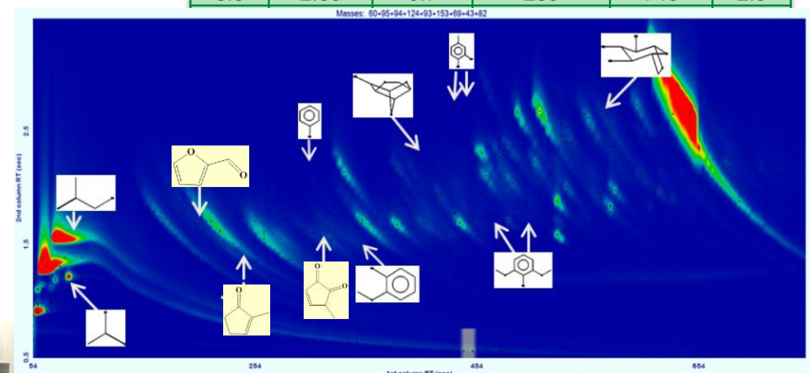
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

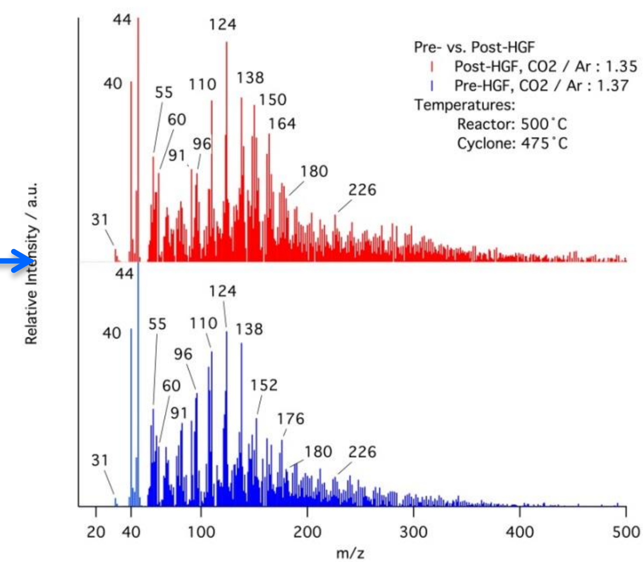
Pyrolyzer systems shakedown during continuous biomass feeding

- Biomass feeder - added variable frequency drive to deliver consistent biomass feeding and vapors
- Validate steam mass balance
- Hot vapor analysis – MBMS, NDIR added to sample vapors pre and post hot gas filter
- Hot Vapor delivery to DCR: installing mass calibration unit for transfer line
- Shakedown pyrolyzer condenser train
- Characterize oils
- Validate vapor composition pre/post hot gas filter: no change in vapor composition (remove alkali, residual char only)
- Deliver vapor to DCR June 2015: evaluate vapor co-feeding with VGO (9.15 MS)

500 °C Pyrolysis, Vary Pyrolyzer Feed to DCR

N_2 (kg/hr)	Biomass (kg/hr)	Biomass /N2	Pyrolysis Vapor (g/hr)	VGO/kero (g/hr)	Ratio
4.5	1.50	0.3	102	898	8.8
4.5	1.50	0.3	255	255	2.9
4.5	1.50	0.3	500	500	1.0
4.0	2.00	0.5	102	830	8.8
4.0	2.00	0.5	255	745	2.9
4.0	2.00	0.5	500	500	1.0
3.5	2.50	0.7	102	898	8.8
3.5	2.50	0.7	255	745	2.9





Jarvis, Olstad, Parent, Carpenter. Powell, Sprague

3 – Progress

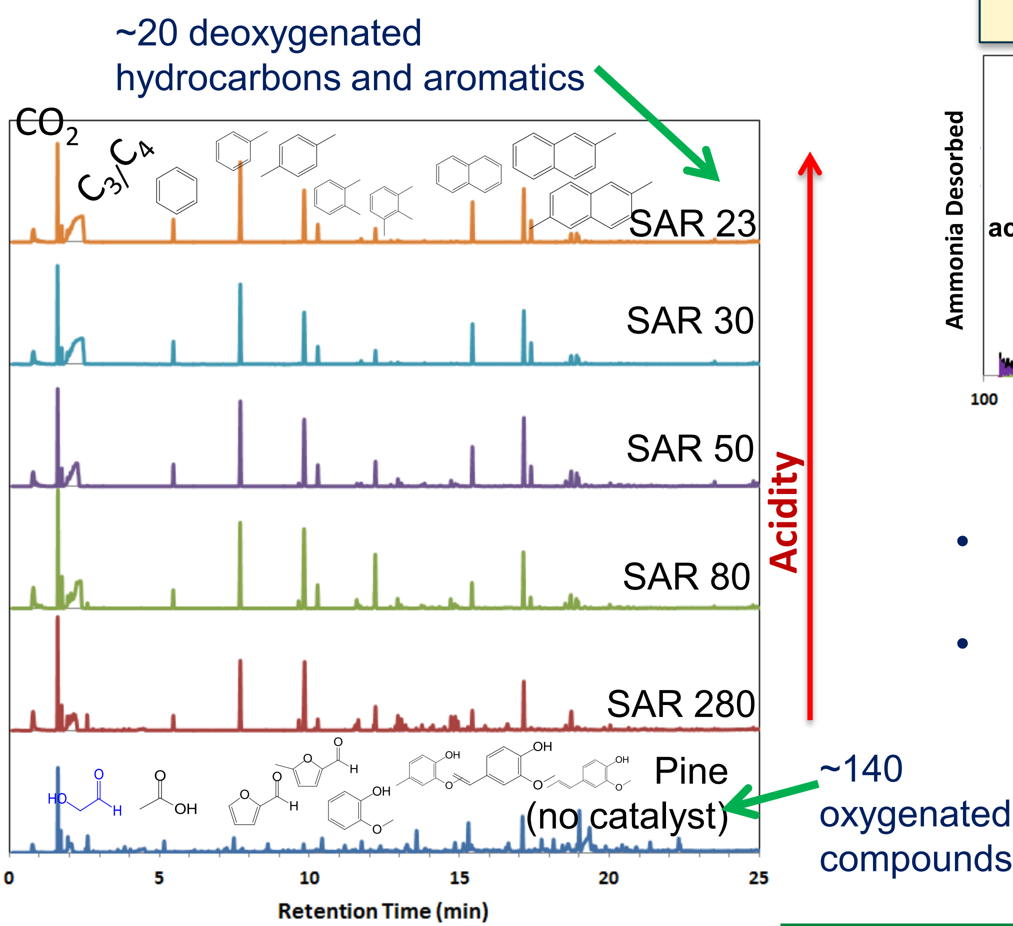
Task 2: Catalyst Development

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

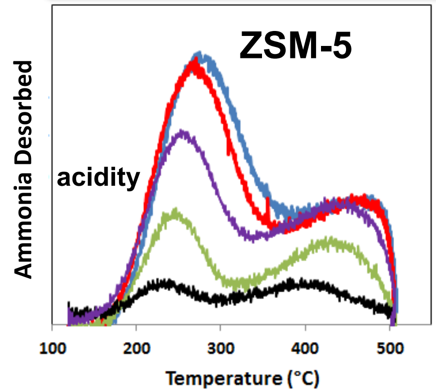
Yung, Engtrakul

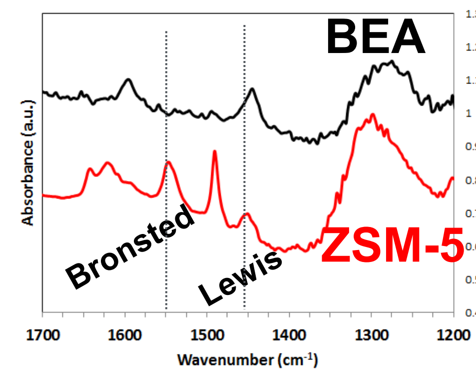
Study effects of acidity (concentration and Brønsted/Lewis ratio) on product distribution

- High acidity zeolites HC and aromatic production

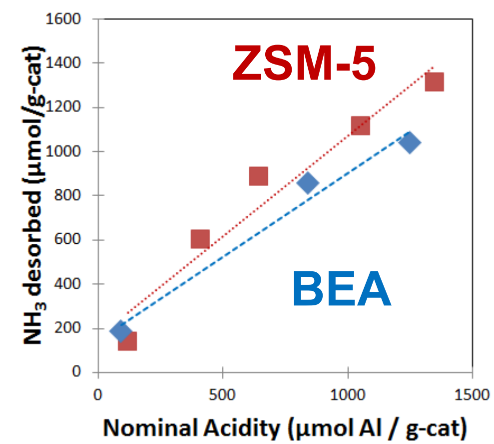


Acid site characterization (NH_3 TPD and pyridine DRIFTS)





- **Higher B/L ratio on ZSM-5 than BEA**
- **NH_3 TPD acidity of zeolites of varying SiO_2/Al_2O_3 ratio**



3 – Progress

Task 2: Catalyst Development

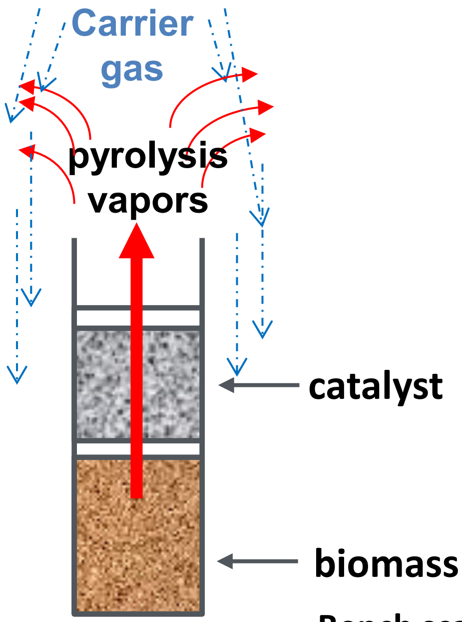
Yung, Engtrakul

- Evaluate how catalyst composition and acid site density affects reactivity for oxygen functional groups (pine vapors and model compounds)
- Synthesis of acidic materials (zeolites and sulfated metal oxides) with incorporation of metallic deoxygenation/hydrogenation functionality
- Catalysts must meet DCR specifications (particle size, density, attrition resistance)

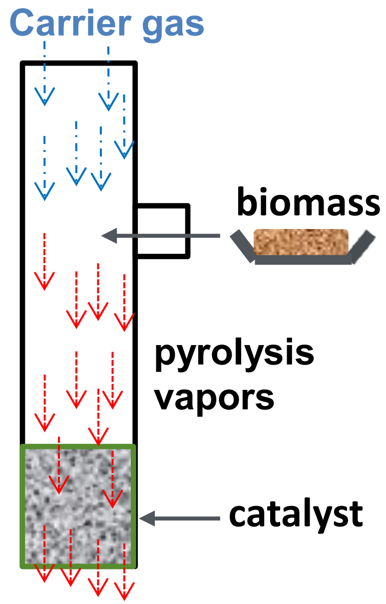
Catalyst synthesis

Ion-exchange and incipient-wetness impregnation synthesis of Ni, Pt, and Cu catalysts for biomass VPU

***In situ* upgrading**



***Ex situ* upgrading**

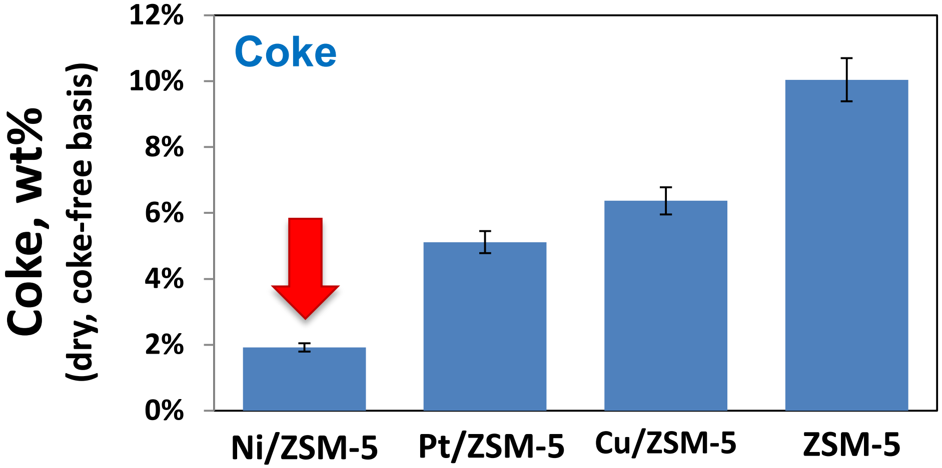


Bench scale reactors (0.01 – 1.0 g catalyst)

3 – Progress
Task 2: Catalyst Development

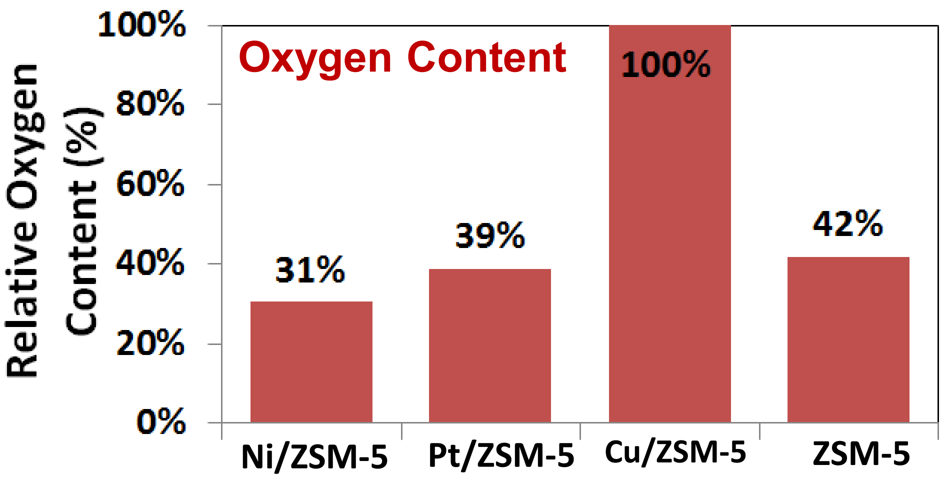
Yung, Engtrakul

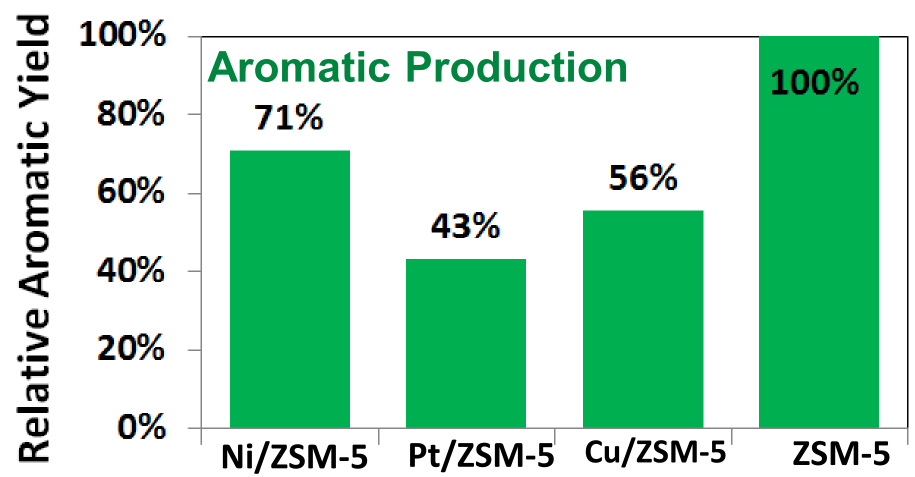
Effect of composition on coke, oxygen, and aromatic yields during pine *ex situ* VPU at 500°C



- Relative to ZSM-5, the addition of metals resulted in:
  - Decreased coke formation by resistance/removal of surface carbon
  - Lower oxygen content in products (Ni, Pt)
  - Lower aromatic yield at low biomass-to-catalyst ratio (0-0.7) but higher stability and aromatic yield at B:C = 0.7-1.0

Reaction conditions: 500°C, 1 atm, 500 mg catalyst , total biomass/catalyst = 1.0 wt/wt, by 35 mg pine pyrolysis at 500°C, 33% H_2, GHSV = 50,000 h^{-1}





3– Progress

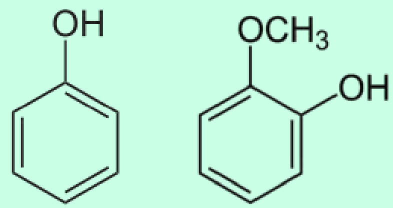
Task 2: Catalyst Development

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

M. Yung

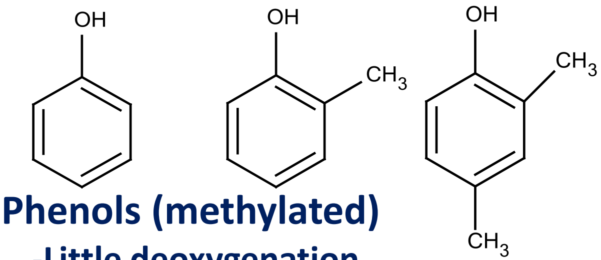
Model Compounds

Phenol, Guaiacol



300-500°C, 1 atm, H_2

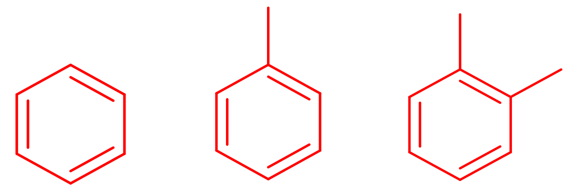
Zeolites (BEA, ZSM-5)



Phenols (methylated)

- **-Little deoxygenation**
- **-Low stability, rapid coking**

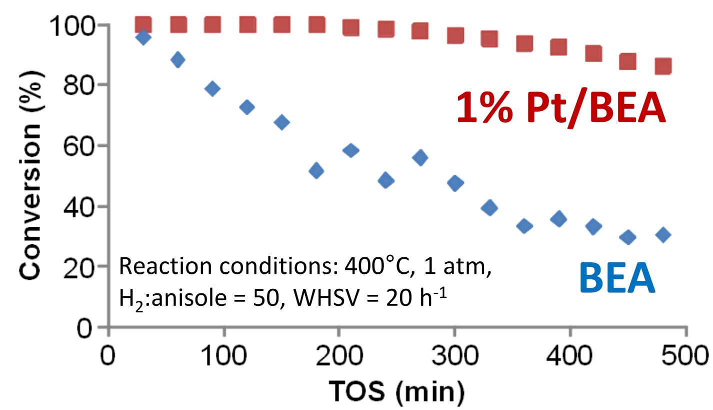
Zeolites with Pt or Ni



Aromatics (B, T, X)

- **-Higher deoxygenation**
- **-Higher stability, decreased coking**

- Evaluate effects of composition on reaction products of various model oxygenates
- Incorporate deoxygenation and/or hydrogenation activity into acidic zeolite support



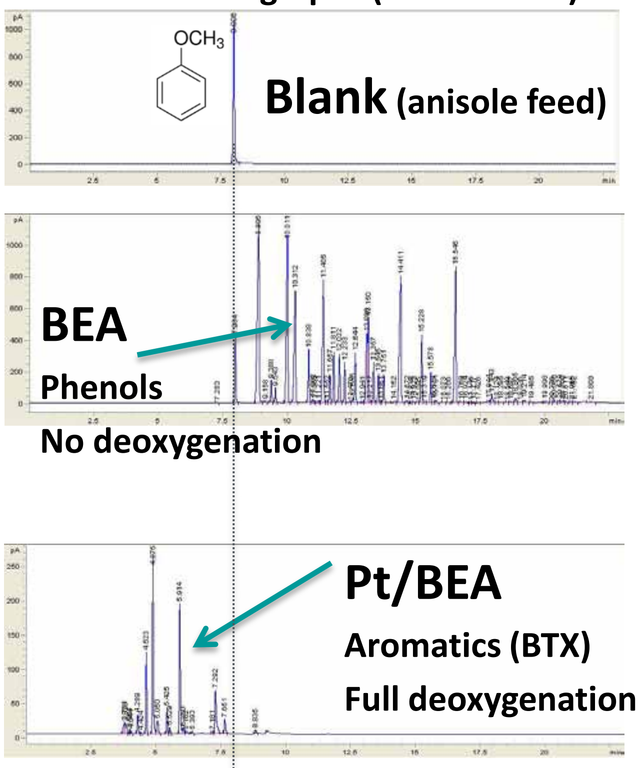
3 – Progress

Task 2: Catalyst Development

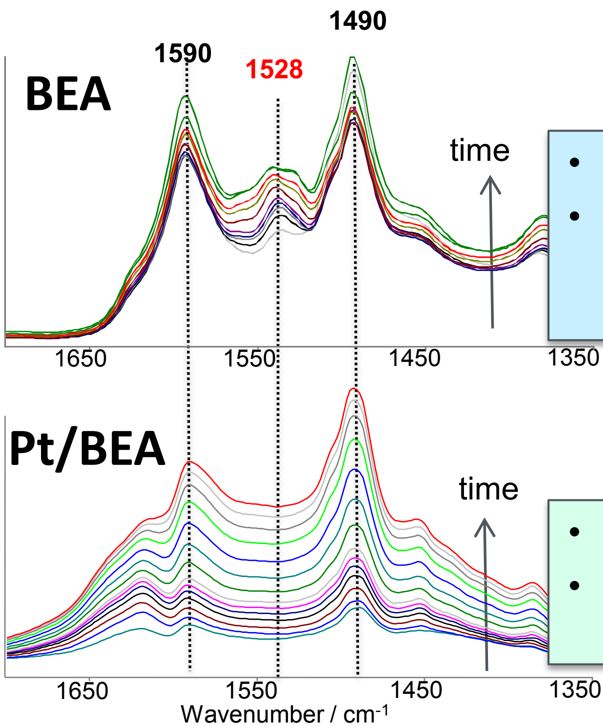
M. Yung

- Study surface chemistry and formation of intermediates
- Use *in situ* techniques to study catalysts under operating conditions (deoxygenation and coke forming reactions)

Gas chromatographs (anisole VPU)



Monitoring surface species via *in situ* DRIFTS (anisole VPU)



- **PAH/coking on surface (1528 cm^{-1})**
- **Ratio of 1590/1490 indicates oxygen attached to aromatic ring (phenol and methoxy species)**

- **Decreased PAH/coking at (1528 cm^{-1})**
- **Ratio of 1590/1490 indicates no oxygen aromatic ring (BTX)**

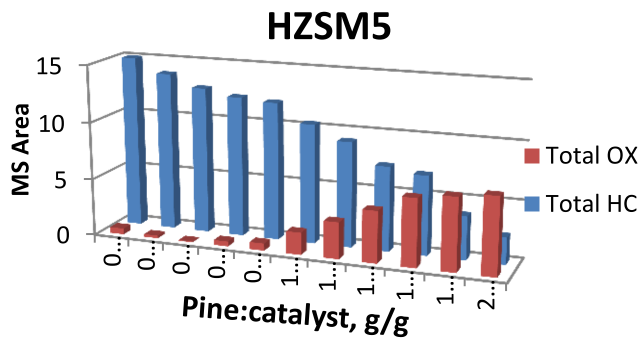
Task 2: Catalyst Development

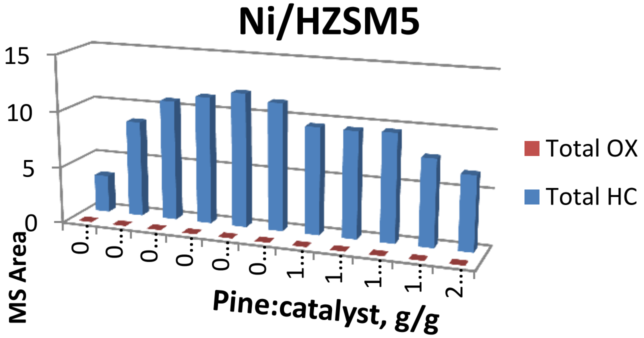
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

lisa, Cheah

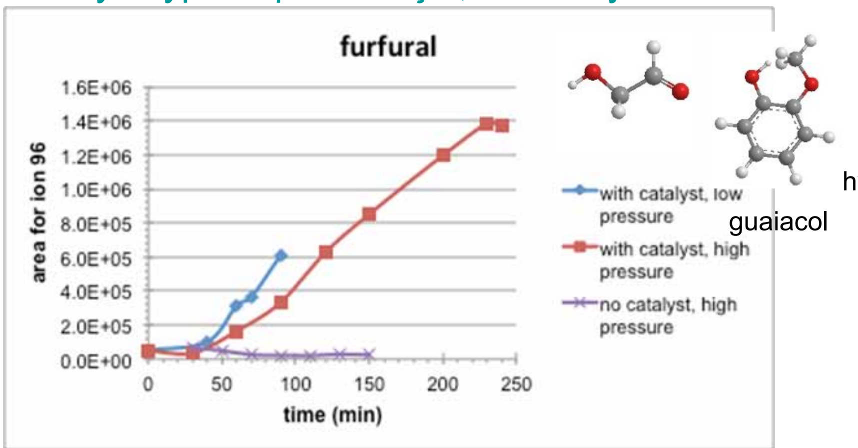
Understanding the impact of ΔP and catalyst on pine vapor upgrading: catalyst performance improved by addition of metals (Ni or Pt) and H_2

- Reduced catalyst deactivation due to lower [coke]
- Higher hydrocarbon formation
- Less oxygenates = lower oil oxygen content
- Active already at low pressure (5 bar)





Understanding carbon coupling reactions with biomass model compounds (guaiacol, hydroxyacetaldehyde) and catalyst type to produce jet, diesel hydrocarbons



Furfural was produced due to C-C coupling reactions of HAA.

CSTR reactor for carbon coupling reactions with biomass compounds.

S. Cheah and Y. Zhao, Doped Pt and Ni catalysts for deoxygenation of biomass pyrolysis vapors, NREL Invention Record (IR) Number ROI-13-00055, May 2013.

4 - Relevance

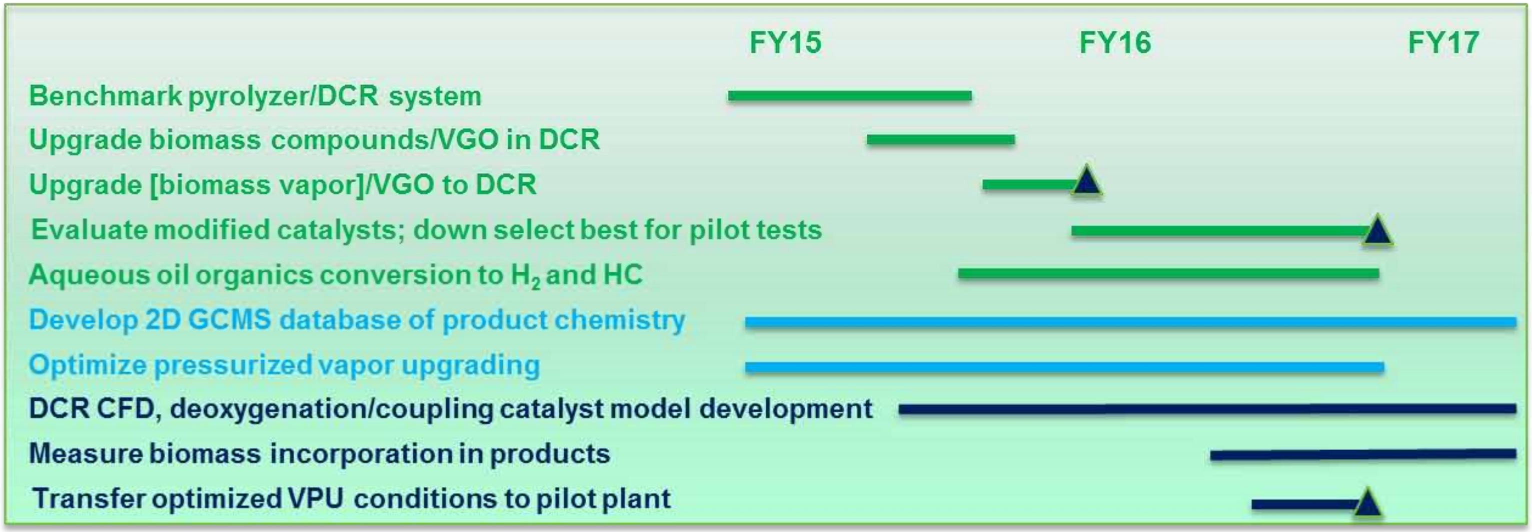
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

- Project supports the development of catalysts that enable biomass pyrolysis vapor conversion to fungible hydrocarbon liquid products that can contribute towards BETO's MYPP goal:
  - *Achieve a conversion cost of $3.31 per gallon of total blendstock via a bio-oil pathway*
  - *DCR results directly transferable to the refining industry*

- For the Bioenergy Industry:
  - *Contribute to the expansion of the biomass pyrolysis industry by developing catalysts that produce oils that can be upgraded in refineries*
  - *Working with Johnson Matthey, NexCeris to develop next generation VPU catalysts for industrial use*
  - *Develop oil characterization database to understand process induced chemical changes (GC TOFS, hot vapor analysis, NMR)*

5 – Future Work

- Move to 100% vapor feeding to the DCR and assess products
- Continued development of 1) reduced coking, hydrogenation and deoxygenation catalysts and 2) structure activity relationships
- Prepare/evaluate/characterize kg quantities of metal modified zeolites and JM catalyst for DCR tests
- Continue developing correlations between bio oil production and liquid and vapor phase chemistry
- Assess vapor incorporation extent in products (C^{14} analysis)
- Down select/prepare best catalyst for VPU use in pilot tests
- Begin emerging catalyst evaluation in 2017



Summary

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

Project develops catalysts that convert biomass pyrolysis vapor to fungible hydrocarbon liquid products that can contribute towards BETO's MYPP goal:

- Achieve a conversion cost of $3.31 per gallon of total blendstock via a bio-oil pathway.
- Selective catalysts being developed by NREL, Johnson Matthey and NexCeris

The coupled pyrolyzer/DCR system is operational for VPU

- Biomass compounds are incorporated into VGO during VPU
- On line hot gas analysis provides vapor feed composition
- Hot gas filtration does not change vapor chemistry
- Catalytic hot gas filtration will be assessed

Process impacts on biomass deconstruction are being understood by chemically characterizing liquid and vapor phase chemistry

- MBMS, 2D GCTOFS, NMR, SIM DIS, TAN, and carbonyl analyses characterize products

Summary

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

Catalyst structure activity relationships and modeling are used to understand deoxygenation, hydrogenation and coupling to develop better catalysts

- Bimetallic alloying controls acidity – controls coking
- Higher acidity improves deoxygenation and hydrocarbon yields
- Hydroxyacetaldehyde favors coupling reaction, guaiacol does not
- Ni modified zeolites combine decreased coking and deoxygenation activity

During catalytic pyrolysis, moderate pressure H_2

- Reduces coking and improves hydrocarbon yields
- Reduces oxygenate content in product composition

Ongoing Work:

- Complete biomass compound study with ECAT and VGO
- Assess metal modified zeolites
- Calibrate vapor mass flow to DCR
- Conduct vapor/VGO then vapor only DCR experiments
- Product characterization (composition, extent of biomass incorporation)

Acknowledgements

Adam Bratis
Haoxi Ben
Danny Carpenter
Earl Christiansen
Singfoong Cheah
Mark Davis
Steve Deutch
Jane Fisher
Doug Herrick
Kristiina Iisa
Whitney Jablonski
Mark Jarvis
Mark Nimlos
Marc Oddo
Jessica Olstad
Yves Parent
Glenn Powell
Mike Sprague
Alex Stanton
Jack Ziegler

NREL Catalysis, DCR and Analysis Team

Zeton Fabrication Team

Casey Hetrick (BP America)
Jeff Lewis (Equilibrium Catalysts)
Matthew Seabaugh (Nexceris)
Gordon Weatherbee (WR Grace)
Mike Watson, Andrew Heavers (Johnson Matthey)
Larry Doyle, Chris Brown, Sean Murray (Zeton)
Carston Sievers (GeorgiaTech)

Johnson Matthey
GRACE Enriching Lives, Everywhere.™
ZETON PILOT PLANT TECHNOLOGY
Nexceris
CPC cpcbiomass.org

A. Dutta

FY2013 Reviewer Comments/Responses

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

Comment: Good group of collaborators, choice of reactors and catalysts. Possibly redundant with other Lab work, and potential for innovation seems limited.

Response: Innovation is possible from the use of emerging catalysts that can be selective for vapor phase upgrading (VPU) reactions and produce hydrocarbons other than BTX compounds from HZSM5 upgrading. Johnson Matthey is developing these kinds of catalysts through the CRADA with NREL. The overarching question is, as always, catalyst cost, selectivity, regeneration extent, and scalability. We will build on other national lab results when available. Also note that this process upgrades biomass pyrolysis vapors – no other labs are doing this to our knowledge.

Comment: Several potential catalyst and support providers are involved, which is good. Not entirely clear how the J-M CRADA impacts the J-M involvement in this task and the IP involved, for example the cost-sharing.

Response: The JM CRADA is structured to provide catalysts tailored for VPU and that target specific functional groups for VPU. The overall goal is evaluating JM catalyst activity at the laboratory scale to determine if further testing is warranted at the DCR scale. The 3 NREL tasks (Hensley, Nimlos, Magrini) work together seamlessly on the CRADA of which the cost structure is each partner funds their own activities.

FY2013 Reviewer Comments/Responses

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

IP has been worked out and can be: 1) each party owns their own IP if developed separately and 2) shared inventions means shared IP. We worked closely with JM on the gasification platform to develop reforming catalysts and in that case they developed and own any IP around the Rh reforming material.

Comment: Catalyst optimization is critical to pyro upgrading. No question. Somewhat redundant with other projects studying catalyst with common goals and success factors.

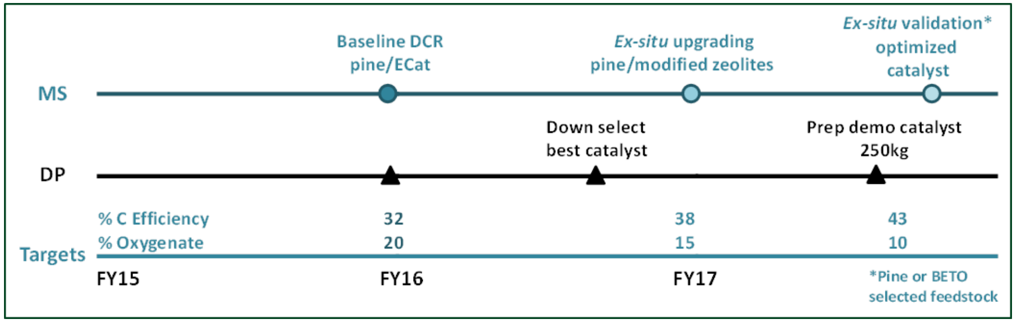
Response: We are targeting the screening of the most promising catalysts with industrially relevant process conditions and scale and will test and characterize promising material developed by industry, other labs and academia if they are interested. Redundancy can be good and we encourage round robin testing of VPU catalysts to better understand how different reactors and process conditions impact product formation. This kind of testing is needed to transfer the technology to industry.

Comment: Project could be more detailed, and with more attention to G/NG decision points.

FY2013 Reviewer Comments/Responses

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

Response: The work plan will be revised yearly with G/NG points as soon as we have enough generated data to make these kinds of decisions. The FY14 AOP has the following decision points:



Comment: CSF's are not specific enough - they read more like a "fishing expedition" It could work out OK if these GET more specific as the project matures; if they stay this vague throughout, it will not drive the project very effectively.

Response: We agree that stringent catalyst performance targets need to be defined and will be once the process model/design case report is completed in FY13. Then we use those targets to assess progress in catalyst performance and then progress to process cost reductions. The FY14 CSF's from the SOT are:

- Catalyst coking $\leq$ 10%
- Products Carbon$_{eff}$ $\geq$ 43%
- Product O_2 content $\leq$ 10%
- Products cost to meet $3.31/gal

Publications, Presentations

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

PUBLICATIONS

1. Magrini, K., Beckham, G., Vardon, D., Catalysis's Role in Bioproducts Update, accepted for publication in "Commercializing Biobased Products: Opportunities, Challenges, Benefits, and Risks", Ed. S. Snyder, publisher Royal Society of Chemistry, January 2015.
2. Talmadge, M.; Baldwin, R.; Biddy, M.; McCormick, R.; Beckham, G. T.; Ferguson, G.; Czernik, S.; Magrini-Bair, K.; Foust, T.; Metelski, P.; Hetrick, C.; Nimlos, M. R., A Perspective on Oxygenated Species in the Refinery Integration of Pyrolysis Oil. *Green Chemistry,* **2014,** 16, 407-453**.**
3. A. Dutta, Jesse Hensley, Richard Bain, Kim Magrini, Eric CD Tan, George Apanel, David Barton[3], Peter Groenendijk, Daniela Ferrari, Whitney Jablonski, Daniel Carpenter. "Techno-economic analysis for the production of mixed alcohols via indirect gasification of biomass based on demonstration experiments", I*ndustrial and Engineering Chemistry Research*, **2014**, 53(30), 12149-12159.
4. Calvin Mukarakate, Michael Watson, Jeroen ten Dam, Xavier Baucherel, Sridhar Budhi, Matthew M. Yung, Haoxi Ben, Kristiina Iisa, Robert M. Baldwin, and Mark R. Nimlos, "Upgrading biomass pyrolysis vapors over β-zeolites: role of Silica-to-Alumina ratio," Green Chemistry 2014, 16, 4891-4905.
5. Richard J. French, James Stunkel, Stuart Black, Michele Myers, Matthew M. Yung, and Kristiina Iisa, "Evaluate Impact of Catalyst Type on Oil Yield and Hydrogen Consumption from Mild Hydrotreating," Energy & Fuels 2014, 28(5), 3086-3095.
6. Richard L. Bain, Kimberly A. Magrini-Bair, Jesse E. Hensley, Whitney S. Jablonski, Kristin M. Smith, Katherine R. Gaston, and Matthew M. Yung, "Pilot Scale Production of Mixed Alcohols from Wood," Industrial & Engineering Chemistry Research 2014, 53, 2204-2218.
7. Yolanda A. Daza, Ryan A. Kent, Matthew M. Yung, and John N. Kuhn, "Carbon dioxide conversion by reverse water gas shift chemical looping on perovskite-type oxides," Industrial & Engineering Chemistry Research 2014, 53 (14), 5828–5837.
8. Allison M. Robinson, Megan E. Gin, and Matthew M. Yung, "Methane Steam Reforming Kinetics on a Ni/Mg/K/Al2O3 Catalyst," Topics in Catalysis, December 2013, 56(18-20), 1708-1715.
9. Qiang Xu, Singfoong Cheah, and Yufeng Zhao. Initial reduction of the NiO(100) surface in hydrogen; *The Journal of Chemical Physics* 139, 024704 (2013); doi: 10.1063/1.4812824
10. G. S. Foo, and C. Sievers, "Synergistic Effect between Defect Sites and Functional Groups in the Hydrolysis of Cellulose using Activated Carbon," *Chemsuschem*, vol. 8, pp. 534-543, 2015.
11. G. S. Foo, D. Wei, D. S. Sholl, and C. Sievers, "Role of Lewis and Brønsted Acid Sites in the Dehydration of Glycerol over Niobia," *ACS Catalysis*, vol. *4*, pp. 3180–3192, 2014.
12. Sarah M. Schimming, Guo Shiou Foo, Onaje LaMont, Allyson K. Rogers, Matthew M. Yung, Andrew D. D'Amico, and Carsten Sievers, "Kinetics of hydrogen activation on ceria-zirconia," Journal of Catalysis (submitted).
13. Guo Shiou Foo, Adam H. van Pelt, Daniel Krotschel, Benjamin F. Sauk, Allyson K. Rogers, Cayla R. Jolly, Matthew M. Yung, Carsten Sievers, "Hydrolysis of Cellobiose over Sulfonated Activated Carbon Catalysts," Green Chemistry (submitted).
14. Singfoong Cheah, Anne Starace, Erica Gjersing, Steven Deutch, Sarah Bernier. Deoxygenation of hydroxyacetaldehyde and guaiacol catalyzed by HZSM-5. To be submitted to Topics in Catalysis.

.

Publications, Presentations

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

MILESTONE REPORTS

1. K. Magrini, Reactor modifications for pyrolysis oil production, BETO Milestone Report, October 15, 2013.
2. M. Yung, Measure Biomass Deconstruction Kinetics, BETO Milestone Report, March 31, 2013
3. S. Cheah, Y. Zhao, W. Michener, Develop Bi-Functional Catalysts, BETP Milestone Report, July 31,2013.
4. S. Deutch, D. Carpenter, R. Evans, R. French, Develop Oil Analysis, BETO Milestone Report, March 31, 2013 K. Iisa, A. Stanton. S. Habas, Determine the impact of pressure on the distribution of carbon between oil, solids, and light cases for three (3) catalysts during pyrolysis intermediate upgrading, BETO Milestone Report, September 30, 2014.
6. M. Yung, C. Engtrakul, C. Mukarakate, A. Starace, J. Olstad, Influence of catalyst acidity for pyrolysis vapor phase upgrading reactions, BETO Milestone Report, March 30, 2014.
7. W. Jablonski, E. Christiansen, Evaluate the equilibrium FCC catalyst for verifying steady state system performance in the DCR, BETO Milestone Report, September 15, 2014.
8. S. Deutch, D. Carpenter, Composition of pyrolysis vapors from pyrolysis oil: Characterize chemical changes to pyrolysis vapors upon condensation to define chemical classes and amounts., BETO Milestone Report, May 30, 2014.
9. S. Cheah, Evaluate the reactions between representative lignin- and cellulose-derived molecules in pyrolysis vapors to determine product types and typical product chain lengths, BETO Milestone Report, November 2014.
10. S. Deutch, E. Christiansen, D. Carpenter, Characterize and compare the chemical composition of raw and upgraded oils as a function of pyrolyzer conditions to baseline product oil composition from pine vapor using 2D chromatography and NMR. Develop PIANO analysis for upgraded oils to assess fungibility, BETO Milestone Report, March 31, 2015, in progress.
11. J. Olstad, M. Jarvis, Y. Parent, K. Magrini, M. Sprague, G. Powell, Establish baseline DCR operations and product composition using WR Grace supplied VGO and ECat and compare product composition when biomass model compounds (guaiacol, sorbitol, and acetic acid) are added to the VGO feed to understand biomass deoxygenation and incorporation into liquid product. Light gas and oil composition and yield and coking extent will be determined and used to establish performance before adding biomass vapors to the DCR feed, BETO Milestone Report, March 31, 2015 in progress.

INVENTION RECORDS

1. S. Cheah and Y. Zhao, Doped Pt and Ni catalysts for deoxygenation of biomass pyrolysis vapors, NREL Invention Record (IR) Number ROI-13-00055, May 2013.

PRESENTATIONS

1. Haoxi Ben, Glen A. Ferguson , Matt Sturgeon , Gregg T. Beckham, Tom D. Foust, Mark Jarvis, Mary J. Biddy, “Aromatic model compounds ring opening on Ir/Al_2O_3 – a mechanistic study by deuterium tracing and NMR”, 247th ACS National Meeting and Exposition, March 16-20, 2014, Dallas TX. Oral
2. Haoxi Ben, Mark Jarvis, Mark Nimlos, David Robichaud, Calvin Mukarakate, Steve Deutch, Aging process of biomass pyrolysis oil and its model compounds – a mechanistic study, 248th ACS National Meeting, August 10-14, San Francisco, CA . Oral.

Publications, Presentations

6. M. Yung, K. Magrini, W. Jablonski, Y. Parent, J. Olstad, A. Steele, S. Poulston, R. Bain, S. Phillips, J. Hensley, K. Smith, C. Feik, K. Gaston, M. Pomeroy, “Pilot Scale Demonstration of Biomass Syngas Cleaning via Catalytic Reforming,” TCS Biomass, Denver, CO September 2014. Oral
4. Matthew Yung, Chaiwat Engtrakul, Calvin Mukarakate, Anne Starace, and Jessica Olstad, “Effects of catalyst acidity on upgrading of biomass pyrolysis vapors,” TCS Biomass, Denver, CO September 2014. Poster
5. Matthew Yung, Chaiwat Engtrakul, Calvin Mukarakate, Anne Starace, and Jessica Olstad, “Effects of catalyst acidity on upgrading of biomass pyrolysis vapors,” International Conference on Environmental Catalysis, Asheville, NC, August 2014. Oral5.
6. Matthew Yung, Calvin Mukarakate, Chai Engtrakul, and Anne Starace, “Upgrading biomass-derived pyrolysis vapors on catalysts of varying acidity,” 248th American Chemical Society Annual Meeting, San Francisco, CA, August 2014. Oral
7. M.M. Yung, E. Gomez, E. Qauuym, and J.N. Kuhn, “Vapor Phase Catalytic Deoxygenation of Acetic Acid,” American Institute of Chemical Engineers Annual Conference, San Francisco, CA, November 2013.
8. John Kuhn, Yolanda Daza, Ryan Kent, Matthew Yung, “Intensified carbon dioxide conversion by reverse water gas shift chemical looping via perovskite-type oxides,” International Conference on Environmental Catalysis, Asheville, NC, August 2014. Oral
9. J. Rorrer and M.M. Yung, “Catalytic Deoxygenation of Pyrolysis Vapors for Biofuel Production” (Undergraduate Poster Session), American Institute of Chemical Engineers Annual Conference, San Francisco, CA, November 2013. Poster
10. Y.A. Daza, R.A. Kent, M.M. Yung, and J.N. Kuhn, “Temperature-programmed studies on lanthanum strontium cobaltites for carbon dioxide reduction” (Poster), SHPE National Conference 2013, Indianapolis, IN, October 2013. Poster
11. M.M. Yung, S. Cheah, K.A. Magrini-Bair, J.N. Kuhn, “Understanding sulfur poisoning and regeneration of nickel biomass conditioning catalysts using X-ray absorption spectroscopy,” ACS National Meeting, Catalysis Division, New Orleans, LA, April 2013. Oral
12. M.M. Yung, “Thermochemical Biomass Catalytic Conversion R&D at NREL,” Ohio State University, Chemical & Biomolecular Engineering Department Seminar, Columbus, OH, August 2013. Oral
13. M.M. Yung, “Thermochemical Biomass Conversion R&D at NREL,” pH Matter LLC Company Seminar, Columbus, OH, August 2013. Oral
14. M. M. Yung, S. Cheah, J.N. Kuhn, “Effect of Regeneration Protocols on Sulfur Species over Nickel-based Biomass Syngas Conditioning Catalysts,” 23rd North American Catalysis Society Meeting, Louisville, KY, June 2013. Oral.
15. Singfoong Cheah, Erica Gjersing, Caitlin Majlinger, Matthew M. Yung, Mark Davis, “Spectroscopic Investigation of Biomass Oxygenates on Zeolites,” 23rd North American Catalysis Society Meeting, Louisville, KY, June 2013. Oral
16. J. Rorrer, M.M. Yung, “Catalytic Pyrolysis of Biomass for Biofuel Production,” (poster) NREL SULI Poster Session, Golden, CO, August 2013. Poster
17. N.H. Elsayed, Y.A. Daza, M.M. Yung, J.N. Kuhn, “Hydrogen purification by catalytic tar reforming of biomass-derived syngas,” (poster) 2013 Florida Energy Summit, Orlando, FL, October 2013. Poster
18. N.H. Elsayed, Y.A. Daza, M.M. Yung, J.N. Kuhn, “Hydrogen purification by catalytic tar reforming of biomass-derived syngas,” (poster) 12th Annual Symposium of the Southeastern Catalysis Society, Asheville, NC, September 2013. Poster