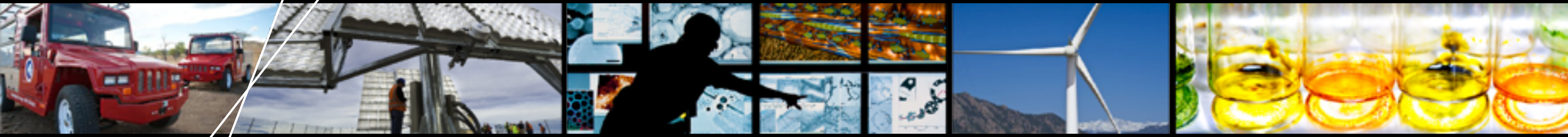
NREL
NATIONAL RENEWABLE ENERGY LABORATORY

2015 DOE Bioenergy Technologies Office (BETO) Project Peer Review

Catalytic Pyrolysis Sciences

WBS 2.3.1.313



Bio-oil Technology Area Review

Mark R. Nimlos

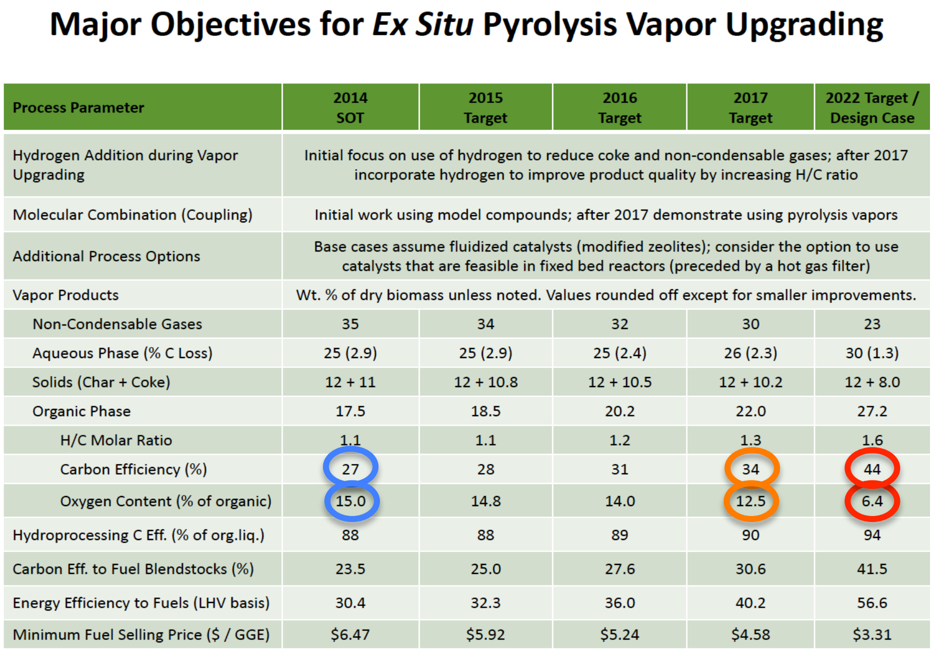
March 27, 2015

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Goal Statement

Improve process economics of Catalytic Fast Pyrolysis (CFP) through understanding of chemistry and physics

- Demonstrate technical targets at a laboratory scale
  - Improve carbon efficiency from 27% to 44% in FY2022
  - Reduce oxygen content in oil from 15% to 6.4% in FY2022
- Build an understanding of underlying science of CFP so as to reduce inefficient walk through Edisonian space to improve the technology
- Provide guidance for development of new catalysts and operation of pilot scale reactors



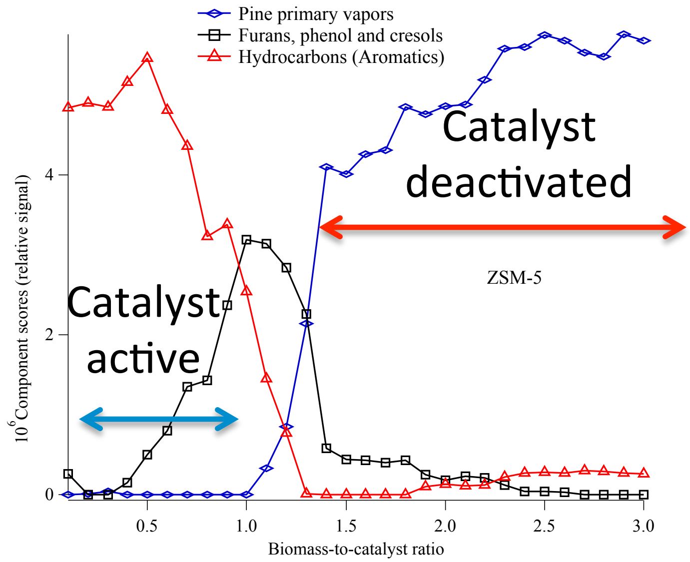
Major Objectives for *Ex Situ* Pyrolysis Vapor Upgrading

Process Parameter	2014 SOT	2015 Target	2016 Target	2017 Target	2022 Target / Design Case
Hydrogen Addition during Vapor Upgrading	Initial focus on use of hydrogen to reduce coke and non-condensable gases; after 2017 incorporate hydrogen to improve product quality by increasing H/C ratio				
Molecular Combination (Coupling)	Initial work using model compounds; after 2017 demonstrate using pyrolysis vapors				
Additional Process Options	Base cases assume fluidized catalysts (modified zeolites); consider the option to use catalysts that are feasible in fixed bed reactors (preceded by a hot gas filter)				
Vapor Products	Wt. % of dry biomass unless noted. Values rounded off except for smaller improvements.				
Non-Condensable Gases	35	34	32	30	23
Aqueous Phase (% C Loss)	25 (2.9)	25 (2.9)	25 (2.4)	26 (2.3)	30 (1.3)
Solids (Char + Coke)	12 + 11	12 + 10.8	12 + 10.5	12 + 10.2	12 + 8.0
Organic Phase	17.5	18.5	20.2	22.0	27.2
H/C Molar Ratio	1.1	1.1	1.2	1.3	1.6
Carbon Efficiency (%)	27	28	31	34	44
Oxygen Content (% of organic)	15.0	14.8	14.0	12.5	6.4
Hydroprocessing C Eff. (% of org.liq.)	88	88	89	90	94
Carbon Eff. to Fuel Blendstocks (%)	23.5	25.0	27.6	30.6	41.5
Energy Efficiency to Fuels (LHV basis)	30.4	32.3	36.0	40.2	56.6
Minimum Fuel Selling Price ($ / GGE)	$6.47	$5.92	$5.24	$4.58	$3.31

Abhijit Dutta, Thermochemical Platform Analysis Project , WBS 2.1.0.302

Example: Deactivation of ZSM-5 catalyst during feeding of biomass pyrolysis vapors

- Laboratory experiments showed ranges of biomass-to-catalyst ratio where catalyst is active
- Suggests riser reactor (NREL's DCR reactor and TCPDU) are ideal reactors for vapor phase upgrading
- Fixed and fluidized bed reactors not ideal
- This experiment was completed in under 2 hours.
- Results are used by Computational Pyrolysis Consortium in CFD simulations to suggest operating conditions for DCR reactor



Catalyst deactivated

Catalyst active

Mukarakate, C., et al. (2014). Real-time monitoring of the deactivation of HZSM-5 during upgrading of pine pyrolysis vapors. *Green Chemistry*, *16*(3), 1444–1461.

Project Quad Chart Overview

Timeline

- **Start Date:** October 1, 2013
- **End Date:** September 30, 2017
- **50% percent complete**

Barriers

Barriers addressed

Tt-H. Bio-Oil Intermediate Stabilization and Vapor Cleanup

Tt-L. Knowledge Gaps in Chemical Processes

Budget

	Total Costs FY 10 – FY 12	FY 13 Costs	FY 14 Costs	Total Planned Funding (FY 15-Project End Date
DOE Funded	$0	$1,777K	$1,816K	$6,970K
Project Cost Share (Comp.)*		$400K JM	$400K JM	$1.2M JM

Partners & Roles

- Johnson Matthey: Catalyst development and characterization (Vapor Phase Upgrading)
- Colorado School of Mines (Richards, Trewyn): Catalyst development and characterization
- University of Colorado (Ellison): mechanisms of pyrolysis
- LBL - Advanced Light Source (Ahmed): pyrolysis
- MIT (Roman): Catalyst development
- ORNL (Daw), ANL (Curtiss): Computational modeling

1- Project Overview

- **Catalytic Fast Pyrolysis (CFP) investigated since 1986**
  - ZSM-5 was first and most effective catalyst to date
  - Done properly it can achieve low oxygen content oil
  - Low C yields (< 15%) have been reported. Loss to coke and light gases
- **Incomplete understanding of the process**
- **We conduct laboratory experiments with model compounds and biomass pyrolysis vapors**
  - Provide understanding of chemical mechanisms to Johnson Matthey to develop new catalysts
  - Provide data for technoeconomic analysis and planned pilot studies at NREL (DCR and TCPDU)
  - Collaborate with Computational Pyrolysis Consortium (WBS 2.5.1.302)

FY17 Targets
C_{eff}: 27% -> 34%
O: 15% -> 12.5%

FY22 Targets
C_{eff}: -> 44%
O: -> 6.4%

2 – Approach (Technical)

- **Critical success factors:**
  - At the laboratory scale, we will reach the following technical targets:
    - Carbon yields of 34% and oxygen content of 12% by 2017 will be achieved by establishing reactor conditions (high biomass-to-catalysts ratio, short residence time), stripping products with steam and the addition of hydrogen (< 5 bar)
    - Carbon yields of 44% and oxygen content of 6% by 2022 will be achieved by developing new catalysts to better utilize added hydrogen and to direct reaction through different products (furans)
  - Discover reaction pathways that reduce search through Edisonian space
  - Provide understanding and data that simplify operation at pilot scale
- **Task plan**
  - **Development and testing of catalysts at lab scale for the Johnson Matthey CRADA** – Data and understanding generated in this project is used by JM to develop catalysts
  - **Laboratory performance testing of CFP improvements** – Experiments are conducted at 100g scale using improvements discovered at 1g scale to measure C yield and O content.
  - **Chemistry of catalytic upgrading** – chemical mechanisms of CFP are studied using reactions of model compounds and biomass.
  - **Biomass, catalyst and bio-oil: changes and characterization** – Measurements of starting material, catalyst and resulting product are used to infer reaction mechanisms.

2 – Approach (Technical cont)

- **Challenges**
  - Pyrolysis vapors contain a mixture of many molecules with different functional groups – condensable and reactive
  - Catalysts deactivate rapidly
  - Heterogeneous chemical reactions are difficult to measure directly
- **Experiments conducted at multiple scales**
  - Small reactors (1g catalyst) and Molecular Beam Mass Spectrometer (MBMS): universal detection in real time
  - Pyroprobe GCMS (5 mg): direct measurement and quantification of products
  - 2" fluidized bed reactor (100g): collection of oils. Being modified for continuous replacement of catalyst
  - Laminar entrained flow reactor (100g): simulation of conditions in a riser reactor
  - Product and catalyst analysis: NMR (600 and 400 MHz), SEM, TEM, light microscopy, etc

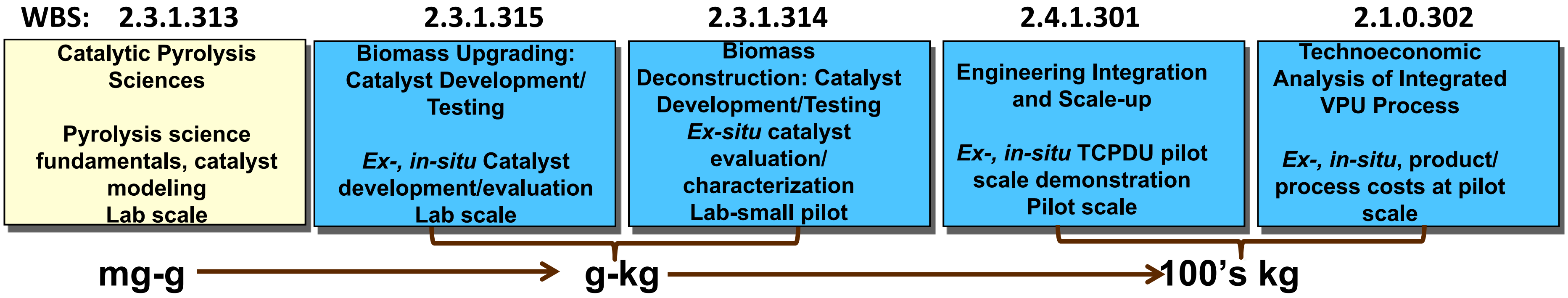
Baseline Experimental conditions: Pine pyrolysis vapors over Nexceris ZSM-5

2 – Approach (Management)

- **Track progress**
    - Quarterly progress reports
    - Quarterly SMART milestones
    - Go/No-Go points to direct research
- **Monthly task meeting**
- **Johnson Matthey CRADA**
    - Monthly teleconferences
    - 1 – 2 face-to-face meetings per year at NREL

Example Milestone (Q3 FY2015): Compare catalysts developed by WBS 2.3.1.314 to determine if hydrogenation can increase yields to 40% at labscale (< 5 g catalysts).

Project integration for the overall NREL/BETO thermochemical platform:



WBS: 2.3.1.313	2.3.1.315	2.3.1.314	2.4.1.301	2.1.0.302
Catalytic Pyrolysis Sciences **Pyrolysis science fundamentals, catalyst modeling** **Lab scale**	**Biomass Upgrading: Catalyst Development/ Testing** ***Ex-, in-situ* Catalyst development/evaluation** **Lab scale**	**Biomass Deconstruction: Catalyst Development/Testing** ***Ex-situ* catalyst evaluation/ characterization** **Lab-small pilot**	**Engineering Integration and Scale-up** ***Ex-, in-situ* TCPDU pilot scale demonstration** **Pilot scale**	**Technoeconomic Analysis of Integrated VPU Process** ***Ex-, in-situ*, product/ process costs at pilot scale**

mg-g → **g-kg** → **100's kg**

3 - Technical Accomplishments/ Progress/Results

Will present progress on the following:

- Our experimental measurements were used by the Thermochemical Platform Analysis Project to determine the SOT
- Studies to address the 2017 technical targets
  - We compared in-situ and ex-situ CFP
  - We determined limits of biomass-to-catalysts ratio for catalyst deactivation
  - The activities of catalysts with different acidities were compared
  - The addition of steam was investigated for increasing the carbon yield

C_{eff}: 27% -> 34%
O: 15% -> 12.5%

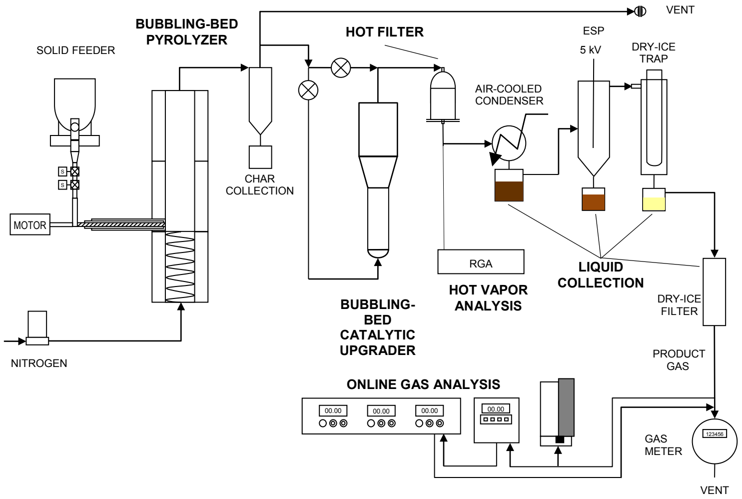
- 2022 Targets: New catalyst development
  - We have screened catalyst provided by Johnson Matthey to identify mechanisms that lead to other products (furans)
  - The selective hydrogenation of C=C bonds has been investigated as a means of increasing carbon yields and reducing light gas formation

C_{eff}: -> 44%
O: -> 6.4%

Results Measured for State of Technology (SOT)

- **2” fluidized bed reactor**
  - In- and ex-situ
  - 150 g h^{-1}
  - Fully characterized
- **Baseline catalysts (Nexceris)**
  - Clay, Al_2O_3 and SiO_2 binder
  - Mass balance 86% - 97%
  - Ex-situ (SiO_2)
    - C yield: 27%
    - O content in oil: 15%
- **Values from this work were used by the Thermochemical Platform Analysis Project to determine the SOT, which is used in the MYPP**

Kristiina Iisa, Rick French, Matt Yung, NREL quarterly milestone, Dec 31, 2014



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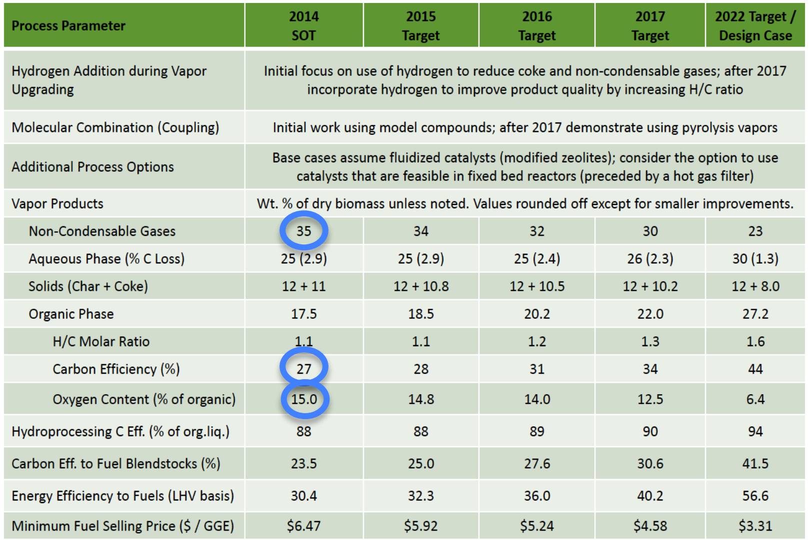

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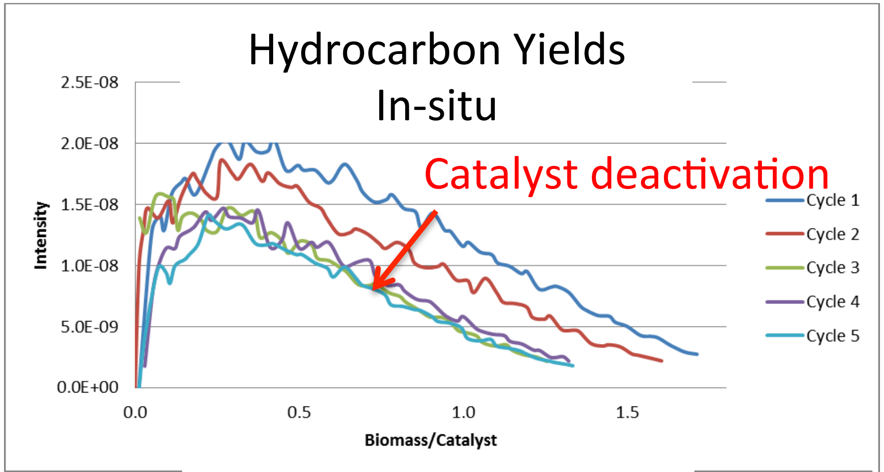
Ex-Situ CFP was compared to In-Situ CFP

- 2” FBR
- Milestone: June 30, 2014
- C yields
  - In-situ: 24%
  - Ex-situ: 20%
- O content
  - In-situ: 21%
  - Ex-situ: 18%

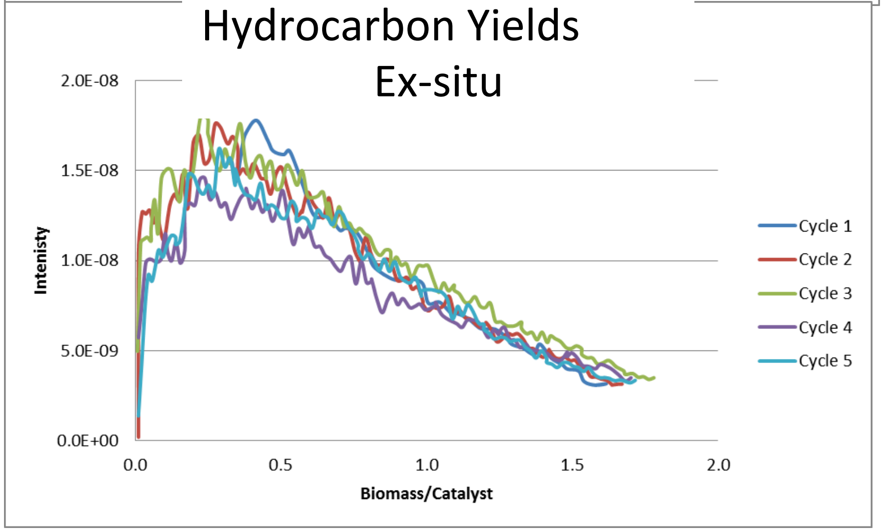
Similar Results

- Reactions were conducted in batch mode with regeneration after each batch of biomass
- Deactivation was observed after each batch in the in-situ configuration and not in ex-situ.
- Filtration in the ex-situ configuration likely removed alkali metals
- This results show that catalyst fouling will be reduced using using filtration and will favor ex-situ CFP



Hydrocarbon Yields
In-situ

Catalyst deactivation



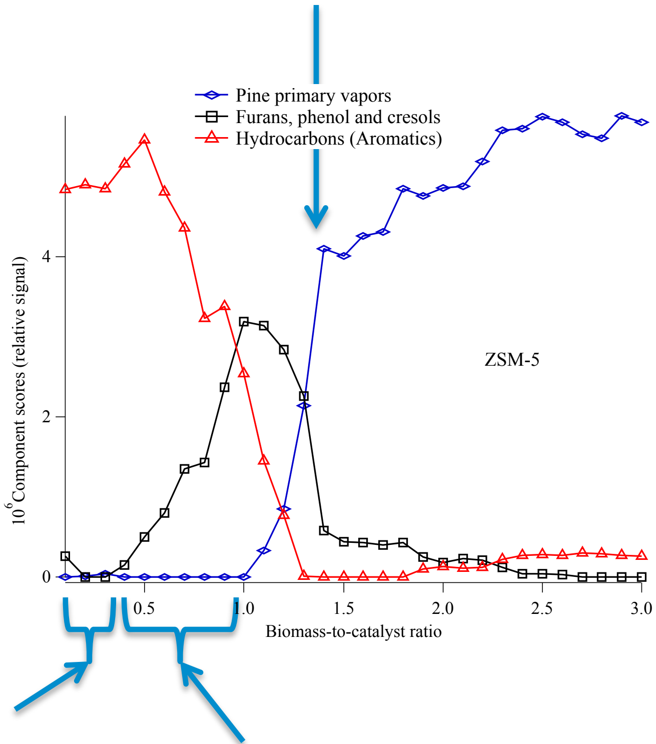
Hydrocarbon Yields
Ex-situ

Kristiina Iisa, Rick French, “Compare in situ and ex situ catalytic pyrolysis at the bench scale. Measure yield, product composition, deactivation and coke/char formation”, NREL Milestone Report, June 30, 2014

Catalyst Deactivation Suggests Reactor Configuration

- Upgrade vapors over HZSM-5
- Fixed bed, sequential addition of biomass pyrolysis vapors
- Monitor products with MBMS
  - Add pulses of pyrolysis vapors
  - Monitor chemical composition of vapors as catalyst deactivates
- Confirmed with pyroprobe GC/MS
- Short reaction time, low biomass-to-catalyst ratio optimal for hydrocarbon production
- Suggests that reactors with tightly controlled biomass/catalyst contact are desirable
  - Risers
  - Entrained flow
  - Continuous catalyst replacement

Catalyst Deactivation



no oxygenates

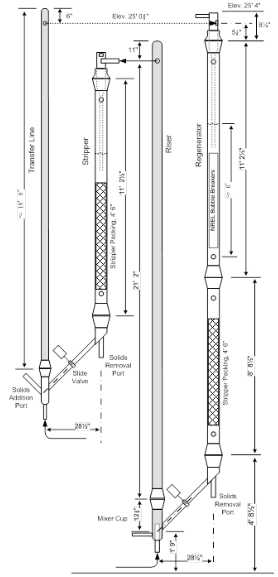
active catalyst

Mukarakate, C., et al. (2014). Real-time monitoring of the deactivation of HZSM-5 during upgrading of pine pyrolysis vapors. *Green Chemistry*, *16*(3), 1444–1461.

Riser Reactors Are Well-Suited for CFP

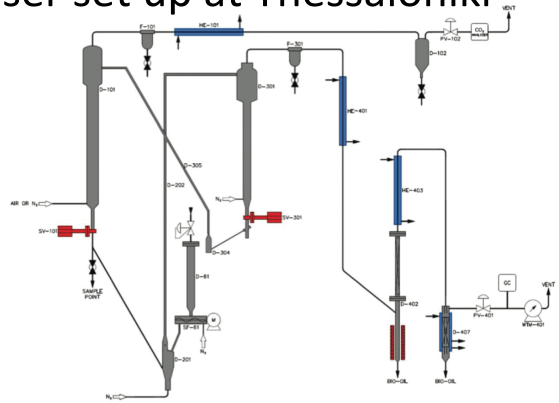
- Findings from laboratory studies suggest that riser reactors are ideal for CFP
- Davison Circulating Riser (DCR) Reactor and riser in TCPDU will be used for larger scale experiments
- Our lab results suggest reaction conditions and residence time required to optimize reactors
- Riser experiments conducted at Aristotle University of Thessaloniki (Greece)* obtained high C yields (34%) with low oxygen content (11%)
- Our results explain the high yields for this experiment and indicate that technical targets are achievable.

NREL's pilot riser reactor



NREL's DCR riser system

Riser set up at Thessaloniki

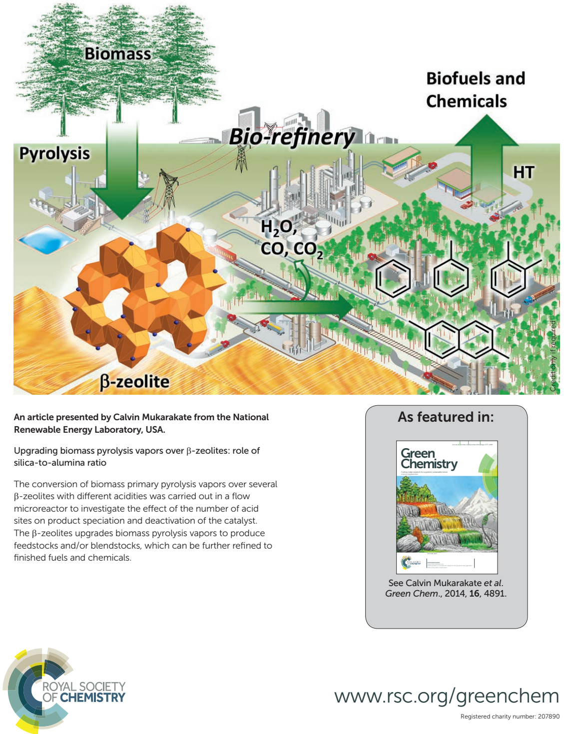


*Iliopoulou, E. F., et al. (2014). *Green Chemistry*, *16*(2), 662–674.

The Effects of Catalyst Acidity on Yields

- Measured deactivation of β-zeolite with different numbers of acid sites
- Determine yields and coke rates
- Hydrocarbon yield increases with number of acid sites
- Provide design criteria for our catalyst partner: Johnson Matthey

Featured on back cover of Green Chemistry



An article presented by Calvin Mukarakate from the National Renewable Energy Laboratory, USA.

Upgrading biomass pyrolysis vapors over β-zeolites: role of silica-to-alumina ratio

The conversion of biomass primary pyrolysis vapors over several β-zeolites with different acidities was carried out in a flow microreactor to investigate the effect of the number of acid sites on product speciation and deactivation of the catalyst. The β-zeolites upgrades biomass pyrolysis vapors to produce feedstocks and/or blendstocks, which can be further refined to finished fuels and chemicals.

As featured in:

Green Chemistry

See Calvin Mukarakate *et al.* *Green Chem.*, 2014, **16**, 4891.

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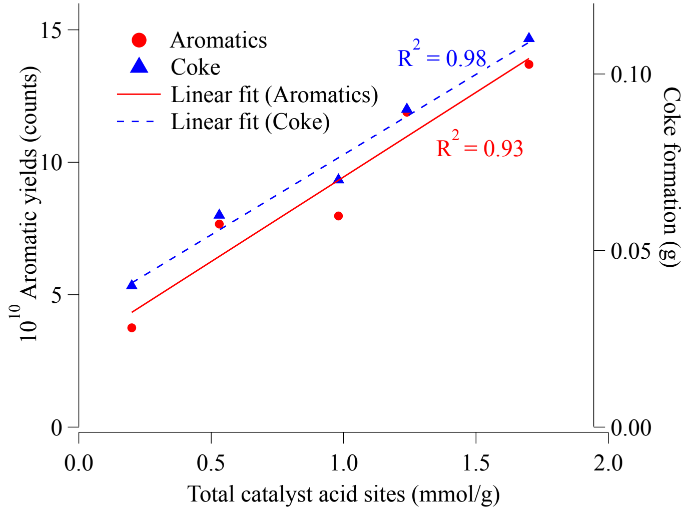
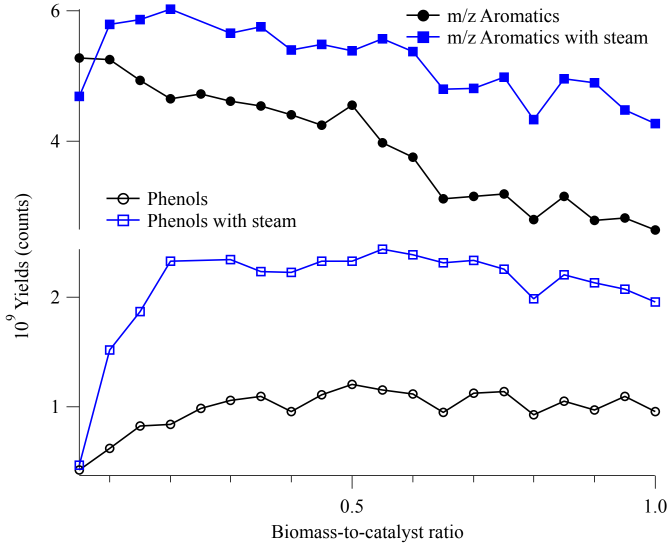
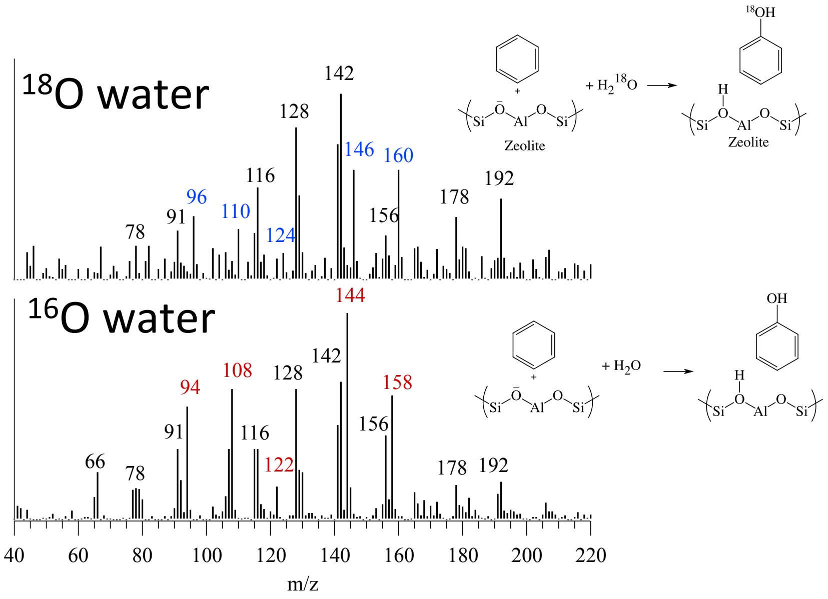


Calvin Mukarakate, et al. *Green Chemistry*, *16*, 4891–4905.

Steam Stripping Increases Carbon Yield

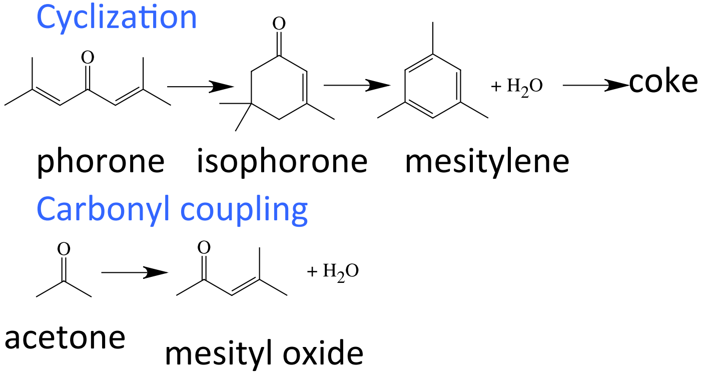
- Addition of steam strips additional product out of ZSM-5 catalyst
- Measurements at lab scale
  - Increased yields (20%)
  - Decreased in Coke (20%)
  - Water reacts with aromatic carbocations to from phenols
  - Manuscript is being prepared for publication
- Steam stripping commonly used in riser systems
- Working with Johnson Matthey to address catalysts stability in steam



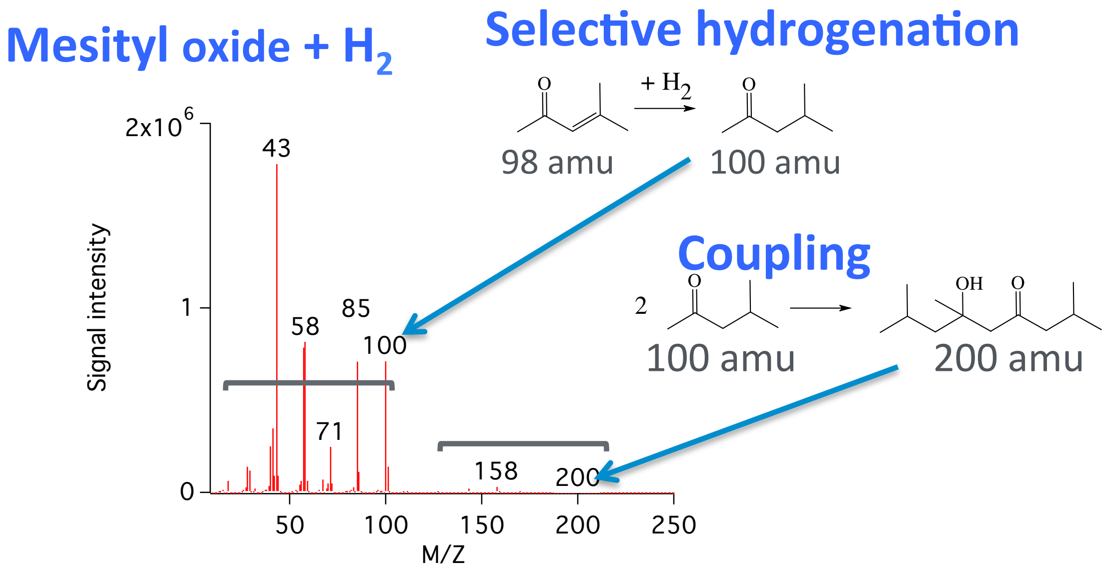


Selective Hydrogenation of C=C Bonds Will Increase C Yields

- Cyclization reactions of C=C bonds are undesirable because they lead to the aromatics and coke
- Carbonyl coupling reactions are desirable because they lead to carbon chain growth and reduce the formation of light gas (CO)
- Selective hydrogenation of C=C bonds with coupling of carbonyls will reduce coke and light gas formation and increase C yield



Catalyst Development for FY2022 Targets



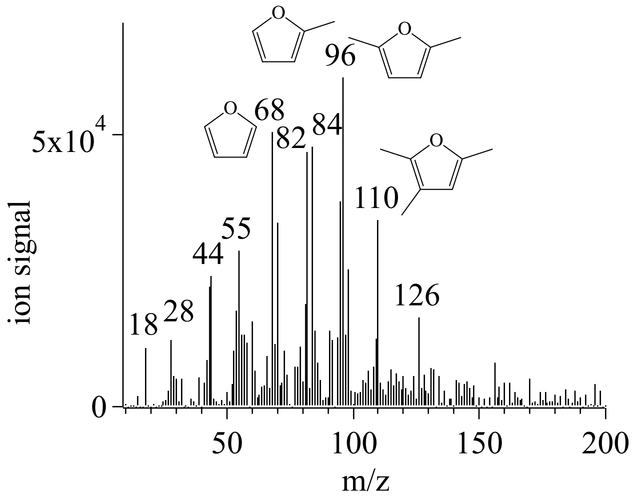
Showed that with selective hydrogenation we can reduce aromatic formation and still allow carbonyl coupling

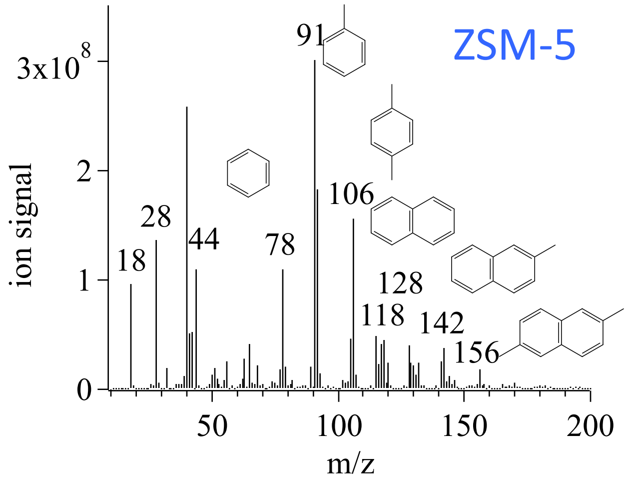
Catalyst Testing for Alternative Products

- Working with Johnson Matthey to test catalysts for products other than aromatic molecules
- Tested several catalysts (zeolites, hydrotalcites, alumina silicates)
- Some catalysts produce furans
- Producing products other than aromatic molecules could cut off pathways to coke formation and lead to products that can be coupled to form diesel-range molecules

Addressing FY2022 Targets

Products from Upgrading with Amorphous Silica Alumina




ZSM-5

4 - Relevance

BETO Barriers:

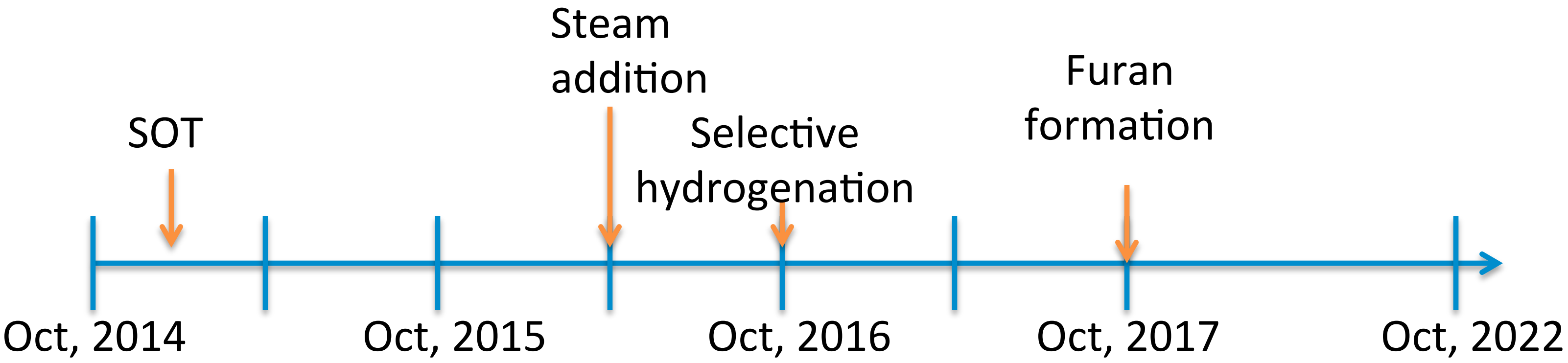
- **Tt-H. Bio-Oil Intermediate Stabilization and Vapor Cleanup**
  - Provided data for SOT for MYPP (C yields, O Content, coke formation, light gas, aqueous carbon)
  - Helping reach FY2022 cost target ($3.31 GGE) through increase C yield and reduced O content
  - Reported limits of Biomass-to-Catalyst ratios
  - Demonstrate steam stripping
  - Fouling of catalysts in *in-situ* operation, hot gas filtration reduces problem
  - Measuring benefits of added hydrogen
  - We provide information about reaction mechanisms that enable strategies to improve catalysts
- **Tt-L. Knowledge Gaps in Chemical Processes**
  - Scientific underpinning allow quicker development of technology
  - Providing information for design of new catalysts to catalyst providers

5. Future Work

- **FY2017 Targets:**
  - Go/NoGo decision for use of steam

Determine whether to continue with research into steam stripping and hot gas filtration for improving yields and cost of vapor phase upgrading. The basis for the Go/No Go will depend upon economic calculations (by WBS 2.8.2.1) using data generated in this project and the metric will be whether or not the cost of the product is reduced. ***3/30/2016***

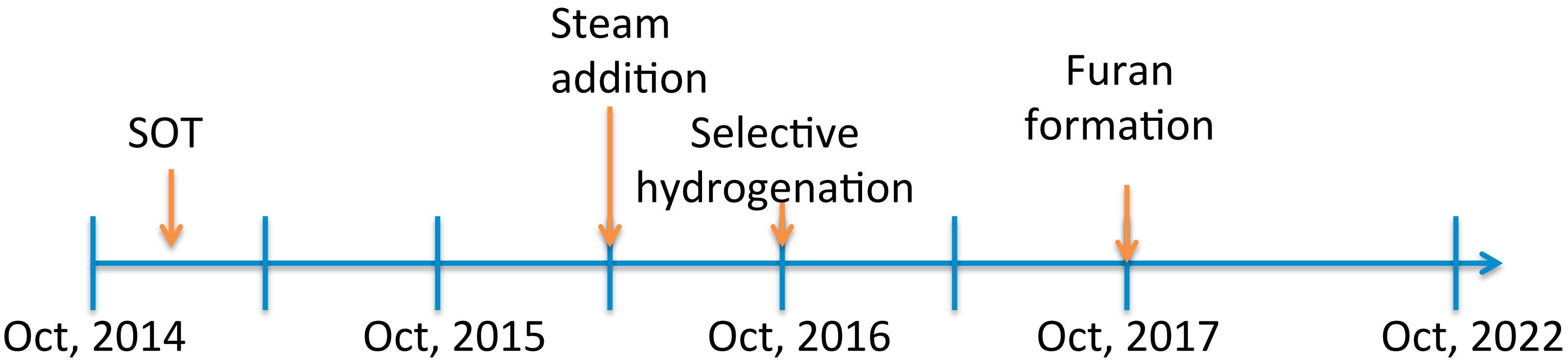
  - Conduct measurements with Laminar Entrained Flow Reactor. Determine if FY2017 C Yield and oxygen content targets can be met.
  - Continue to study the effects of added hydrogen (< 5 bar). Determine increases in yield and decreases in coking.
- **Work with Johnson Matthey to select catalyst to scale up for experiments in DCR and pilot plant**



5. Future Work (cont)

FY2022 Targets:

- **Select bifunctional catalyst that can selectively hydrogenate olefines and allow C-C coupling of carbonyl compounds**
  - Use computational modeling (Computational Pyrolysis Consortium) to help identify low cost catalysts, with high efficiency hydrogenation and C-C coupling
- **Select catalysts that produce furans in high yields**
  - Determine yields and coking and light gas formation



SOT

Steam addition

Selective hydrogenation

Furan formation

Oct, 2014

Oct, 2015

Oct, 2016

Oct, 2017

Oct, 2022

Summary

- Helping reach technical targets (increase C yield to 44% decrease O content to 6% by 2022) for CFP by increasing our understanding of chemical reaction mechanisms
- Conducting laboratory experiments in collaboration with computational modeling to explore mechanisms, effects of catalyst composition and reactor conditions
- Produced results that help establish SOT, compared in-situ to ex-situ, establish operating ranges, compare catalyst acidity, increased yields with steam and hydrogen, and different reaction pathways with other catalysts.

Additional Slides

Publications

1. Biomass Particle Models with Realistic Morphology and Resolved Microstructure for Simulations of Intraparticle Transport Phenomena, Ciesielski, P. N., Crowley, M. F., Nimlos, M. R., Sanders, A. W., Wiggins, G. M., Robichaud, D., et al. (2015) *Energy & Fuels*, *29*(1), 242–254.
2. Bimolecular Decomposition Pathways for Carboxylic Acids of Relevance to Biofuels, Jared M. Clark, Mark R. Nimlos, and David J. Robichaud, *J. Phys. Chem. A*, Articles ASAP, December 16, 2014, DOI: 10.1021/jp509285n
3. Pyrolysis of Cyclopentadienone: Mechanistic Insights from a Direct Measurement of Product Branching RatiosThomas K. Ormond, Adam M. Scheer, Mark R. Nimlos, David J. Robichaud, Tyler P. Troy, Musahid Ahmed, John W. Daily, Thanh Lam Nguyen, John F. Stanton, and G. Barney Ellison, *J. Phys. Chem. A*, Articles ASAP, January 15, 2015, DOI: 10.1021/jp511390f
4. Synthesis and Characterization of Molybdenum Incorporated Mesoporous Silica Catalyst for production of bio-fuels and value added chemical, Sridhar Budhi, Calvin Mukarakate, Peter Ciesielski, Mark Nimlos and Brian Trewy, Green Chemistry, In Press.
5. An Experimental Study of the Thermal Decomposition of the Benzyl Radical in a Heated Micro-Reactor, Grant T. Buckingham, Thomas K. Ormond, Jessica P. Porterfield, Patrick Hemberger, Oleg Kostko, Musahid Ahmed, David J. Robichaud, Mark R. Nimlos, John C. Daily, G. Barney Ellison, J. Chem. Phys., In Press.
6. Upgrading biomass pyrolysis vapors over β-zeolites: role of silica-to-alumina ratio, Calvin Mukarakate, a Michael J. Watson, Jeroen ten Dam, Xavier Baucherel, Sridhar Budhi, Matthew M. Yung, Haoxi Ben, Kristiina Iisa, Robert M. Baldwin and Mark R. Nimlos (2014). *Green Chemistry*, *16*, 4891–4905.
7. Comparison of Unimolecular Decomposition Pathways for Carboxylic Acids of Relevance to Biofuels, Clark, J. M., Nimlos, M. R., & Robichaud, D. J. (2014) *Journal of Physical Chemistry A*, *118*(1), 260–274.
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2. Iisa, K., Stanton, A., Baer, A., French, R., Czernik, S. C. Mukarakate, B. Evans, Light Hydrocarbons as Hydrogen Transfer Agents for Catalytic Pyrolysis, Oral presentation TCBiomass 2013, Chicago, IL, September 3-6, 2013.
3. Abhijit Dutta, Michael Talmadge, Stefan Czernik, Calvin Mukarakate;TCBiomass 2013 at Chicago, IL. Process considerations for the feasibility of upgrading vapors from the fast pyrolysis of biomass to benefit downstream products, TCBiomass 2013, Chicago, IL, September 3-6, 2013.
4. Mark Nimlos, Improvements in Vapor Phase Upgrading of Biomass Pyrolysis Vapors, TCBiomass 2013, Chicago, IL, September 3-6, 2013.
5. Calvin Mukarakate, Xiaodong Zhang, David Robichaud and Mark Nimlos. Effects of Hot Gas Filtration on HZSM-5 during Ex-situ Catalytic Fast Pyrolysis of Biomass, 246th ACS meeting in Indianapolis, IN, September 8 -12, 2013.
6. Sridhar Budhi, Calvin Mukarakate, Mark Nimlos and Brian Trewyn, Catalytic Fast Pyrolysis of Biomass Using Molybdenum Supported in 3-D Mesoporous Silica Catalyst, 246th ACS meeting in Indianapolis, IN, September 8 -12, 2013.
7. David Robichaud, Mark Nimlos, Calvin Mukarakate, Bryan Donohoe, Kristiina Iisa, and Gregg Beckham, Catalytic fast pyrolysis for the production of hydrocarbon biofuels, 246th ACS meeting in Indianapolis, IN, September 8 -12, 2013.
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12. Sridhar Budhi, Calvin Mukarakate Mark R. Nimlos and Brian Trewyn, Catalytic fast pyrolysis of biomass using molybdenum supported in mesoporous silica; effect of pore structure on catalyst activity, ACS National Meeting in Dallas, TX, March 16-20, 2014.
13. Mark R. Nimlos, Calvin Mukarakate, David J. Robichaud and Robert J. Evans, Steam stripping during upgrading of biomass Pyrolysis vapors, ACS National Meeting in Dallas, TX, March 16-20, 2014.
14. Mark R. Nimlos, Calvin Mukarakate, David J. Robichaud, Kristiina Iisa, Robert M. Baldwin,, "Laboratory Studies of Upgrading of Biomass Pyrolysis Vapors", EU BC&E 2014, Hamburg, Germany, June 26, 2014
15. Mark R. Nimlos, "Upgrading of Biomass Pyrolysis Vapors", CNRS, Nancy, France, June 18, 2014.
16. Kristiina Iisa, Alexander R. Stanton, Richard J. French, Mark R. Nimlos, Catalyst Deactivation in *Ex Situ* and *In Situ* Catalytic Pyrolysis of Biomass, *Preprints, 248th American Chemical Society National Meeting & Exposition*, San Francisco, CA, August 10-14, 2014.
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