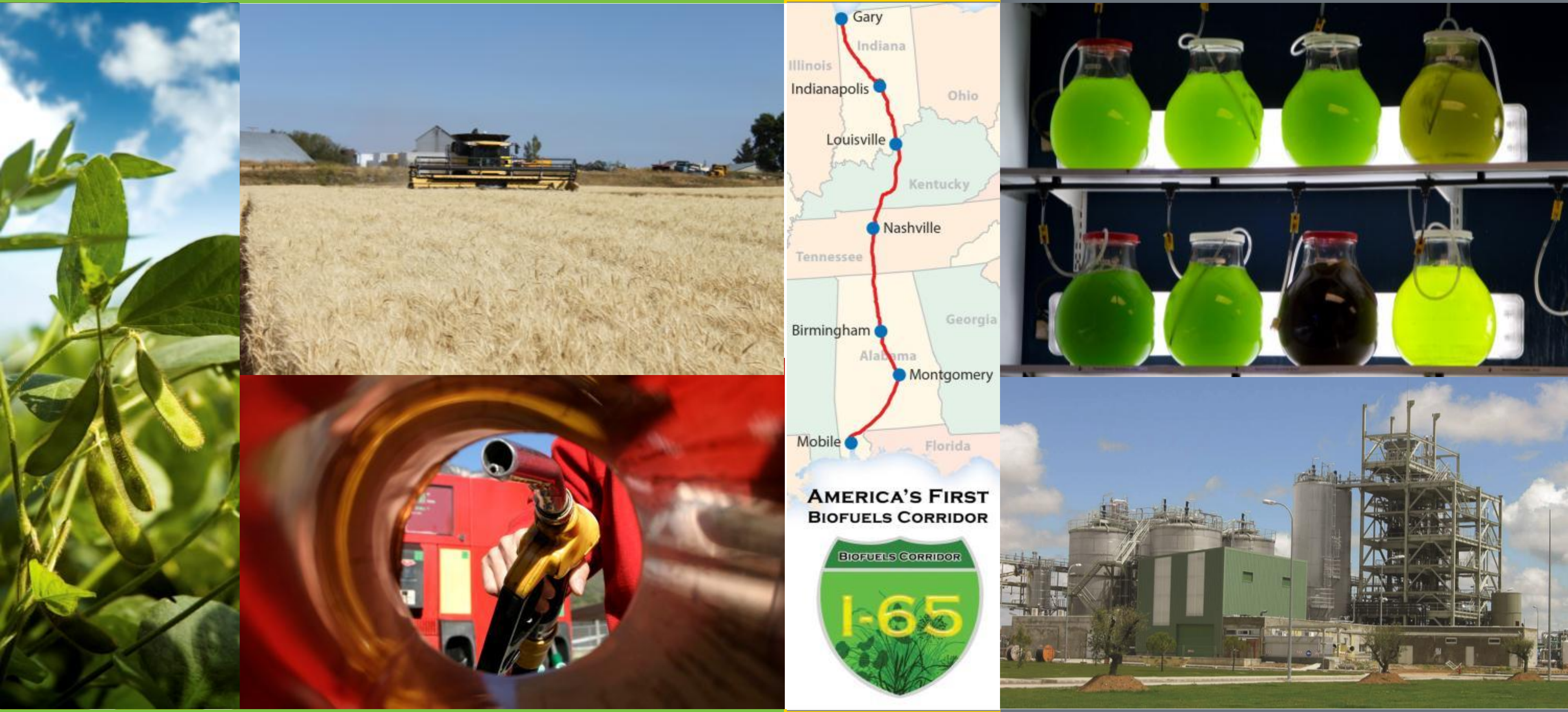
2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

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



3.1.1.14 - Biomass Deconstruction: Catalyst Development and Testing

May 22, 2013

Kim Magrini

Goal/Objectives

- ***Program mission:*** *Develop and transform our 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 catalysts for economical, efficient deconstruction of biomass into stable intermediates suitable for further upgrading or blending into petroleum feedstocks

- **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)

Project Quad Chart Overview

Timeline

- Project start date: 10/2012
- Project end date: 9/2022
- Percent complete: 6%

Barriers

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

Budget

- Total project funding: $2M
- Funding received in FY 2011: $0M
- Funding in FY 2012: $0M
- Funding in FY 2013: $2M
- ARRA Funding: $0M
- Years the project has been funded & average annual funding: 1y at $2M

Partners & Roles

- NREL: catalyst development, evaluation and characterization
- Johnson Matthey: VPU catalyst development
- NexCeris – modified catalyst preparation
- CoorsTek – fluidizable catalyst development

Task Structure

Catalytic Pyrolysis Sciences

Mark Nimlos

Catalyst Development/Testing
Deconstruction

Kim Magrini

Catalyst Development/Testing
Upgrading

Jesse Hensley

Engineering Integration and Scale-up

Esther Wilcox

Work Flow

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

- Catalyst development (existing and emerging)
- Catalyst characterization
- Catalyst regeneration
- Catalyst preparation (kg)
- Commission and run ACE and DCR systems

- Pilot modifications
- Product fractionation
- Pilot scale runs
- Hot gas filtration

Scale

mg-g **g-kg** **100’s kg**

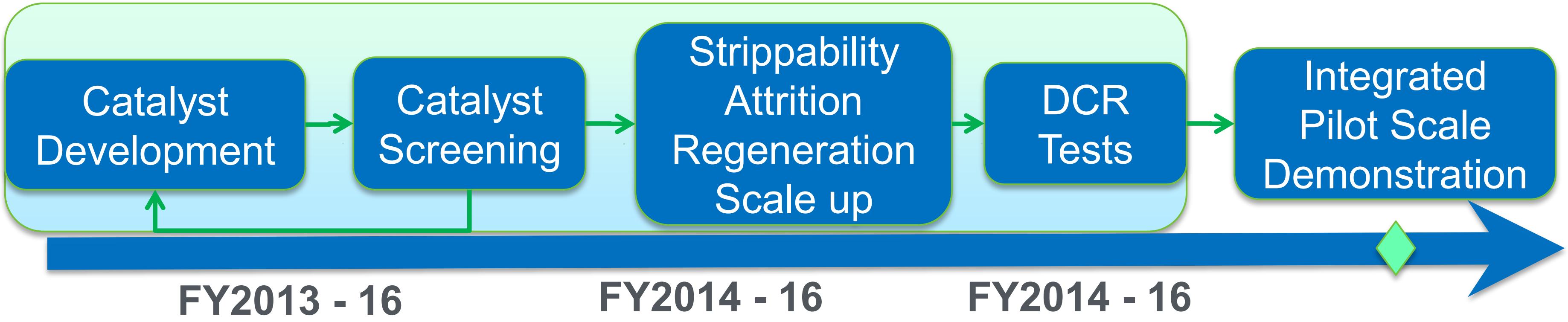
Synergistic Activities:

Catalyst development
Hydrogen donor molecules
Hot gas filtration
Reaction kinetics

Analytical tool development
Reactor design
Product characterization
TEA

1 - Approach

Goal: Demonstrate $3/gal renewable fuel



Catalyst Development → Catalyst Screening → Strippability Attrition Regeneration Scale up → DCR Tests → Integrated Pilot Scale Demonstration

FY2013 - 16

FY2014 - 16

FY2014 - 16

Supporting Activities:

- Techno-economic Analysis (TEA)
- Catalyst Science
- Feedstock Modification
- Johnson Matthey CRADA
- 2D GCMS oil analysis

1 – Approach

Task Structure

1a) Pyrolysis reactors modification

1b) Johnson Matthey catalyst evaluation

1c) Chemical effects of biomass vapor/oil phase transition

1d) Characterize and correlate catalyst structure and reactivity

1e) Catalyst development for targeted biomass deconstruction

1f) Impact of pressure on pyrolysis intermediate upgrading

2 – Progress

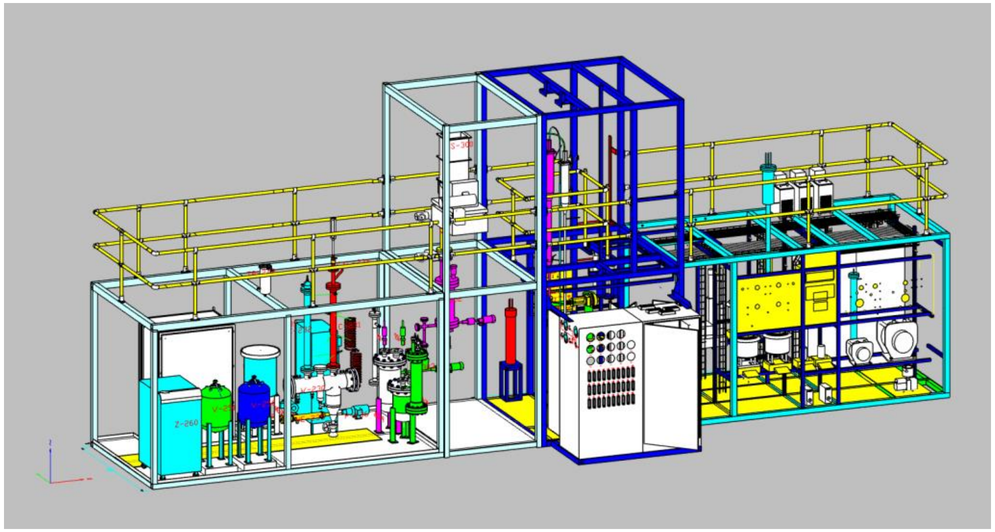
Pyrolysis reactors

Jablonski and Magrini

Vapor Phase Upgrading for FCC-type processing

- Capability: Davison Circulating Reactor (DCR)
- Advantage: Continuous coke removal to keep catalyst active
- Description: Pyrolysis liquids and vapors fed to continuously circulating catalyst for linear hydrocarbon production with no added hydrogen or preliminary deoxygenation

DCR pilot unit



NREL DCR pilot unit schematic

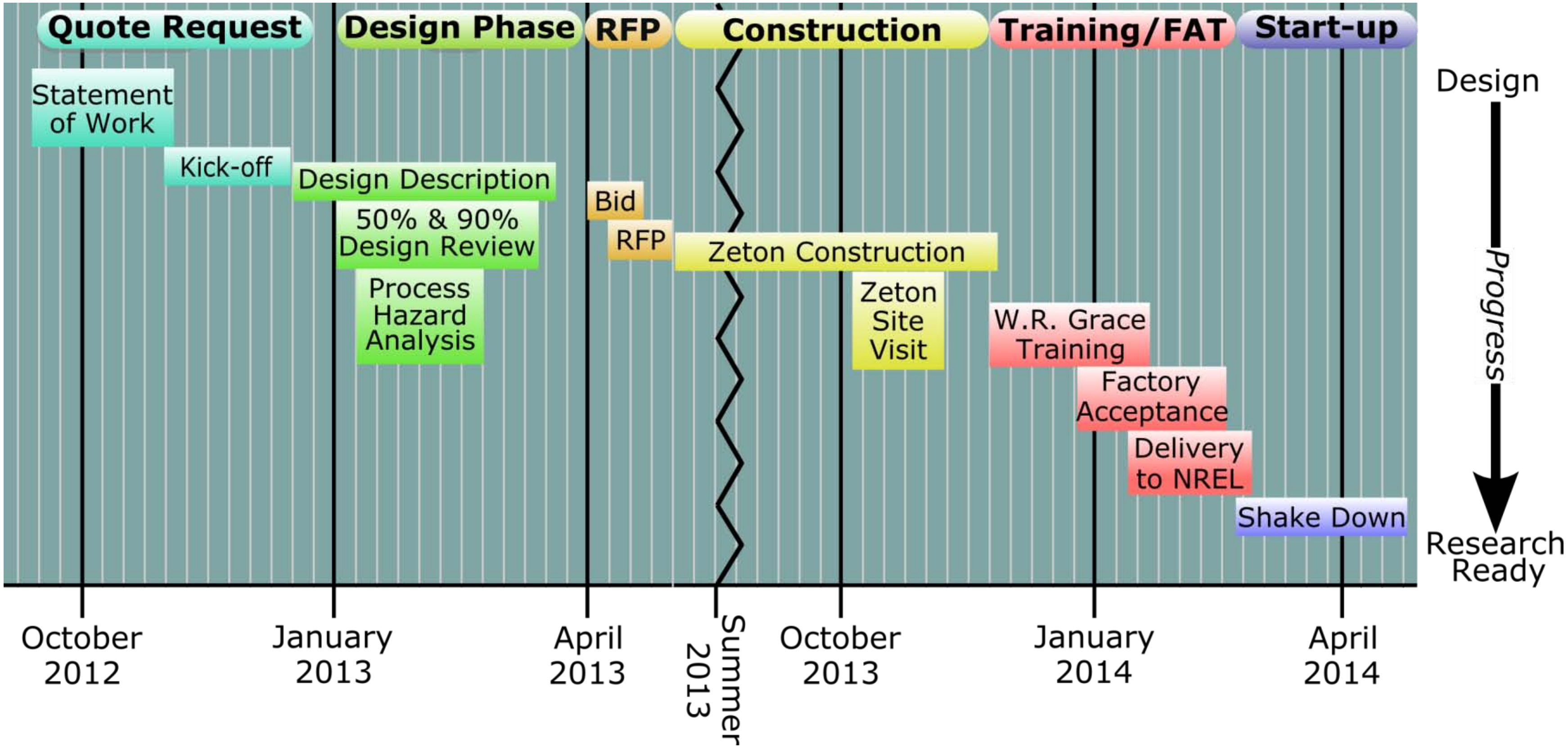
2 – Progress

Pyrolysis reactors

Jablonski and Magrini

Pyrolyzer-DCR Design Complete

- Catalyst Development: Small pilot scale FCC catalyst screening for DCR
- Py-DCR Operation: Develop methods for feeding pyrolysis oil, biomass, *and* cracking pyrolysis vapors (DCR can do both)



2- Progress

Pyrolysis reactors

Lab Scale Catalyst Testing and Screening – ACE (Advanced Cracking Evaluation) Unit

Research Applications:

- Screen catalysts for DCR use
- Measure coke yields
- Define process parameters
- Kinetic model development
- Variable riser residence time - mimics short contact time FCC
- Catalyst strippability (rate of HC removal from catalyst)
- Catalyst regeneration measurements

- Attrition test unit – catalyst DI (Davison Index)

Laboratory scale reactor to evaluate catalyst performance and regenerability

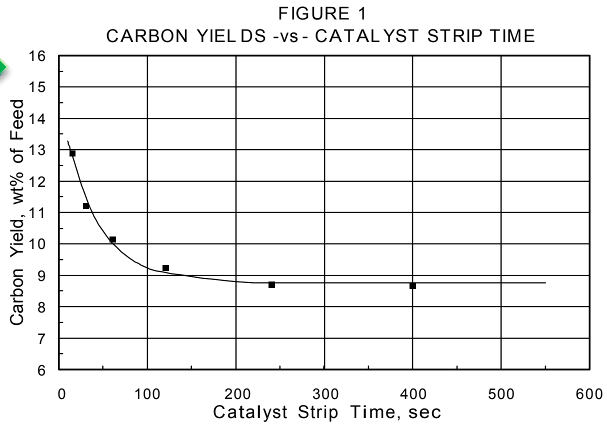
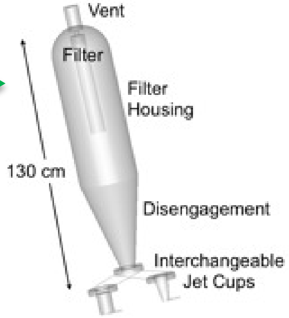


FIGURE 1
CARBON YIELDS -vs- CATALYST STRIP TIME



www.kaysertech.com

Jablonski and Magrini

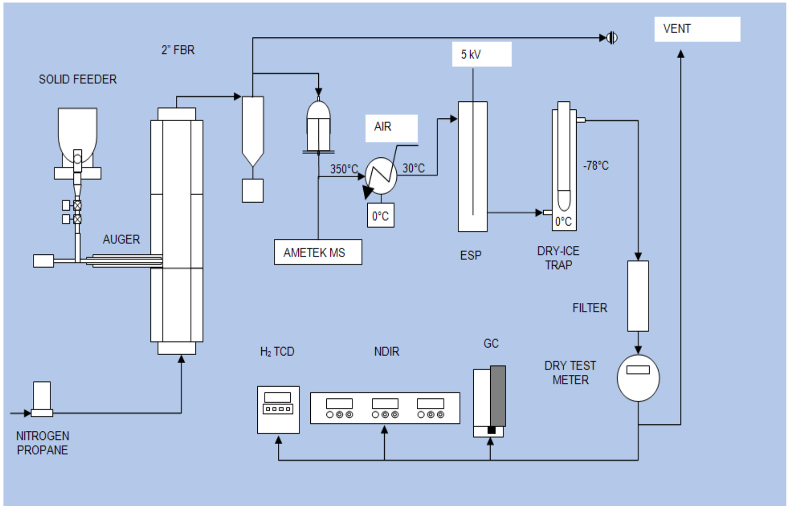
2 – Progress

Vapor oil transition

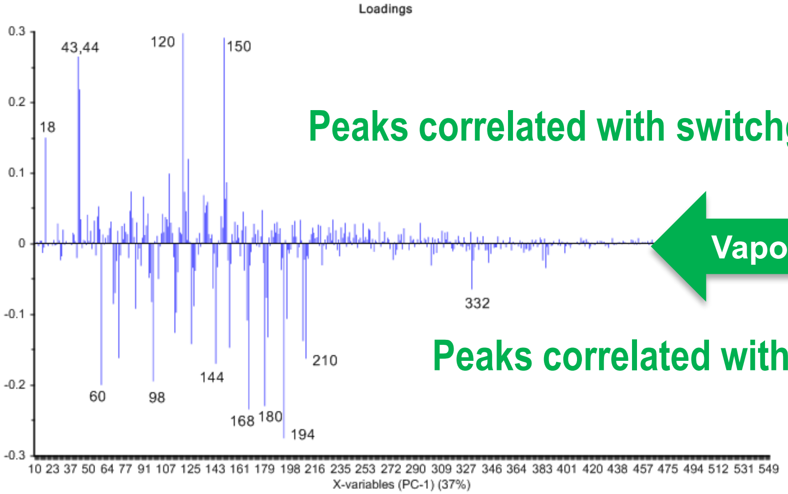
Development of feedstock/vapor/oil correlations

Carpenter and Deutch

- Can high throughput py-MBMS screening tie marker compounds in the vapor to desired oil qualities?
- Generate oil with 2” fluid bed reactor
- Analyze by 2D GC
- Conduct multivariate analysis on *very* complex data sets to uncover latent correlations



2” Fluidized Bed Reactor system (~2 kg/day)

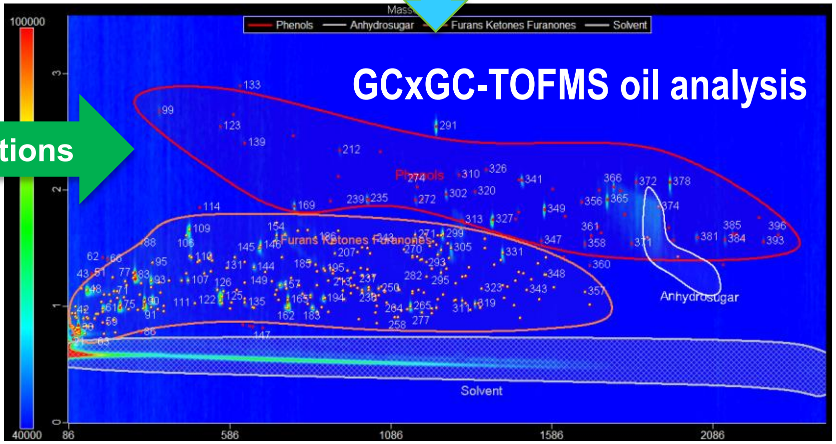


Peaks correlated with switchgrass

Vapor/oil correlations

Peaks correlated with oak

Principal component analysis of py-MBMS data



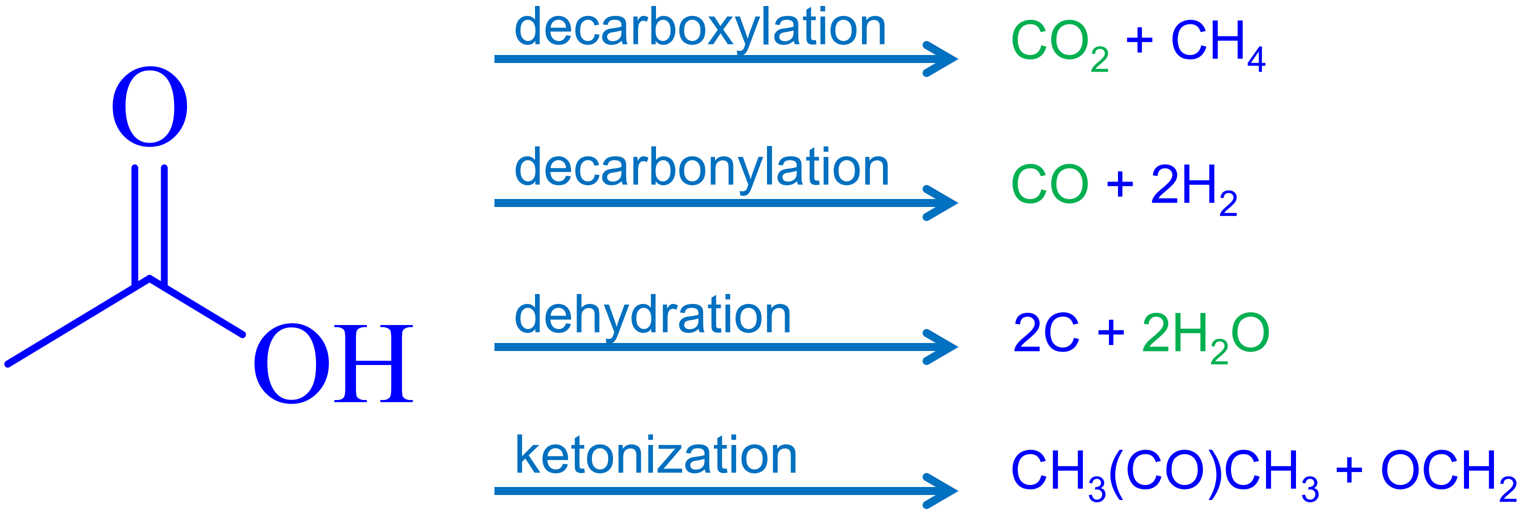
GCxGC-TOFMS oil analysis

2 – Progress

Catalyst structure/activity correlations

M. Yung

- Evaluate how catalyst composition affects reactivity for various oxygen functional groups
- Use carboxylic acids (acetic acid) as a probe molecule due to their abundance in bio-oil



$\xrightarrow{\text{decarboxylation}} CO_2 + CH_4$

$\xrightarrow{\text{decarbonylation}} CO + 2H_2$

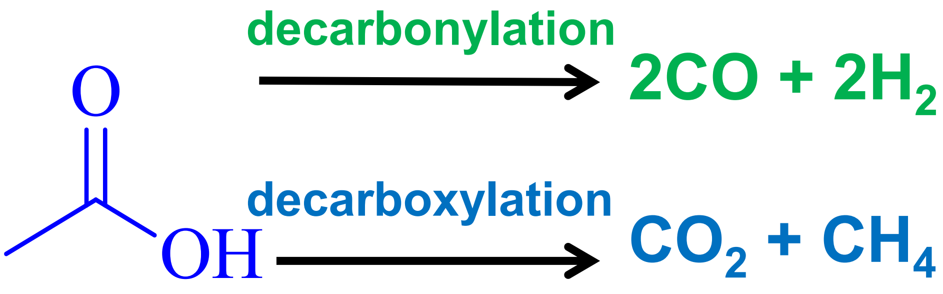
$\xrightarrow{\text{dehydration}} 2C + 2H_2O$

$\xrightarrow{\text{ketonization}} CH_3(CO)CH_3 + OCH_2$

2 – Progress

Catalyst structure/activity correlations

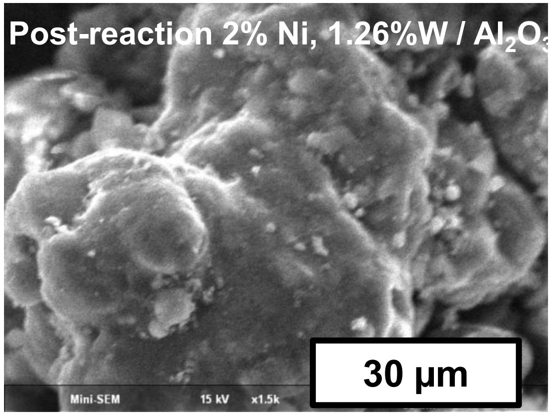
M. Yung



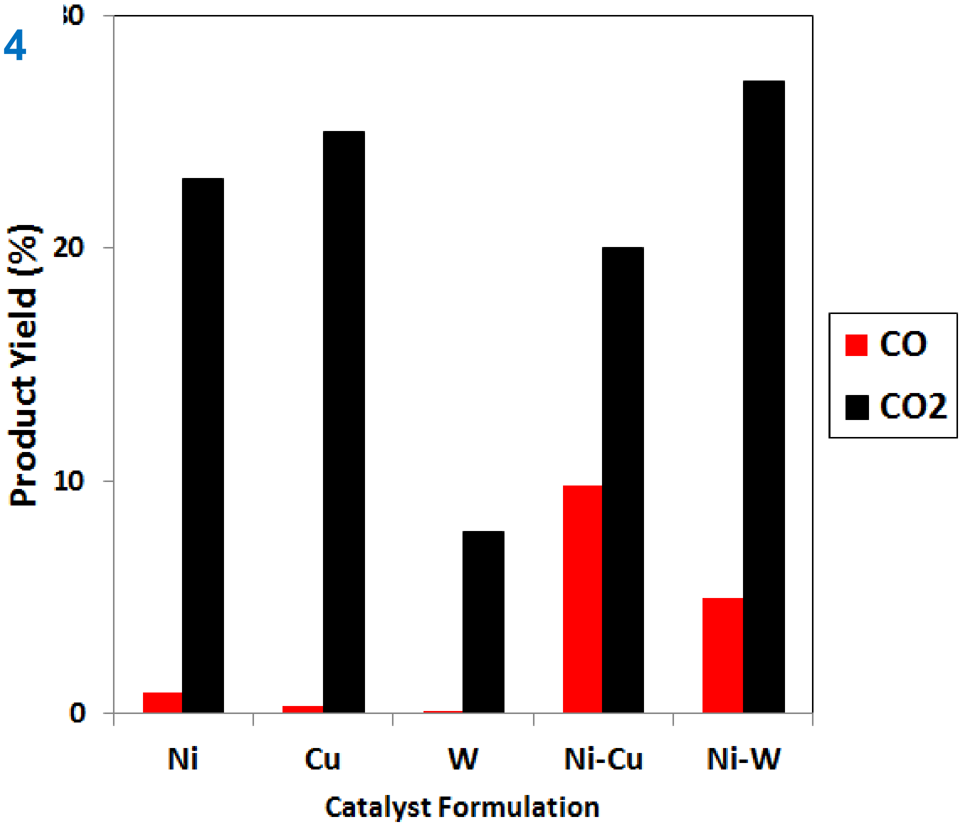
decarbonylation $\rightarrow$ $2CO + 2H_2$

decarboxylation $\rightarrow$ $CO_2 + CH_4$

- Evaluate how catalyst composition affects reactivity for various oxygen functional groups
- Start with carboxylic acids (acetic acid) as a probe molecule



Bimetallic alloying enhances decarbonylation reaction



Product yields during acetic acid deoxygenation. Reaction Conditions: 100mg catalyst, 100 sccm total flow, 5% Ar, 2.3% acetic acid, 92.7% He, 400°C.

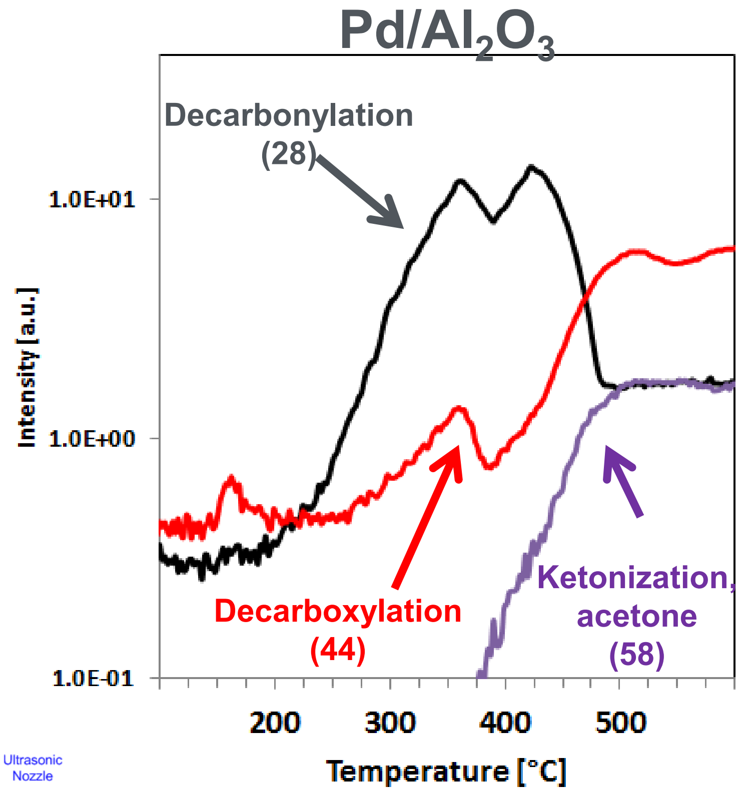
2 – Progress

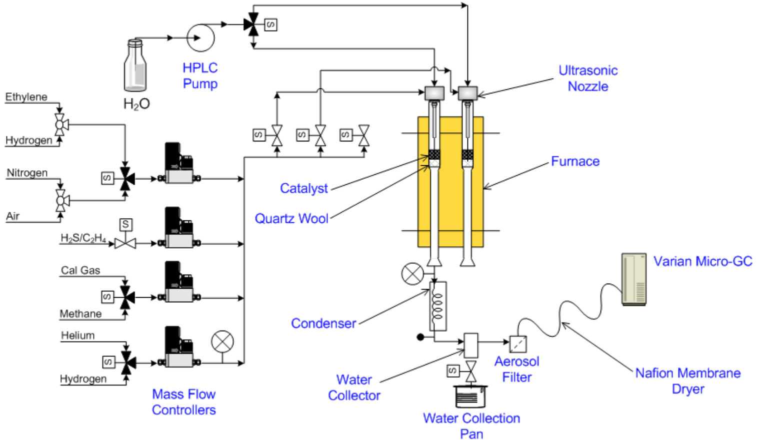
Catalyst structure/activity correlations

- Temperature-programmed reaction is used to determine how kinetics of competing reactions are affected by temperature
- Tested precious metals, transition metals, and bimetallics (Pt, Pd, Rh, Ni, W, Cu, Ni-Cu, Ni-W)

Freshly synthesized catalysts

M. Yung





Catalyst test system

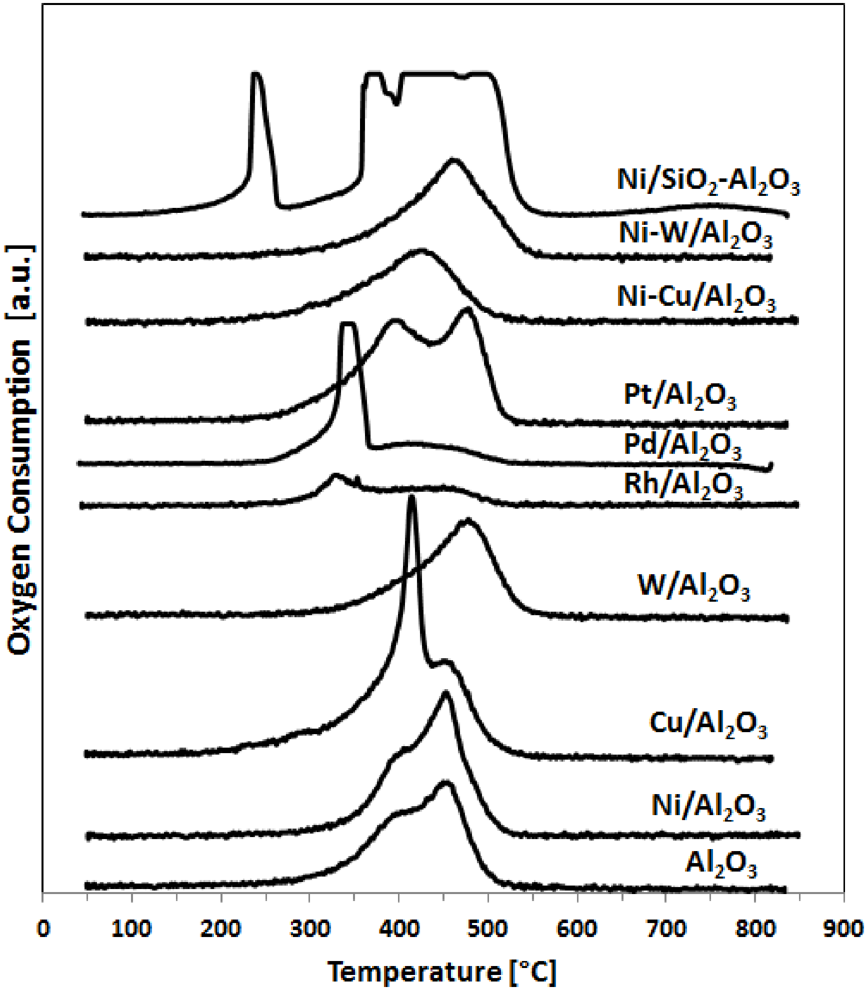
On Pd/Al_2O_3, decarbonylation and decarboxylation are favored over ketonization

2 – Progress

Catalyst structure/activity correlations

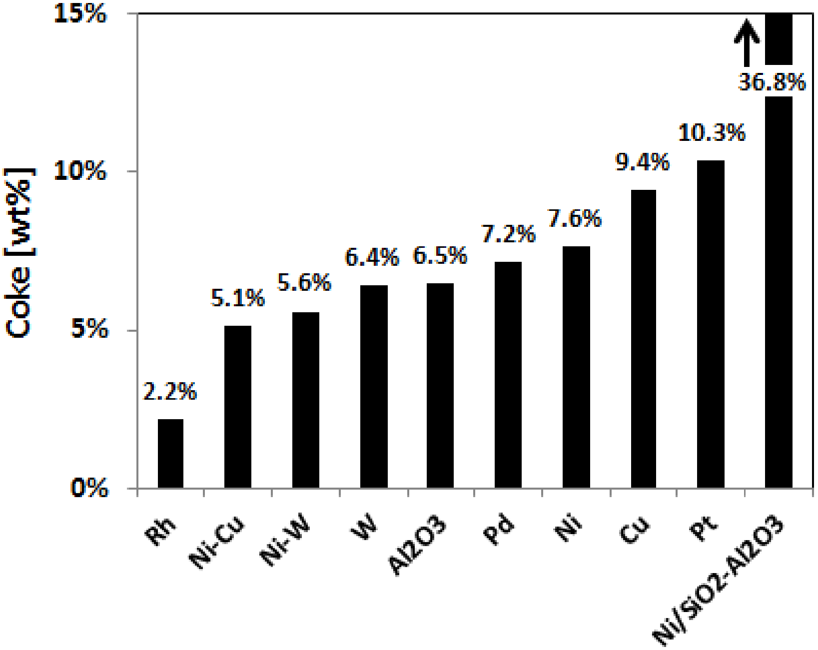
M. Yung

Post-reaction TPO measuring coke burn-off following acetic acid deoxygenation



Coke formation, coke types, and carbon yield during acetic acid deoxygenation depend on catalyst composition

Coke yield based on catalyst composition

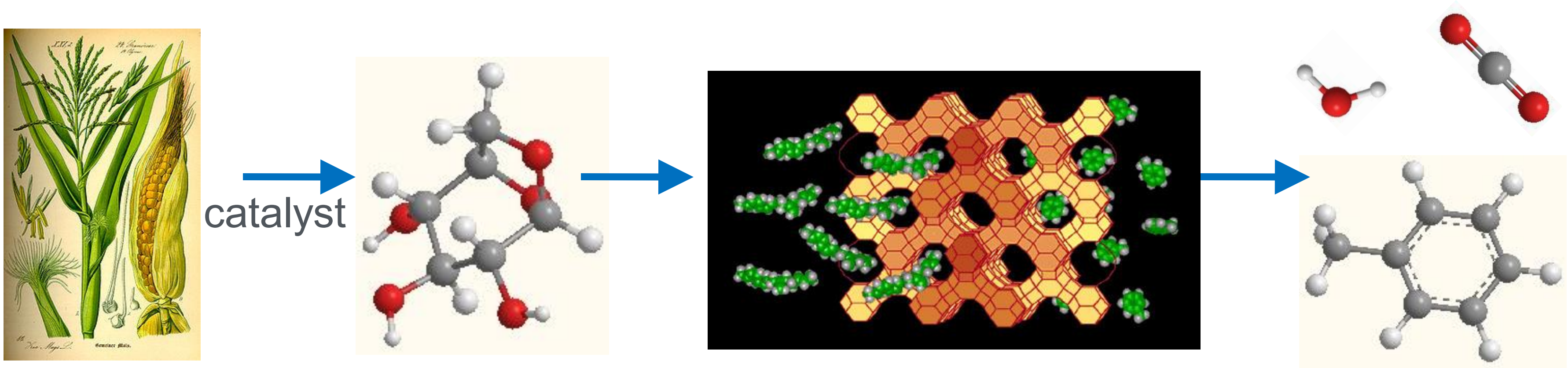


2 – Progress

Deconstruction Catalyst Development

S. Cheah

- Deconstructing biomass while removing oxygen is crucial for producing stable intermediates
- Developing catalysts and process conditions through combination of experimentation and modeling
  - Modeling can help select low cost, high activity catalyst


catalyst

oxygenates

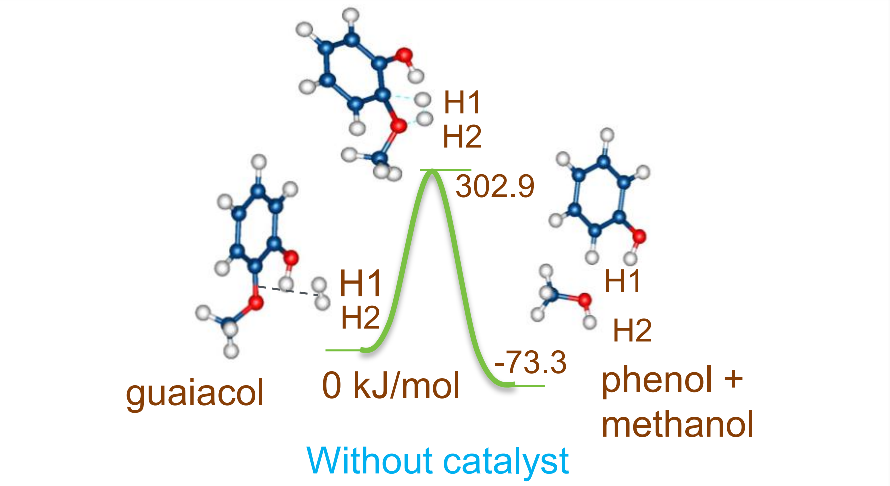
catalyst

hydrocarbon

2 – Progress

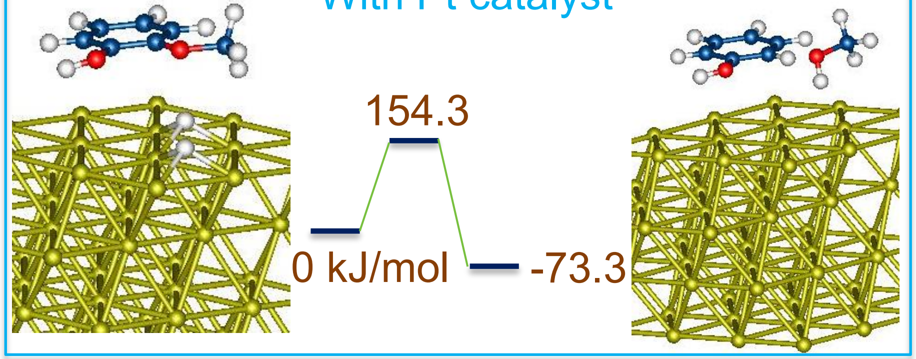
Catalyst structure/activity correlations

- Work with model compounds: bio-oil and monomers derived from lignin.
- Modeled three guaiacol deoxygenation pathways with different H_2 usage, +/- catalyst
- With catalyst, for guaiacol, the pathways and reaction barriers are:
  1. Deoxygenation without H_2: 260 kJ/mol
  2. H_2-aided direct breaking of C-O bond: 150 kJ/mol
  3. Two steps reaction, first with hydrogenation of aromatic ring followed by breaking of C-O bond: 105 kJ/mol
- Currently designing catalysts that favor pathway 2



Similar barrier for guaiacol → anisole + H_2O

With Pt catalyst



S. Cheah

2 – Progress

Catalyst structure/activity correlations

S. Cheah

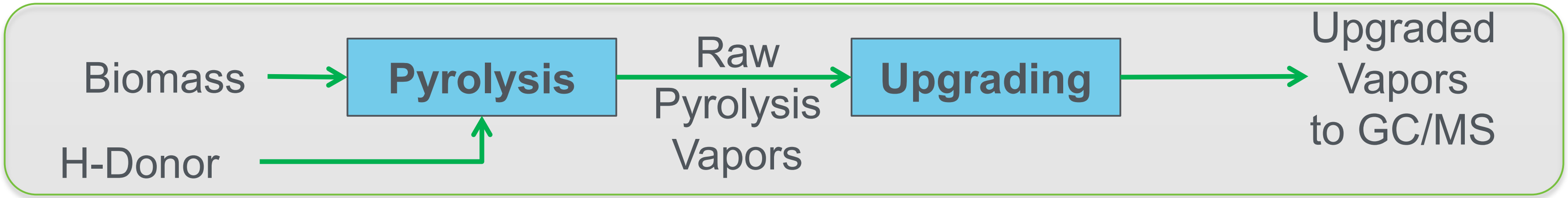
- NREL proprietary catalyst formulation, derived from modeling, that can select reaction, e.g., reaction 2. ROI filed
- Experimental work on the catalyst is in progress
- Next step: study model compounds similar to those from cellulose to determine the impact of different catalysts and H_2 on the deoxygenation kinetics and pathways

2 – Progress

H_2, P Impacts on Catalytic Pyrolysis

K. Iisa

- **Goal: to determine if moderate pressures enhance catalytic pyrolysis in the presence of hydrogen donor molecules.**
  - Biomass has low H:C →coke formation
  - Can be abated by addition of hydrogen or other hydrogen donor molecules
  - Operation at elevated pressures may be required
- **Impact: increase yields by abating coke formation; decrease cost by need for less frequent catalyst regeneration**
- **Future Plans:**
  - FY13: Test impact of moderate pressures (~10 bar) in pyroprobe-GC/MS on presence of H_2 and other H donors
  - Go/no-go decision: Sept. 2013
  - Future years: Optimize conditions; Bench-scale tests



Biomass

H-Donor

Pyrolysis

Raw Pyrolysis Vapors

Upgrading

Upgraded Vapors to GC/MS

2 – Progress

H_2, P Impacts on Catalytic Pyrolysis

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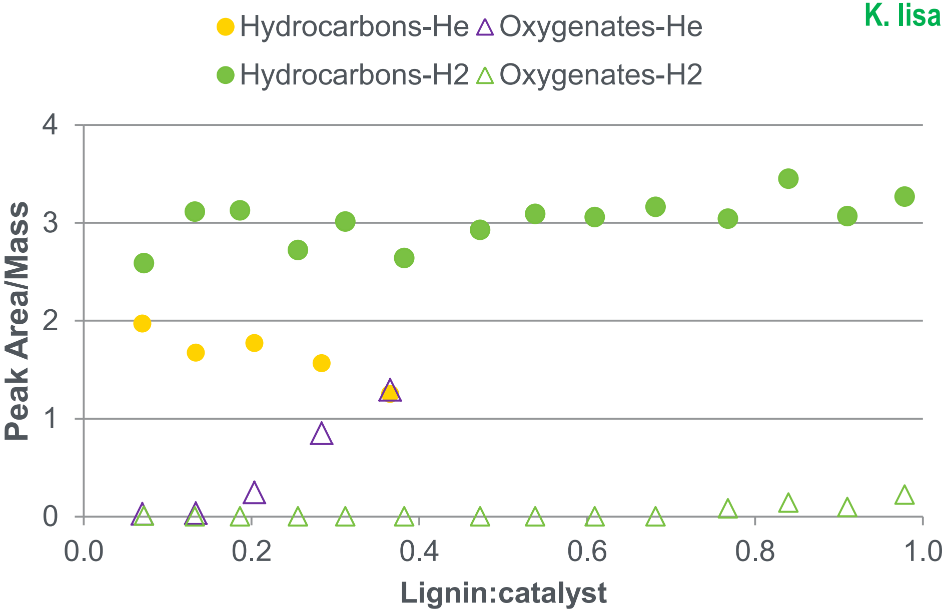
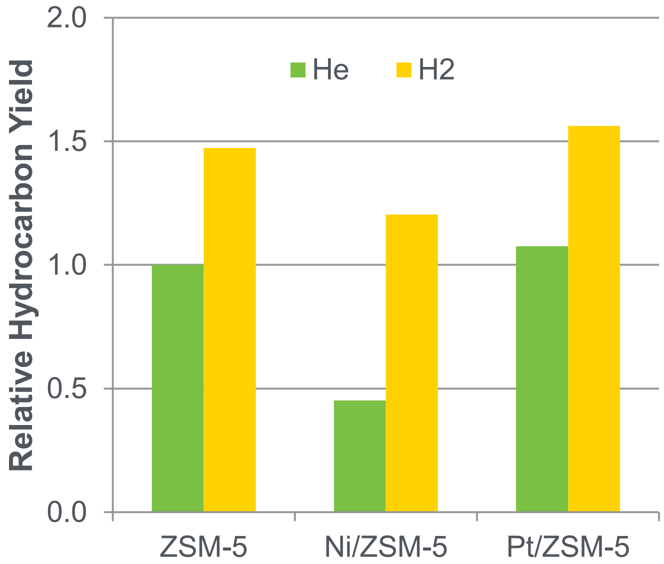
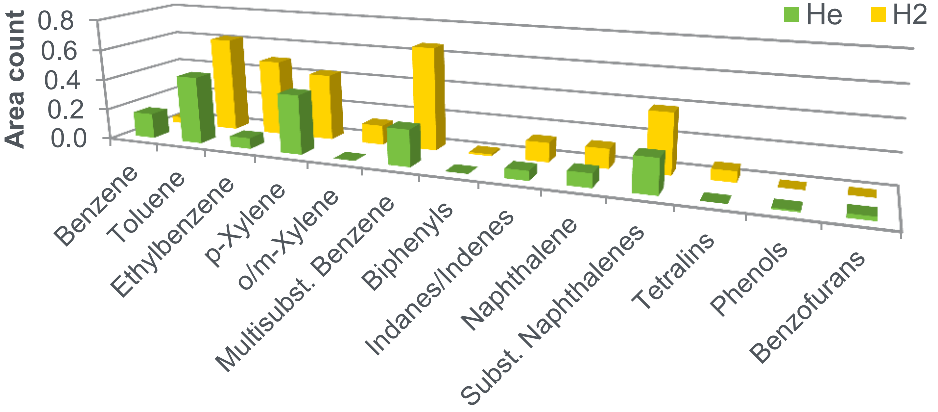
K. Iisa

Hydrogen at moderate pressures

- Delays catalyst deactivation
- Improves hydrocarbon yields
  - Greatest improvement with Ni-modified catalyst
- Changes product composition







Py-GC/MS, 14 bar, pyrolysis 600°C, upgrading 450°C

3 - Relevance

- Project supports the development of catalysts that enable biomass conversion to fungible hydrocarbon bio oils that can contribute towards BETO’s MYPP goal:
  - *Achieve a conversion cost of $3 per gallon of total blendstock via a bio-oil pathway.*

- 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*

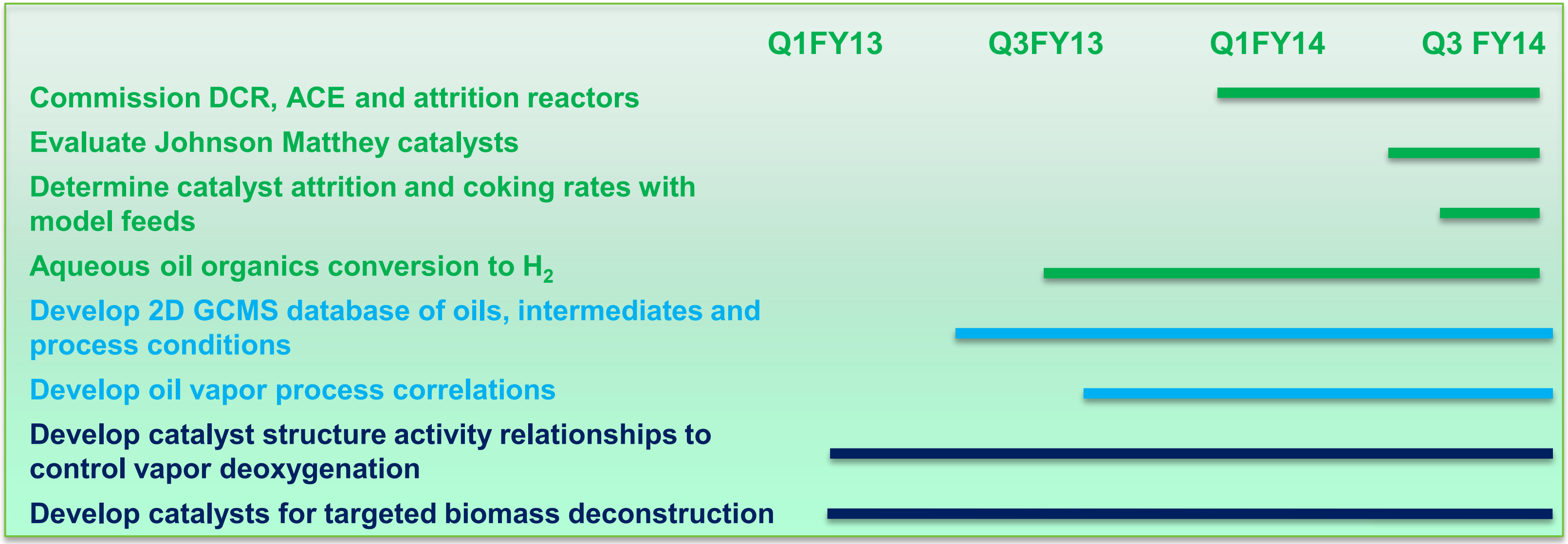
4 - Critical Success Factors

- **Technical**: Develop/identify/evaluate deconstruction and deoxygenation catalysts that are selective for fungible hydrocarbon intermediates at (g-kg scale)
- **Market**: Produce bio-oil or intermediates that can be processed in a conventional refinery with acceptable cost
- **Business**: Technology that is technically and economically superior to other biomass conversion process

- Demonstrate viability of selective catalytic processes to convert biomass to fungible oils
- Develop oil characterization to understand process induced chemical changes
- Successful project could positively impact commercial viability of biomass pyrolysis intermediates for petroleum refining use

5 – Future Work

- Bring the DCR and supporting reactors on-line for evaluating biomass deconstruction and upgrading catalysts
- Continue deconstruction and deoxygenation catalyst development and develop structure activity relationships
- Down select laboratory identified catalysts for steady state performance and regeneration extent
- Continue developing correlations between bio oil production and liquid and vapor phase chemistry



Commission DCR, ACE and attrition reactors

Evaluate Johnson Matthey catalysts

Determine catalyst attrition and coking rates with model feeds

Aqueous oil organics conversion to H_2

Develop 2D GCMS database of oils, intermediates and process conditions

Develop oil vapor process correlations

Develop catalyst structure activity relationships to control vapor deoxygenation

Develop catalysts for targeted biomass deconstruction

Summary

- Lab- and small pilot scale reactors to study biomass deconstruction, vapor phase upgrading, and catalyst performance will be operational in 2014
- Process impacts on biomass deconstruction are being understood by chemically characterizing liquid and vapor phase chemistry
- Catalyst structure activity relationships and modeling are used to understand deoxygenation and deconstruction activity to develop better catalysts
  - bimetallic alloying enhances decarbonylation reactions
  - decarbonylation and decarboxylation are favored over ketonization on Pd/Al_2O_3
- During catalytic pyrolysis, moderate pressure H_2
  - Delays catalyst deactivation
  - Improves hydrocarbon yields
  - Changes product composition

Publications, Presentations

1. Q. Xu, S. Cheah, and Y. Zhao. Initial reduction of the NiO(100) surface in hydrogen. *The Journal of Chemical Physics* (submitted).
2. Y. Zhao, Q. Xu, and S. Cheah. "Deoxygenation of lignin-derived monomeric compounds: computational and experimental results." Abstract accepted for poster presentation at the 23rd North American Catalysis Society Meeting, Louisville, KY, June 2–7, 2013.
3. Y. Zhao, Q. Xu, and S. Cheah. "Modeling hydrogen reduction and hydrodeoxygenation of oxygenates." Invited oral presentation at the Theory and Simulation in Energy and Fuel Production and Utilization special session, Division of Energy and Fuels, 245th ACS National Meeting, New Orleans, LA, April 7–11, 2013.
4. C. Majlinger, S. Cheah, M. Yung, "Reactions of Oxygenated Compounds over ZSM-5 Catalysts", NREL Science Undergraduate Laboratory Internship Research Symposium, Golden, CO, August 2012.
5. E. Gomez, M. Yung, "Vapor phase catalytic deoxygenation of acetic acid as a model biomass compound," American Institute of Chemical Engineers Annual Meeting, Pittsburgh, PA, October 2012.
6. M.M. Yung, E. Gomez, M. Jarvis, J.N. Kuhn, "Vapor phase catalytic upgrading of model biomass-derived oxygenated compounds," ACS National Meeting, Catalysis for Renewable Energy Session, Philadelphia, PA, August 2012.
7. E. Gomez, M.M. Yung, "Vapor phase catalytic deoxygenation of model pyrolysis compounds", Colorado Center for Biorefining and Biofuels Research Symposium, Boulder, CO, August 2012.
8. M. Yung, E. Gomez, C. Majlinger, K. Magrini, "Vapor phase catalytic upgrading of model biomass-derived oxygenate compounds," American Institute of Chemical Engineers Annual Meeting, Pittsburgh, PA, October 2012.
9. Stanton, A., Iisa, K., Effect of Hydrogen on the Vapor-Phase Upgrading of Lignin Pyrolysis Product, ACS Rocky Mountain Regional Meeting, Westminster, Co, October 17-20, 2012.