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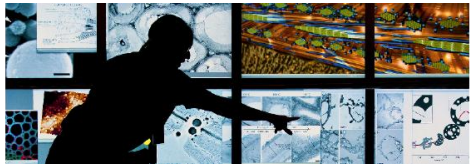
DOE Bioenergy Technologies Office 2015 Project Peer Review

Catalytic Upgrading of Sugars

March 24th, 2015

Technology Area Review: Biochemical Conversion

Principal Investigator: David K. Johnson

Organization: National Renewable Energy Laboratory

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Goal Statement

Direct support for BETO's Multi-Year Program Plan (MYPP) objectives:

- This project directly supports BETO's MYPP objectives to demonstrate "converting intermediates derived from cellulosic feedstocks to hydrocarbon fuels via biological or chemical pathways".
- This Project is identifying chemical/catalytic routes to efficiently upgrade sugar-derived intermediates into fuel products or value-added co-products.

Support goal of Biochemical Conversion R&D to reduce cost of converting cellulosic-derived intermediates to hydrocarbon fuels:

- Project is developing processes to hydrocarbon fuels and is working with process engineers to evaluate if costs are in line with BETO goals.
- Co-products are being developed to enable an overall MFSP of $5/GGE by 2017.

Benefits to the United States:

- Demonstrate processes at laboratory scale that decrease the risk of commercializing production of advanced biofuels and organic acid co-products from lignocellulosic feedstocks.

Quad Chart Overview

Timeline

- Project start date - 2012
- Project end date - 2017
- Percent complete - 50%

Barriers

- Bt-I. Catalyst Efficiency
- Bt-K. Product Acceptability and Performance
- Im-E: Cost of Production

Budget

	Total Costs FY 10 –FY 12	FY 13 Costs	FY 14 Costs	Total Planned Funding (FY 15-Project End Date
DOE Funded	$1,470K	$1,450K	$1,175K	$5,039K
Project Cost Share (Comp.)*	0	0	0	0

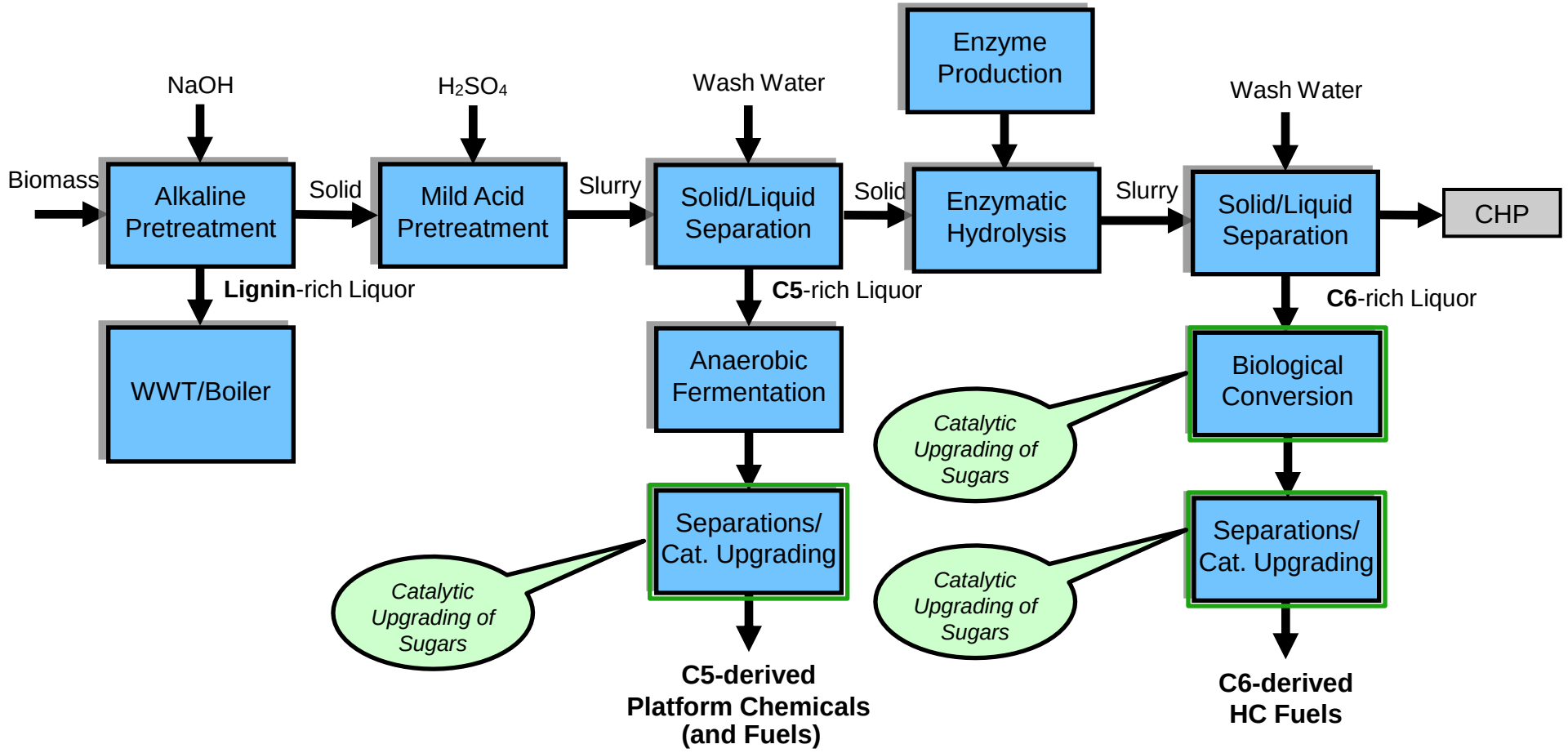
Partners

- Partners
  - None
- Other Collaborations
  - North Carolina State University (Subcontract)
  - University of Waterloo, Canada
- The project is managed under the Biochemical Platform at NREL

1 - Project Overview

- Develop chemical transformation routes that efficiently upgrade sugar-derived intermediates into fuel products or value-added co-products.
- The fuel products will be hydrocarbons compatible with blending into the existing fuel distribution infrastructure, to fit within the specifications for gasoline, jet or diesel fuels.
- Co-products will be higher value chemicals that permit us to meet the 2017 goal of a minimum fuel-selling price (MFSP) near $5/GGE.
- The research being performed is developing catalytic upgrading routes for sugar-derived intermediates such as polyhydroxybutyrate, succinic acid, fatty acids, and furans.

Biochemical Platform – Advanced Biofuels Process

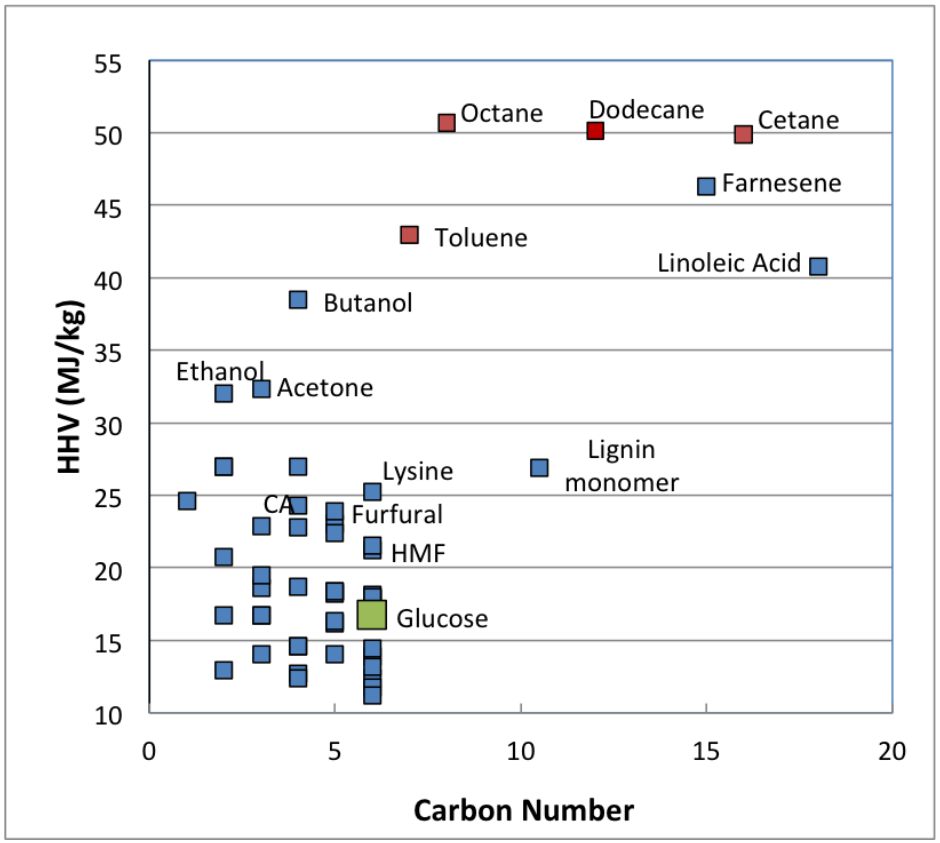


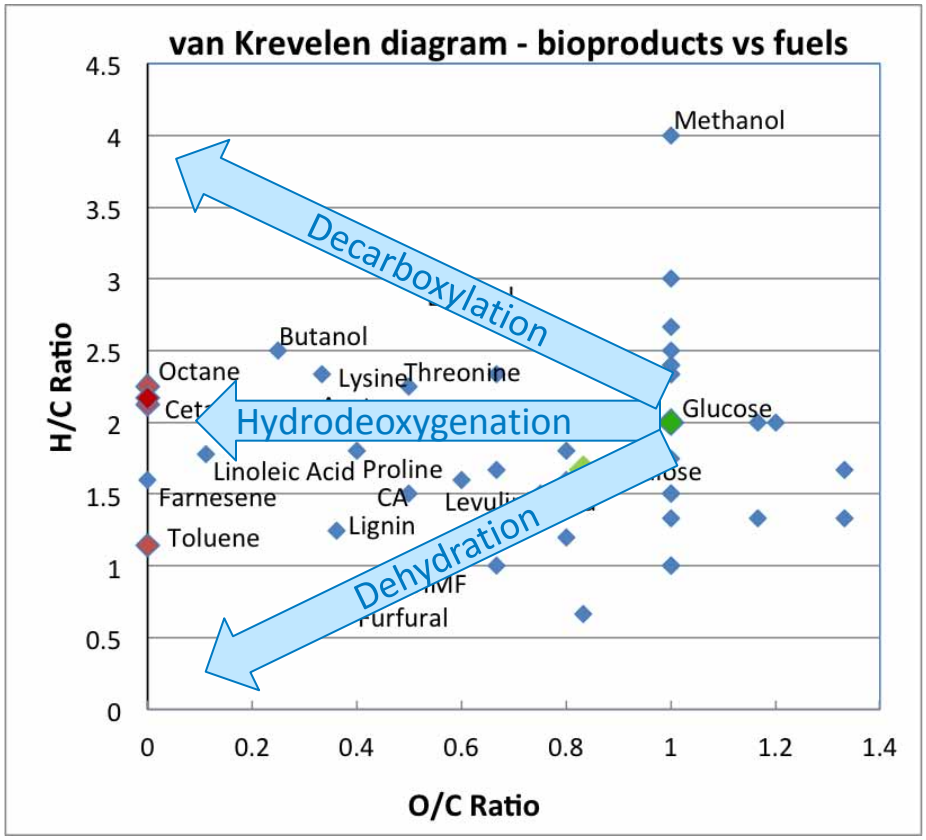
Operations impacted by this Project's research

2 - Approach (Technical)

How to make hydrocarbons from biomass-derived components

- Increase energy content - Decrease oxygen content
- Increase carbon chain length – especially needed for jet and diesel fuels





Top Value Added Chemicals from Biomass Volume I - Results of Screening for Potential Candidates from Sugars and Synthesis Gas (2004). Top 30 chemicals + others

2 - Approach (Technical/Management)

- **Technical challenges - Oxygen removal**
  - Decarboxylation – significant mass and C loss
  - Dehydration – unsaturated products and tars produced
  - Hydrodeoxygenation (HDO) – uses expensive H_2/catalysts, severe conditions
- **Critical Success Factors**
  - Cost drivers – Yield, catalyst cost/lifetime/recycle, process complexity, feeds
  - Product acceptability/performance – Fuel properties - oxygen content, mpt, etc
  - Advanced biofuel GHG reduction requirement – 50% (but not less than 40%)
- **Management plan has well-defined performance targets**
- Detailed Annual Operating Plan (AOP) at task Level
  - FY15 plan has 5 tasks
  - Quarterly milestones/deliverables – SMART milestones
  - Project has 6 milestones in FY15
  - GO/ NO GO decision point March 2016
  - Performing TEA and tracking of research results against TEA determined process performance targets

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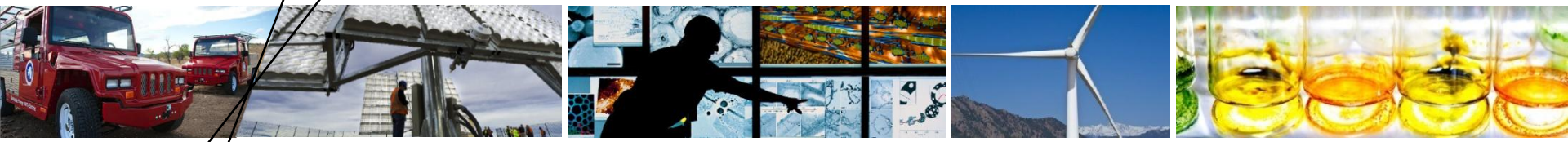
3 - Technical Accomplishments/Progress/Results



- Hybrid biochemical/thermochemical decarboxylation pathway to convert sugars to hydrocarbons via polyhydroxybutyrate
- Production of hydrocarbons using furfural-derived intermediates
- Nanoparticle bimetallic catalysts to reduce cost of catalysts for hydrogenation/hydrodeoxygenation

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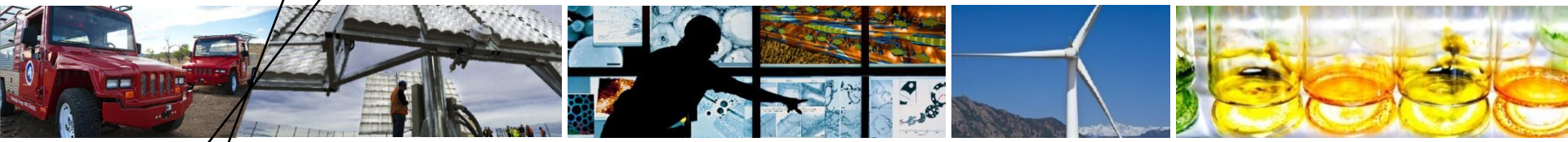

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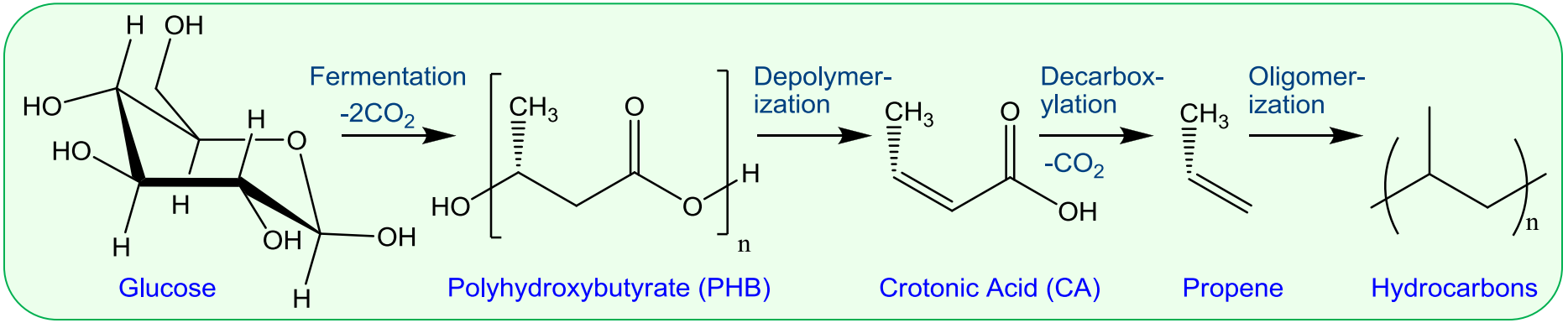
Hybrid biochemical/thermochemical pathway from sugars to hydrocarbons via polyhydroxybutyrate



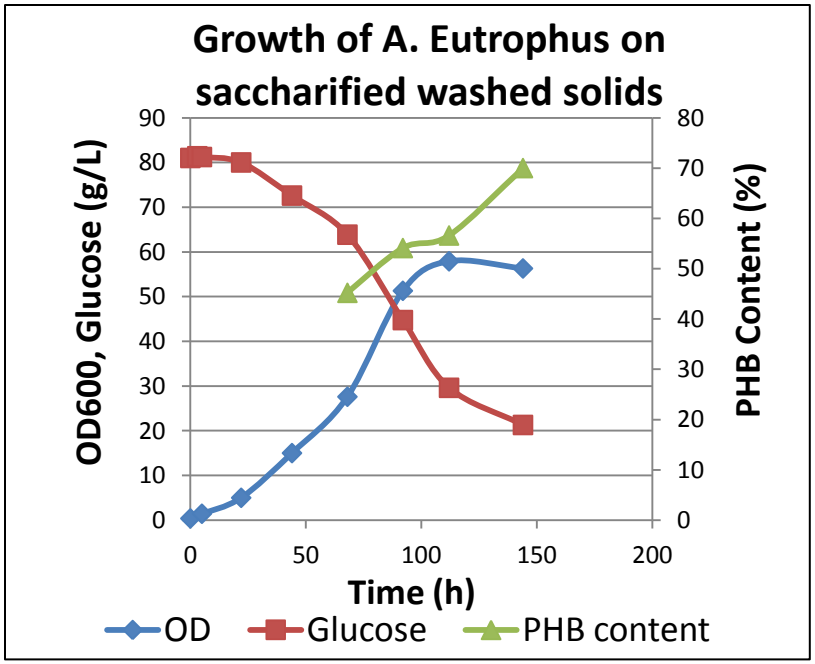
Process converts sugars to HC by decarboxylation only route

- Bacterial fermentation of glucose gives product with up to 75% PHB
- Depolymerization and decarboxylation combined at 400 ^{o}C to give propene in 70-80% molar yield in small tubing reactors
- Production of PHB on biomass hydrolyzates studied in FY13/14
- Kinetics of PHB depolymerization to crotonic acid studied in FY13
- Kinetics of crotonic acid decarboxylation to propene studied in FY13
- Scale-up of conversion of PHB to propene undertaken in FY13/14
- TEA of biomass to PHB to hydrocarbon process performed in FY14

Hybrid biochemical/thermochemical pathway from sugars to hydrocarbons via polyhydroxybutyrate

Biological production of PHB from biomass-derived sugars

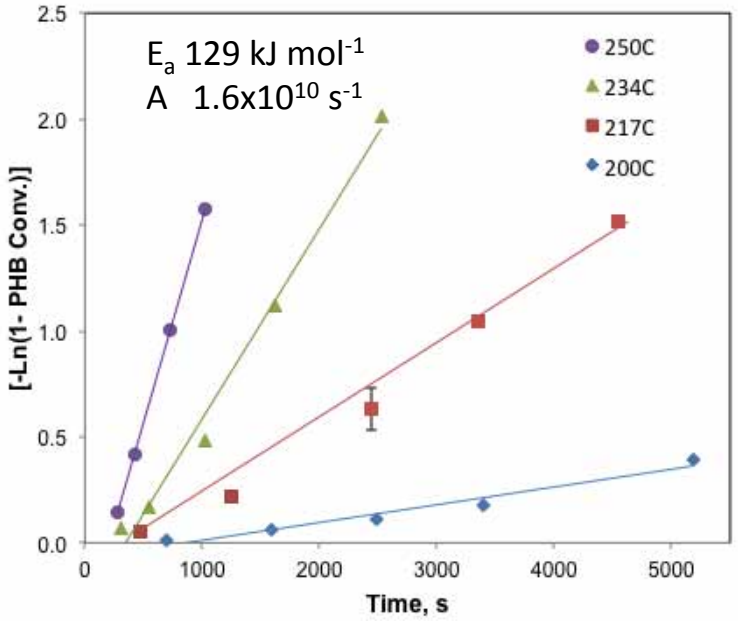
- Evaluated different PHB-producing strains grown on biomass-derived sugars, selected *Alcaligenes eutrophus NCIMB 11599* as our working strain
- Corn stover hydrolyzate slurry proved inhibitory to cell growth
  - Activated carbon effectively removed most chemical inhibitors, however they were not the vital factor leading to inhibition
  - Treatment of slurry with advanced enzymes improved growth indicating oligo-saccharides, most likely accounted for much of the inhibition
  - Cell growth and PHB production (44 wt%) improved with enzyme treated slurry in 2-L fermentor
  - Lag phase up to 48 h still present in 2-L fermentations
- No lag phase using saccharified washed solids.
  - Cell growth and PHB production improved with cell mass 22 g/L and 70 wt% PHB content in 2-L fermentor



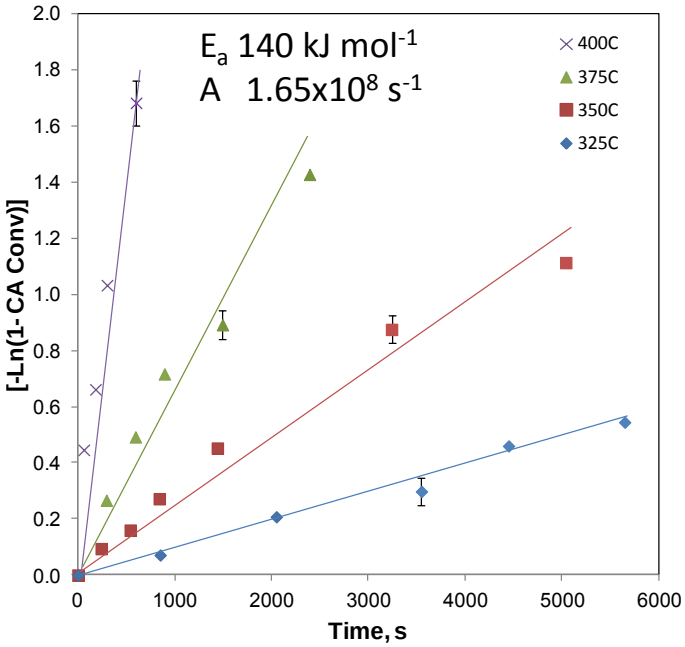
Hybrid biochemical/thermochemical pathway from sugars to hydrocarbons via polyhydroxybutyrate

Kinetics of depolymerization and decarboxylation (FY13 Q2 milestone)

PHB Depolymerization



CA Decarboxylation

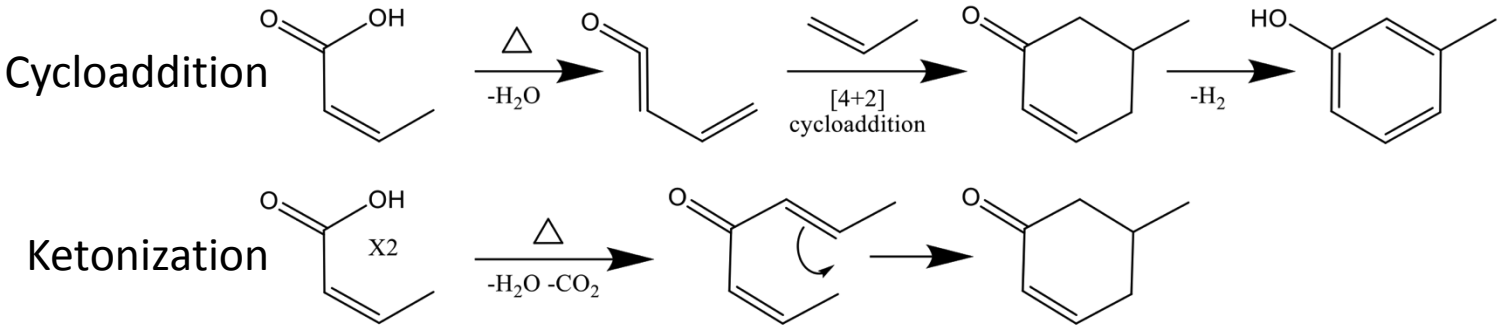


- Kinetics measured in small tubing reactor experiments
- PHB depolymerization and CA decarboxylation followed 1st order kinetics
- Rate constants fit with a simple Arrhenius dependency on temperature
- Decarboxylation was rate-limiting, 500-900X slower than depolymerization in the 350 - 550 ^{o}C range

Hybrid biochemical/thermochemical pathway from sugars to hydrocarbons via polyhydroxybutyrate

Scale-up of PHB thermolysis (FY13 Q4 milestone)

- Initial scale-up in 1 L batch reactor to convert 20-50 g PHB/CA
  - Long heat-up (70 min) and higher pressures (>300 psi)
  - Propene yields much reduced to 20-40%; CO_2 still 70-80%
  - Liquid product formed 5-20 wt% containing H_2O 10-30%
  - Liquid product contained cyclic ketones and even phenols

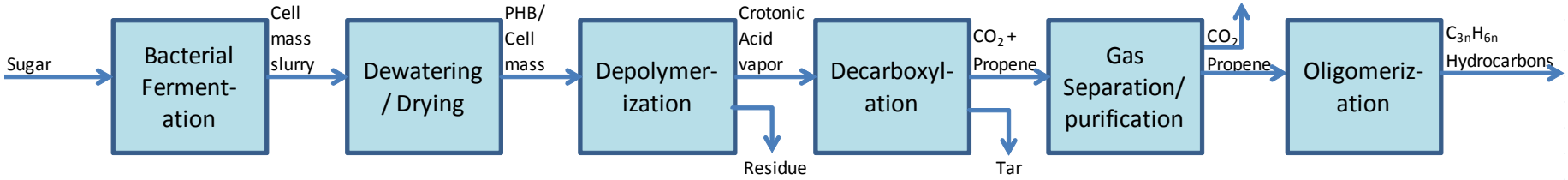


- Scale-up using atmospheric pressure tubular flow reactor (300 mL)
  - Low pressure and short residence time (~30 min) gave similar propene and CO_2 yields (~75%, 375 ^{o}C), no liquid product
  - Comparable yields to those obtained in small tubing reactors

Hybrid biochemical/thermochemical pathway from sugars to hydrocarbons via polyhydroxybutyrate

Technoeconomic analysis (TEA) of PHB to hydrocarbons process
(FY14 Q4 milestone, Joint w/ Biochemical Platform Analysis Project)

PHB Process Flow Diagram



Preliminary TEA of PHB to hydrocarbon process conducted

- PHB process compared to lipid process in FY13 Design Report
- Major finding - lower carbon yield of PHB vs fatty acid (FA) processes
  - PHB process all O rejected as CO_2, resulting loss of 3 carbons/glucose
  - FA process most O rejected as CO_2, but some O rejected as H_2O
  - Max C yield - PHB process 50%; FA process 62%
- Capital investment costs higher for PHB compared to FA process
  - Bioconversion cost lower for PHB because of high microbial activity 2.4 g/L-h
  - Propene oligomerization costs added significantly to capital costs
  - Overall capital costs were higher for PHB process by $65MM
- Decision made to discontinue research on PHB process.

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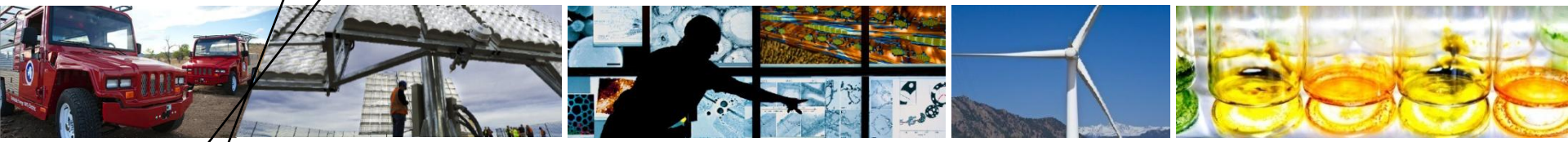

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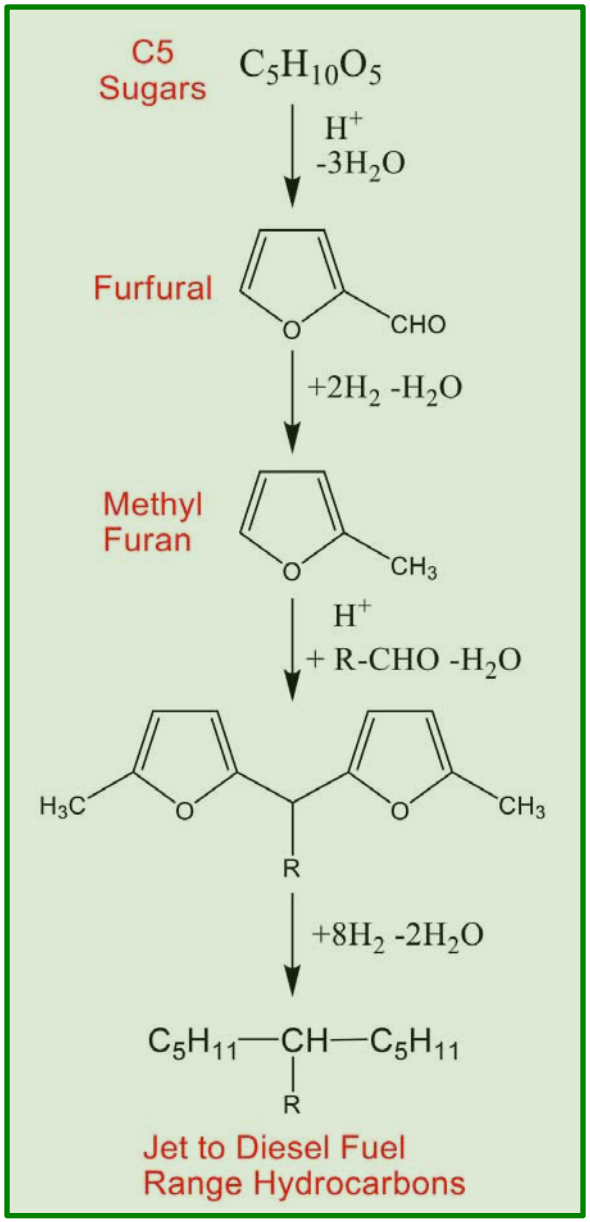
Production of hydrocarbons using furfural-derived intermediates

Chemical route from pentoses to advanced hydrocarbon biofuels

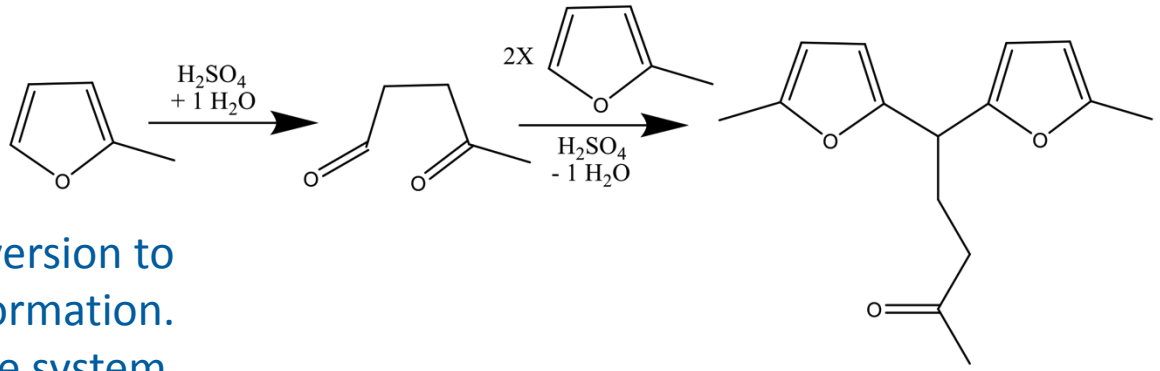
- Known reactions for converting pentoses into furfural and then methyl furan (MF) in high yield (>95%, Lessard and Chornet, 2010), present an opportunity to go from pentoses to renewable jet and diesel fuels with excellent properties.
- Known acid catalyzed condensation of MF with aldehydes and ketones result in products with higher carbon numbers. (Brown & Sawatzky, 1956; Corma et al, 2011; Li et al, 2012)
- HDO of condensation products leads to C12 to C15 hydrocarbons that can be blended into jet and diesel fuels.



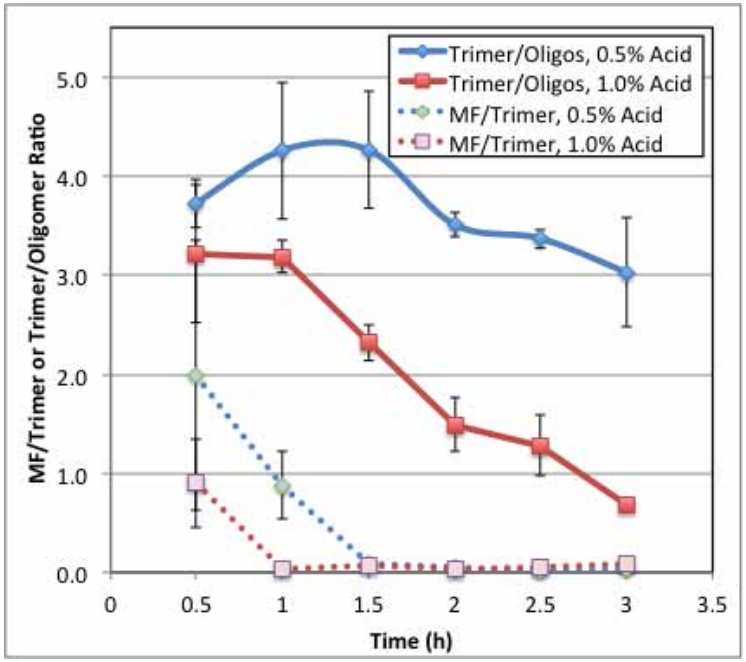
J. Lessard, E. Chornet, et al., Topics in Catalysis (2010) 53:1231–1234.
Brown, Sawatzky, Can J Chem (1956) 34 (9), 1147
A. Corma et al., Chem Sus Chem (2011) 4, 1574
Li et al. Chem Sus Chem (2012) 5, 1958

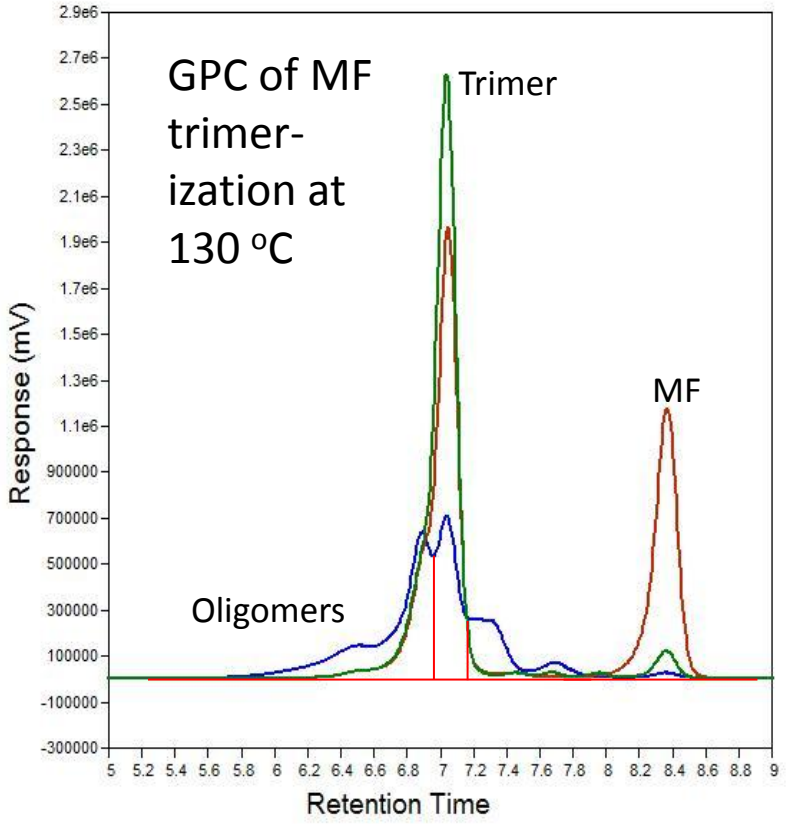
Methyl furan trimerization

- Condensation of methyl furan studied in robotic microwave heated reactor system.
- Analysis by GPC.
- Optimized for maximum MF conversion to trimer with minimum oligomer formation.
- HDO studied in multiple autoclave system.
- 5g of HC produced for FY13 Q3 milestone



Trimerization of MF at 130 °C





Scale-up of methyl furan to C15 hydrocarbon

Produce at least 50 g of hydrocarbon (FY14 Q2 Major Milestone)

Preparation of C15 Adduct

Methyl furan reacted at 130 ^{o}C with 0.5% H_2SO_4

Produced 400 g of MF trimer (molar yield 83%)

Hydrodeoxygenation of C15 Adduct

HDO at 300 ^{o}C, 100 bar H_2, 2 h,

4% Pt-SiO_2/Al_2O_3, 300 mL batch autoclave

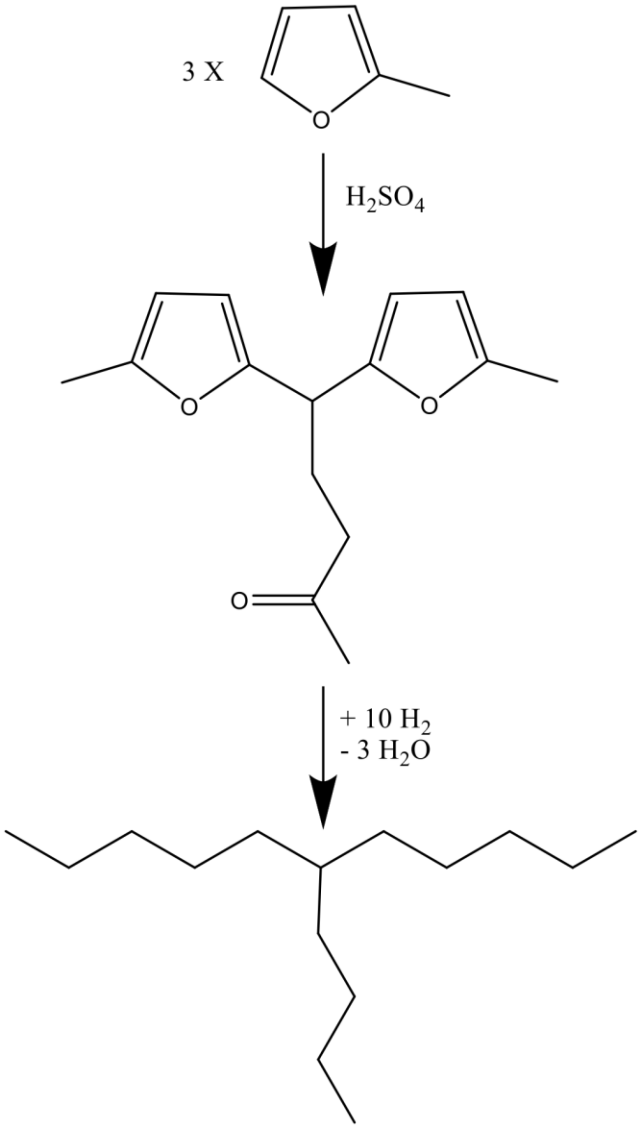
Mass yield 80% (molar yield 92%)

C15 HDO Product Analysis

CHO Analysis (Expected)

C% 84.9 (84.9) H% 14.3 (15.1) O% 0.2 (0.0)

^{13}C NMR and GC/MS analyses agreed that product was mostly 6-butyl undecane



Methyl furan C15 hydrocarbon diesel fuel properties

Diesel Fuel Properties Measured by NREL Fuel Performance Group

Property	MF trimer HDO product	Typical Diesel
Cetane Number	74	45 - 55
Boiling Point (°C)	255 #	200 - 350
Freezing Point (°C)	<-80	
Cloud Point (°C) *	-47.7	-45.4
Density (kg/L)	0.78	0.83
Net heating value (MJ/kg)	44.0	43.1

* Product decreased cloud point of No 1 diesel as a 20 vol% blend

Could also be a jet fuel blending component (JP-8 spec 150-290 °C)

Methyl furan/acetaldehyde adduct to jet fuel hydrocarbon

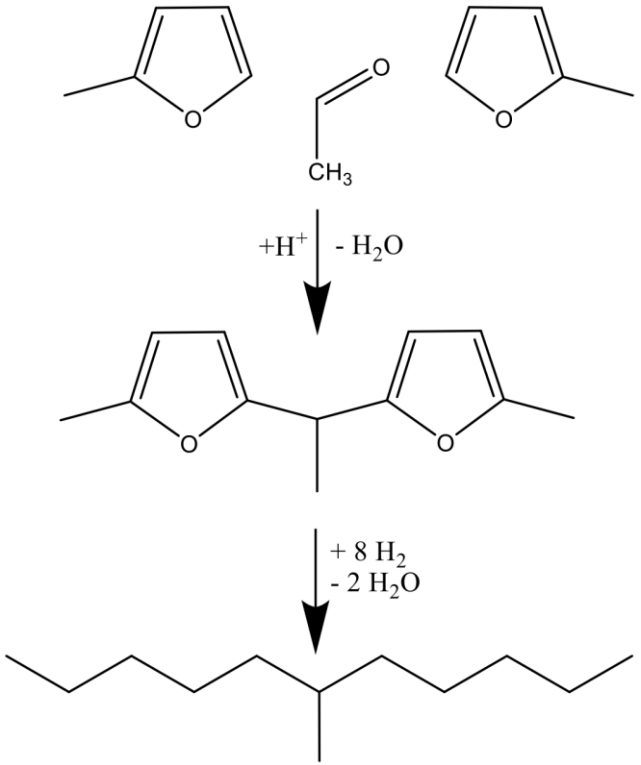
Preparation of C12 Adduct

MF (164 g) reacted exothermically with Acetaldehyde (50g) in an ice bath.

4 aliquots (total 17.7g) Amberlyst 15 (H^+).

Crude yield 191 g, 100% molar yield based on MF

Distilled yield 172 g, 91% molar yield



Hydrodeoxygenation of C12 Adduct

HDO at 300 °C, 100 bar H_2, 2 h

4% Pt-SiO_2/Al_2O_3 catalyst, 300 mL autoclave

Mass yield 81% (91% molar yield)

Properties C12 Hydrocarbon

CHO Analysis (Expected)

C% 84.6 (84.7) H% 15.3 (15.3) O% 0.2 (0.0)

Freezing Point -68 °C (JP-8 spec. -52 °C)

Boiling Point 200 °C (JP-8 spec. 150-290 °C)

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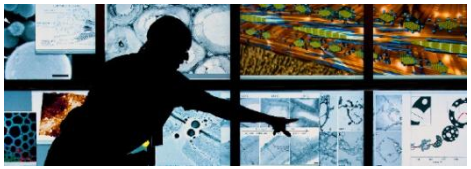

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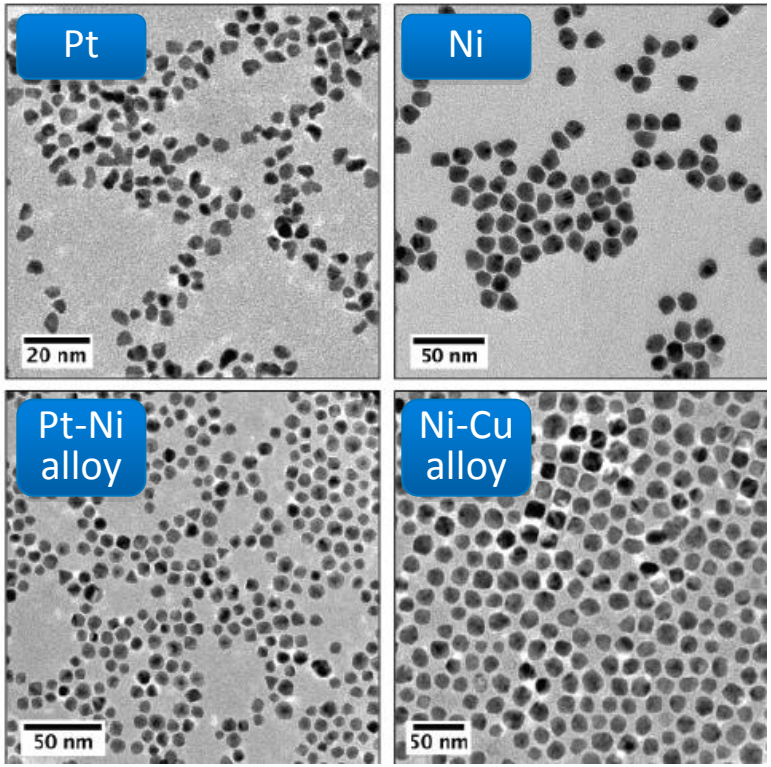
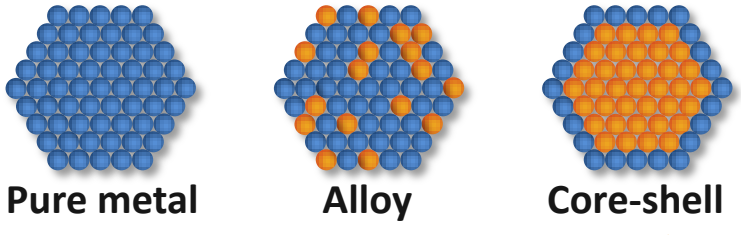
Nanoparticle bimetallic catalysts

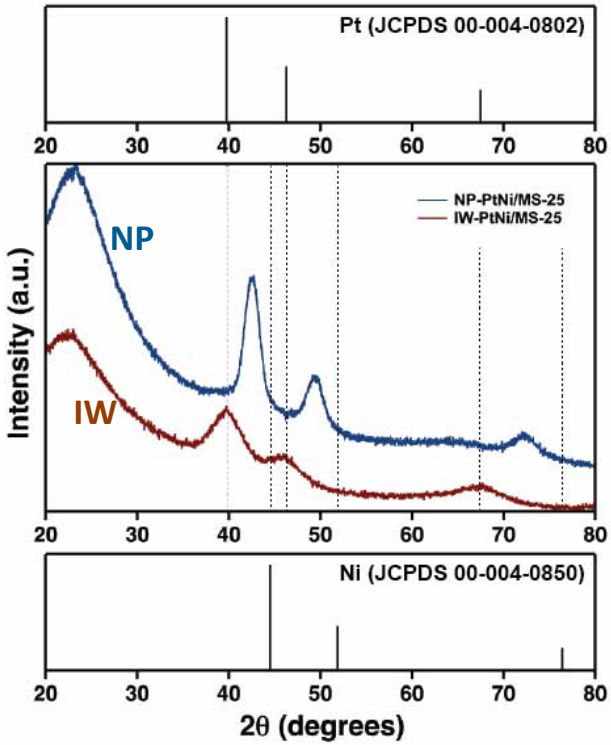
Reduce cost of HDO and hydrogenation catalysts

- Decreased noble metals content
- Controlled size, shape, and *composition*
- Increase activity and possibly selectivity



Different NP morphologies

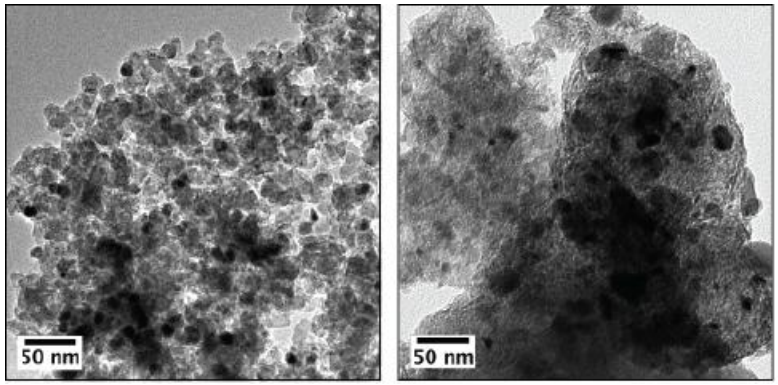




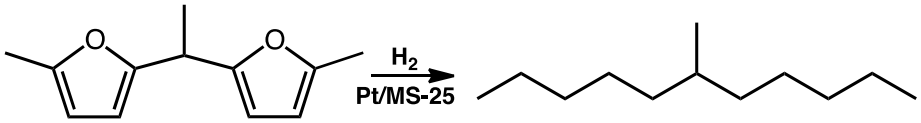
Nanoparticle bimetallic catalysts

Prepare and characterize 10 relevant NP catalysts (FY14 Q1 milestone)

NP-Ni/MS-25 IW-Ni/MS-25



TEM images of supported NP-Ni catalyst and analogue prepared by incipient wetness

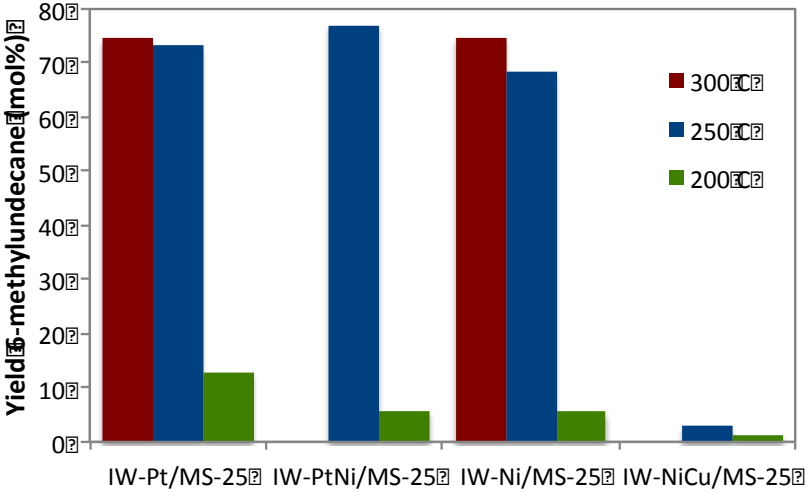


- Ni-Pt and Ni/MS-25 give comparable performance to Pt/MS-25 at 250 °C
- NP catalysts comparable to IW for small and/or polar molecules

  without any pretreatment to remove organic ligands

- Synthesized Pt, Ni, Ni-Pt, Ni-Cu, and Ni-P NPs *with controlled size*
- Supported on carbon, SiO_2, and SiO_2/Al_2O_3 (5 wt%, > 1 g each)
- Characterized by TEM and XRD
- Catalyst activity testing with furan adducts (FY15 Q1 milestone)

Molar yields of 6-methylundecane produced from HDO of methylfuran adduct



4 – Relevance

- Project is developing processes that could be used to produce hydrocarbons for blending into the existing fuel distribution infrastructure, into gasoline, jet and diesel fuels
  - Fuel products are aimed at meeting MYPP 2017 goal of an MFSP of $5/GGE, an interim target on the path to 2022 goal $3/GGE.
- Beginning catalyst R&D to expand platform of valuable co-products that can be made from succinic acid
  - Co-products will enable an overall MFSP of $5/GGE by 2017
- Provide comprehensive bench-scale data in batch and flow reactor conditions to allow detailed TEA models to be built to evaluate potentially new advanced biofuels and co-products.
- Successful projects are anticipated to attract industrial organizations interested in commercializing production of third generation advanced biofuels and co-products from cellulosic feedstocks.

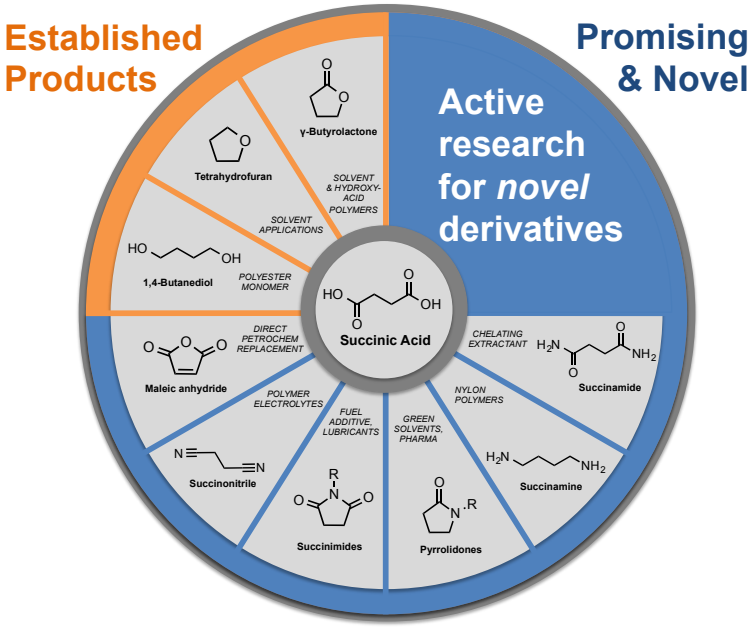
5 - Future Work - Hydrocarbons from furan intermediates

- Test use of Amberlyst-15 H^+ resin for making C15 furan intermediate
  - Reaction takes place at 90 – 130 ^oC with resin
  - High level of conversion at 130 ^oC in 1 hour
- Test reaction of methyl furan with other biomass-derived aldehydes
  - Reaction takes place with HMF, furfural, methyl furfural
- Looking for lower cost and more active HDO catalysts
  - Testing IW and nanoparticle catalysts containing non-precious metals with furan adducts
- Demonstrate production of furfural from C5 sugar stream in >75% yield for FY15 Q2 milestone
  - Batch and continuous reactions being run with pure xylose solutions and pretreatment hydrolyzates
- TEA of C5 sugar to C15 hydrocarbon performed for FY15 Q4 milestone
- GO/NO GO Point FY16 Q2 Hydrocarbon production from furfural
  - Downselect between routes from furfural to hydrocarbons based on theoretical yield, which should be at least 50%.

5 - Future Work – Succinic acid : Expanding the platform

Conducting catalysis R&D to build reliable TEA models to expand the SA platform

- Employing batch and flow reactor systems to track succinic acid conversion, product yields, selectivity, and catalyst lifetime with model and bio-derived SA
- Conducting basic separations research to determine effect of impurities on catalytic upgrading and subsequent end uses
- Developing detailed TEA models and corresponding separations/catalytic approaches for established and promising targets for succinic acid upgrading
- FY15 Q3 milestone - Report TEA on a minimum 3 SA catalytic upgrading pathways coupled to upstream separations



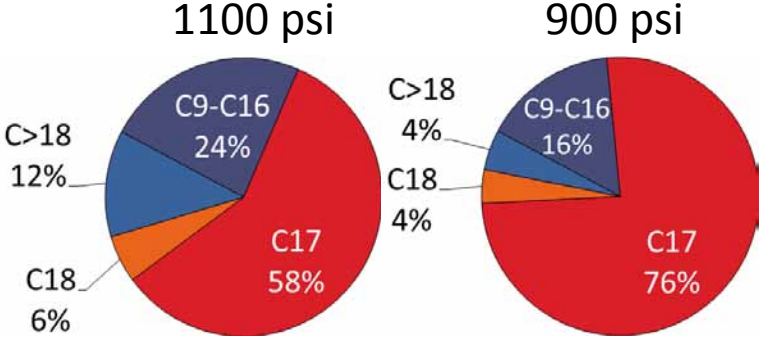
Batch and flow reactor systems with in-house catalyst synthesis

5 - Future Work - Yeast lipid upgrading

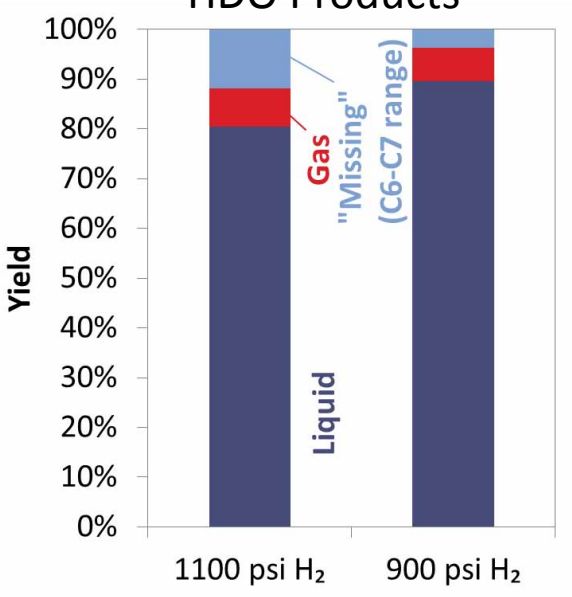
- Primary upgrading work with extracted yeast lipids
  - Leverage experience with algae lipid deoxygenation
    - Deoxygenated products 80+% paraffins
  - Similar conditions likely needed for yeast lipids
- Preliminary shakedown runs with model compound: oleic acid (~50% of yeast lipids)
- Hydroisomerization to produce branched alkanes with lower cloud point
- FY15 Q4 milestone - Yeast lipid HDO

Oleic Acid HDO

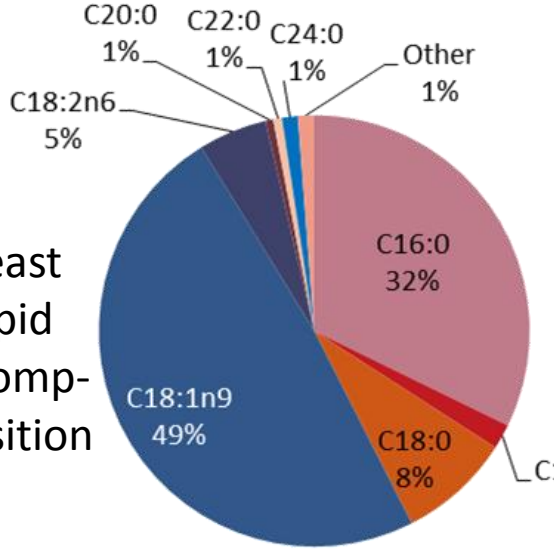
Liquid Product Compositions



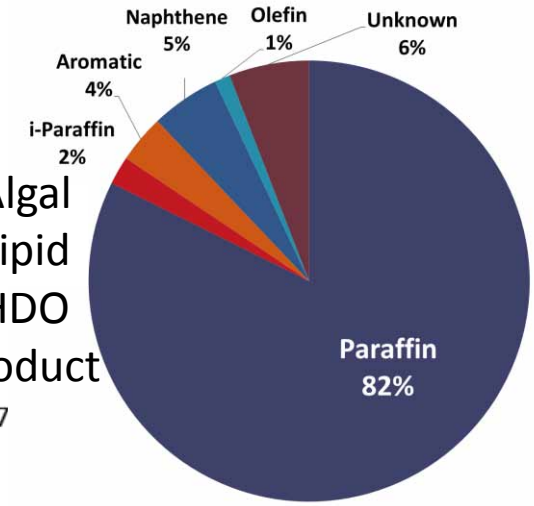
HDO Products



Yeast Lipid Comp-osition



Algal Lipid HDO Product



Summary

- Research focused on chemical transformation routes to upgrade sugar-derived intermediates into hydrocarbon fuel products that fit within the specifications for jet or diesel fuels.
  - Have examined decarboxylation, dehydration and hydrodeoxygenation routes
  - Route involving only decarboxylation appears too costly
  - Route using dehydration and hydrodeoxygenation utilizes high yield reactions that retain C by rejecting O as H_2O
- Hydrocarbon products made from methyl furan adducts could be excellent components for blending into jet and diesel fuel
  - C15 hydrocarbon has a cetane number 74, freezing pt <-80 ^oC
  - C15 and C12 hydrocarbons fit in BPt range for JP-8 and have freezing pts below JP-8 spec (-52^oC)
- In FY15 a TEA will assess the cost of the furfural route to hydrocarbons
- New projects in FY15
  - Expand platform of products that can be made from succinic acid
  - Assess upgrading of yeast lipids to renewable diesel hydrocarbons

Acknowledgements

- Task Leaders
  - S. Habas
  - G. Beckham

NREL Biochemical Platform Analysis Project

NREL Fuel Performance Group

- Staff
  - E. Karp
  - R. Katahira
  - J. Kruger
  - W. Michener
  - A. Mittal
  - L. Moens
  - A. Mohagheghi
  - H. Pilath
  - D. Vardon
  - T. Vinzant
  - W. Wang

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Additional Slides

Previous Reviewers Comments

2013 Biochemical Platform Peer Review

At the last review the work related to the Catalytic Upgrading of Sugars was in a subtask that was part of a much larger task (Pretreatment and Enzymatic Hydrolysis). I have tried to parse out the reviewers comments that seemed to be more directly related to the work that has been ongoing in the Catalytic Upgrading of Sugars Project since 2013.

Comment	Response
Project Approach Milestones could be improved by converting them to SMART goals (i.e. Specific, Measurable, Achievable, Relevant, Timely). The advanced biofuels work is still in the very early stages of development. Many key variables have been identified (leveraging ethanol work); however, much work remains to establish boundary conditions and refine key assumptions for the production of hydrocarbon fuels. The work to date has been sound. The future work involving conversion of sugars to hydrocarbons is somewhat vague.	We appreciate the reviewers' comments regarding the applicability of objectives, timeline, collaboration and approach. We expect subtle differences in the development of strategies for utilizing sugars for HC relative to ethanol. Sensitivity of HC producing organisms to inhibitors already appears slightly different compared to ethanologens from preliminary work looking at the inhibition of these organisms to acetate. We agree with the reviewers that estimation of costs and energy requirements will be very important, as will be the identification of viable sugar upgrading strategies. Milestone tables in the presentation did not show the SMART goals we use, to save space, but these are always included in the *Performance Measure* for each milestone. We agree with the reviewers that much remains to establish boundary conditions and refine the research path to producing HC from sugars. In the accomplishment slides many of the slides showed the milestones that the work had been related to, however, this was not emphasized verbally during the presentation.
Technical Progress, Accomplishments, and Plans HC production via catalysts and/or organisms. carbon chain length vs energ content also O-content (decarboxylation is mechanism used by biology to remove O). furans to hydrocarbons (but furans about $3000/ton vs $900/ton for HC fuel). PHA breakdown into HC. estimates that sugar costs about $0.26/kg It was slightly confusing why some of the tasks, e.g., preliminary work of chemical synthesis were carried out by this pretreatment group.	We appreciate that the reviewers recognized the progress made by the task since the last review. We agree that the current market cost of furans is much greater than the value of the fuels we are looking to produce so we need a lower cost process for their production. Chemical Transformation subtask was added to the task to allow closer interaction of synthesis group with the groups producing sugars and those testing for inhibition and catalyst deactivation.

Previous Reviewers Comments

2013 Biochemical Platform Peer Review (cont.)

Comment	Response
Project Relevance transition to HC meeting program goals Data looks positive but understanding the cost needs to be included A preliminary feasibility analysis for the Furan to HC route should be performed. This would help to identify the key success factors and target metrics for the proposed metrics. Similarly, a preliminary feasibility analyses for the proposed PHB to propene route should also be completed.	We agree with the reviewers that feasibility and technoeconomic analyses are essential for the further development of routes from all sugar intermediates to HC, and these are planned to occur in the next year.
Critical Success Factors Need to stay on top of latest developments and also be aware of older literature Seems to be the case - based on presentation Need to identify quantifiable metrics to drive RDD&D work in support of HC program. Additional guidance from BETO would be valuable to ensure efficient and effective use of resources toward DOE's mission.	We agree with the reviewers that staying abreast of the latest developments in pretreatment science and the development of HC pathways will be essential to the success of our program and BETO/DOE's mission. As the pathways from sugars to HC products become better defined, technical targets will be identified and their achievement will become the targets for our research. Overall, the measurable metric will be the cost of producing HC fuels, but the technical targets will be the subsidiary targets that our research will focus on.
Future Work chemical transformations but cost of substrate is greater than value of product ($3/gal = ~$900/ton whereas furans about $3000/ton) TEA of furfural and PHB	We agree with the reviewers that well described and appropriate milestones are essential to the direction of our research. We agree that the current market cost of furans is much greater than the value of the fuels we are looking to produce. To reach target furfural costs, will require higher yields and lower feedstock costs than are used in traditional furfural production processes. Again TEA of furfural and PHB processes will be essential and are planned. Preliminary cost estimations are performed as soon as we believe process changes are sufficiently well defined and that we can get access to a process engineer to perform them.

Previous Reviewers Comments

2013 Biochemical Platform Peer Review (cont.)

Comment	Response
Technology Transfer and Collaborations This group could benefit from greater interaction and collaboration with the engineering modeling teams.	We agree with the reviewers that greater interaction with process engineers would be beneficial. At NREL their time is highly sought after so we have taken the approach to generate data that can be used in engineering evaluations before involving the engineers.
Overall Impressions need more interaction with the TEA people to drive them It is acknowledged that the initial work plans and feasibilty experiments in support of the new HC production platform are very early stage. That being said, this group could benefit from additional direction from BETO and from greater interaction with the engineering modeling group. The establishment of appropriate goals and milestones for the HC program will be critical to the success of this work. The hydrocarbon work is well-targeted, but it is very early to assess viability. Success depends greatly on the downstream operations.	We agree with the reviewers that more interaction with the TEA people will be beneficial to the direction of our research, and this is planned to occur in the next year. It is our expectation that these interactions will lead to technical targets that will become the focus of our research.

Publications and Presentations: FY2013-14

Publications

"A Route from Biomass to Hydrocarbons via Depolymerization and Decarboxylation of Microbially Produced Polyhydroxybutyrate," by Heidi Pilath, Ashutosh Mittal, Luc Moens, Todd Vinzant, Wei Wang and David K. Johnson has been accepted for inclusion in the book "Direct Microbial Conversion of Biomass to Advanced Biofuels".

Connecting lignin-degradation pathway with pre-treatment inhibitor sensitivity of Cupriavidus necator by Wei Wang, Shihui Yang, Philip T. Pienkos, and David K. Johnson, was published in Frontiers in Microbiology 2014; 5: 247.

Presentations

"Conversion of sugars to hydrocarbons via depolymerization and decarboxylation of polyhydroxyalkanoates (PHA)" was presented by Heidi Pilath at the C2B2 Annual Meeting, in Boulder, CO, and at the 35th Symposium on Biotechnology for Fuels and Chemicals, Portland, OR, April 29, 2013.

"Conversion of biomass-derived furans into hydrocarbon fuels" at the Bioenergy and Biofuels Symposium, by Luc Moens was presented at the Division of Energy and Fuels at the Spring Annual Meeting of the American Chemical Society, New Orleans, LA, April 2013.

"A decarboxylation route from sugars to hydrocarbons via polyhydroxybutyrate" by D. K. Johnson was presented at the AIChE annual meeting in San Francisco, CA, in November 2013.

"Using Furfural as an Intermediate for Making Gasoline, Jet and Diesel Fuel Components" by David K. Johnson, was presented at the 36th Symposium for Biotechnology for Fuels and Chemicals, at Clearwater Beach, FL in April 2014.

"Biological production of a hydrocarbon fuel intermediate polyhydroxybutyrate (PHB) from a process relevant lignocellulosic derived sugar stream, by Wei Wang, Ashutosh Mittal, and David K. Johnson,was presented at the 36th Symposium for Biotechnology for Fuels and Chemicals, at Clearwater Beach, FL in April 2014

"Impact of Pretreatment Inhibitors on Microorganisms for Advanced Biofuel Production" by Shihui Yang, Wei Wang, Glendon Hunsinger, Yat-Chen Chou, Min Zhang, Philip T. Pienkos, and David K. Johnson, was presented at the 36th Symposium for Biotechnology for Fuels and Chemicals, at Clearwater Beach, FL in April 2014.

"A decarboxylation route from sugars to hydrocarbons via polyhydroxybutyrate" by Heidi Pilath, Ashutosh Mittal, Wei Wang, Todd Vinzant, and David K. Johnson, was presented at the 36th Symposium for Biotechnology for Fuels and Chemicals, at Clearwater Beach, FL in April 2014.

"Thermochemical conversion of PHB into intermediates for fuel production" by L. Moens*, R. Katahira, and D. K. Johnson was presented at the Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products, Denver, Sept. 2-4, 2014.

"Conversion of Furfural into Hydrocarbons for Blending in Jet And Diesel Fuels" by David K. Johnson was presented at the 3rd Frontiers in Biorefining conference at St Simons Island, GA on October 24, 2014.

"Conversion of Sugars into Hydrocarbons by Decarboxylation and Hydrodeoxygenation by David K. Johnson was presented at the AICHE Meeting in Atlanta, GA, on November 16, 2014.

Supplementary Slides

Milestone Schedule for Catalytic Upgrading of Sugars Project

FY 13/14 Milestones

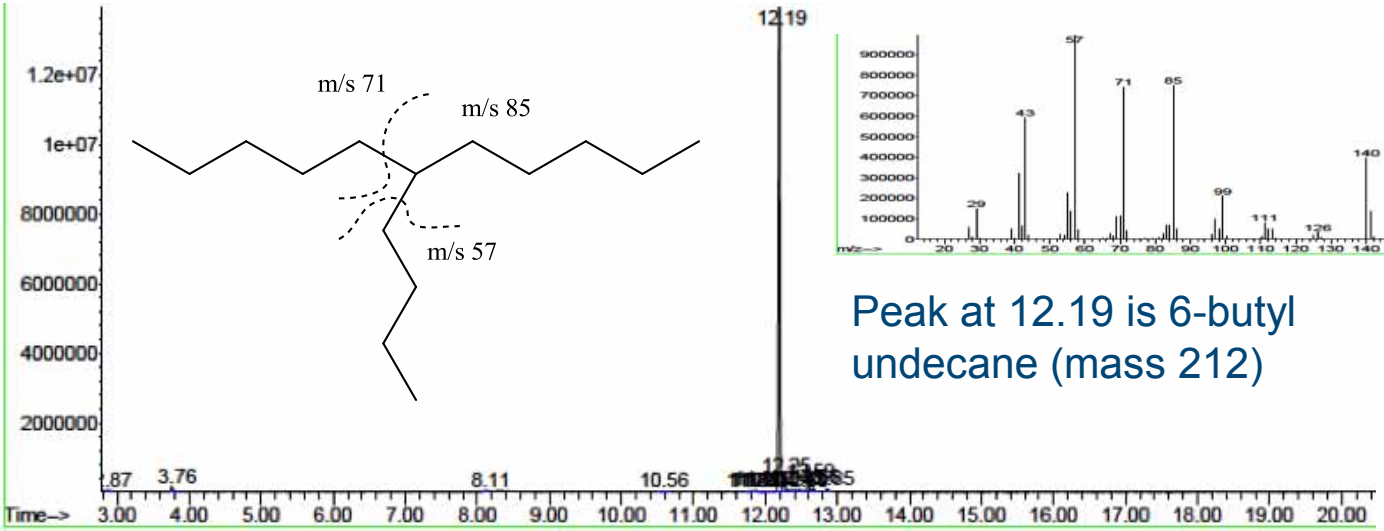
Type	Title/Performance Measure	Due Date
E	Operate scaled-up reactor for conversion of polyhydroxybutyrate to propylene (Subtask B) *Performance Measure:* Build and operate reactor capable of processing at least 50g of substrate.	3/31/13
E	Demonstrate experimentally a new pathway from furfuraldehyde to a liquid hydrocarbon with a chain length of C9 or higher. (Subtask B) *Performance Measure:* Produce at least 5g of hydrocarbon in the jet or diesel fuel range.	6/30/13
D	Demonstrate production of a hydrocarbon fuel intermediate from a process relevant lignocellulosic derived sugar stream. *Performance Measure:* Hydrocarbon fuel intermediate should be produced at a minimum theoretical yield of 50% based on processing 50g of substrate from a process relevant lignocellulosic derived sugar stream. (Subtask B)	9/30/13
Regular	Deliverable: Prepare and characterize 10 relevant monometallic and bimetallic (e.g. Ni, Ni-Pt, Ni-Cu, Ni-Fe) nanoparticle catalysts with controlled size and composition. The catalysts will be dispersed on alumina/silica supports and yield ~1 g quantities at 5 wt.% metal loading.	12/31/13
Major	Deliverable: Scale-up of furan oligomerization to C10+-C15+ hydrocarbons at a 50g scale.	3/31/14
Regular	Deliverable: Prepare 5 g of diol from a polyhydroxyalkanoate through direct reduction methods and convert to olefinic hydrocarbons through thermocatalytic dehydration of the diols.	6/30/14
Regular	Joint Milestone (with Biochemical Platform Analysis task) Preliminary assessment of the economic viability of utilizing sugars in a process relevant lignocellulosic derived sugar stream to produce polyhydroxybutyrate that is subsequently converted to hydrocarbons by thermal depolymerization and decarboxylation.	9/30/14

FY15 Milestones

Type	Title/Performance Measure	Due Date
Regular	Nanoparticle catalyst testing (Task 5) Identify characteristics that promote high catalyst activity, selectivity, and stability during furan compound upgrading by screening at least 10 catalyst materials. Compare their performance to the currently used Pt/silica-alumina catalyst to identify lower cost alternatives.	12/31/14
Regular	Demonstrate 75% furfural yield from a C5 sugar stream (Task 3) The conversion of a C5 sugar stream to furfural will be demonstrated at the bench scale using a furfural production method selected from a literature search of high yielding methods.	3/31/15
Annual	Report TEA on a minimum of three succinic acid catalytic upgrading pathways that are coupled to upstream separations (Task 1) Report preliminary TEA and sensitivity analyses based on product yield, selectivity, and recycle. Based on TEA results, down select catalytic upgrading pathways and collect initial screening data with a minimum of three catalytic materials. Model succinic acid solutions will be tested that are representative of post-separation composition. Catalysts will be characterized before and after reactions to normalize reactivity to active site densities and evaluate material stability and potential fouling issues.	6/30/15
Stretch	PHB productivity on saccharified slurry (Task 4) Demonstrate PHB productivity on saccharified biomass slurry of 1.0 g/L/h in a 5 L fermenter with a yield of 0.3 g PHB/g glucose.	6/30/15
Regular	Complete lipid HDO conversion (Task 2) Determine HDO conditions that allow complete conversion of lipids to straight-chain alkanes, and remove heteroatoms to below detection limit on model FFAs representative of those derived from biomass.	9/30/15
Regular	Conduct preliminary TEA assessment for catalytic conversion of carbohydrate intermediates to fuels (Task 3) Conduct a "preliminary feasibility level" TEA assessment of a catalytic conversion pathway for carbohydrate intermediates (furans) to hydrocarbon fuels, based on new focus under NREL's catalytic sugar upgrading project considering catalytic oligomerization and hydrodeoxygenation of furans-to-hydrocarbons. Analysis will consider at least 3 experimentally validated process metrics, and will extrapolate out to plausible targets to understand aspirational MFSP cost potential in comparison to NREL's catalytic conversion of sugars design report (FY14, under development) and ultimately relative to potential to achieve MFSP costs of $5/GGE or less by 2017. (Joint with catalytic sugar upgrading project)	9/30/15

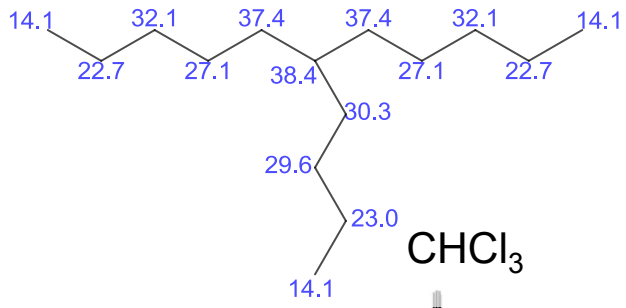
Methyl Furan Trimer HDO

GC/MS and ^{13}C NMR of product made by HDO of MF Trimer in 300 mL autoclave is a C15 hydrocarbon (most probably 6-butyl undecane)



Peak at 12.19 is 6-butyl undecane (mass 212)

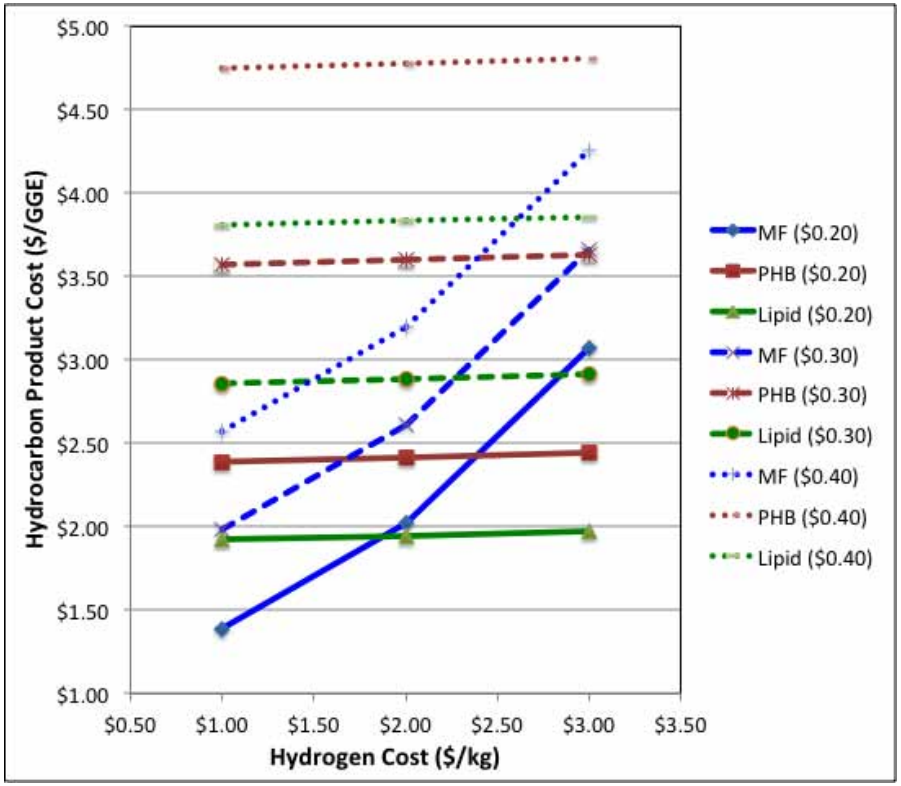
- ^{13}C NMR shows virtually all C in alkane region
- No peaks in 60-90 ppm region indicate no C-O
- Small peaks in 120-140 ppm region from alkenes



Which Pathway to Hydrocarbons is Best

Cost

- Biochemical Platform Analysis project perform detailed TEA
- Many factors contribute to final cost
  - yields, process conditions, capital equipment, catalyst longevity
- Simple comparison based on theoretical yield and H_2 consumption
- PHB pathway less favored because too much C lost in decarboxylation
- Lipid pathway favored because not all O rejected as CO_2
- HDO in MF pathway favored by low cost H_2

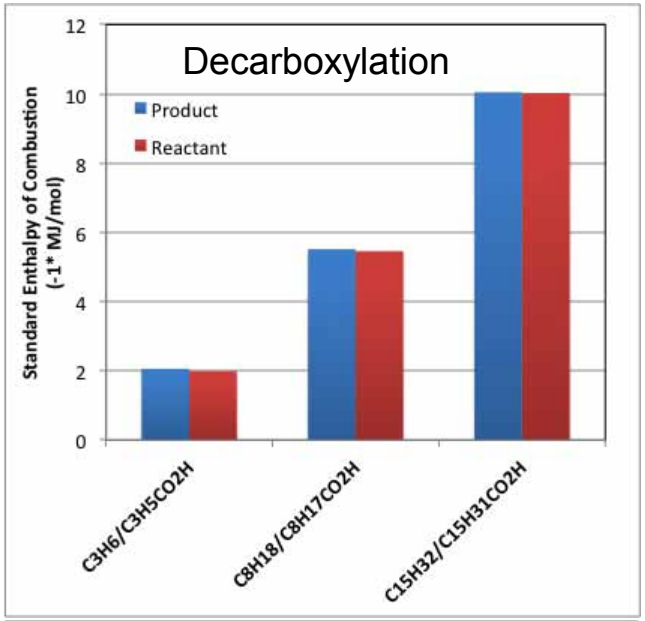


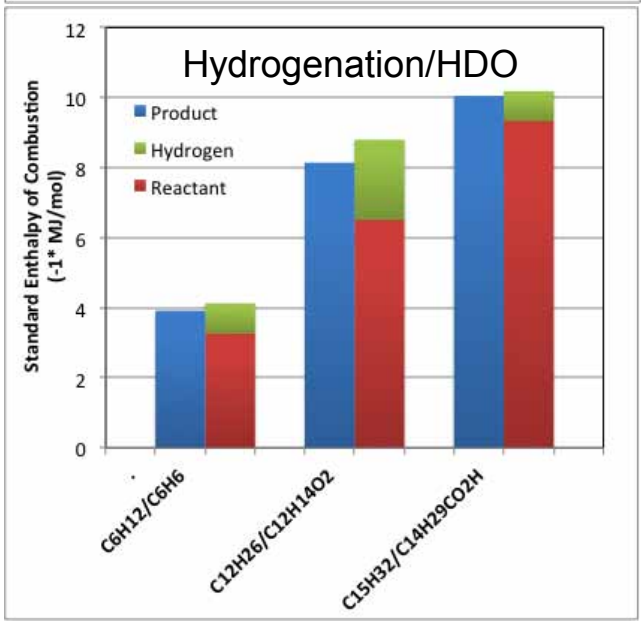
MF = Methyl furan pathway
PHB = Polyhydroxybutyrate pathway
Lipid = Lipid pathway
(Sugar cost $/kg)

Which Pathway to Hydrocarbons is Best

Energy

- How much of the energy in the reactants is retained in the products
- Many factors contribute to energy balance
  - yields, process conditions, integration
- Simple comparison based on exo/endo-thermicity of the reactions
- Decarboxylation reactions tend to be very slightly endothermic
- Hydrogenations and HDO reactions tend to be strongly exothermic
- Heat content of hydrocarbons relative to starting materials (incl. H_2)
  - decarboxylation ~1% higher
  - hydrogenation/HDO 1-7% lower

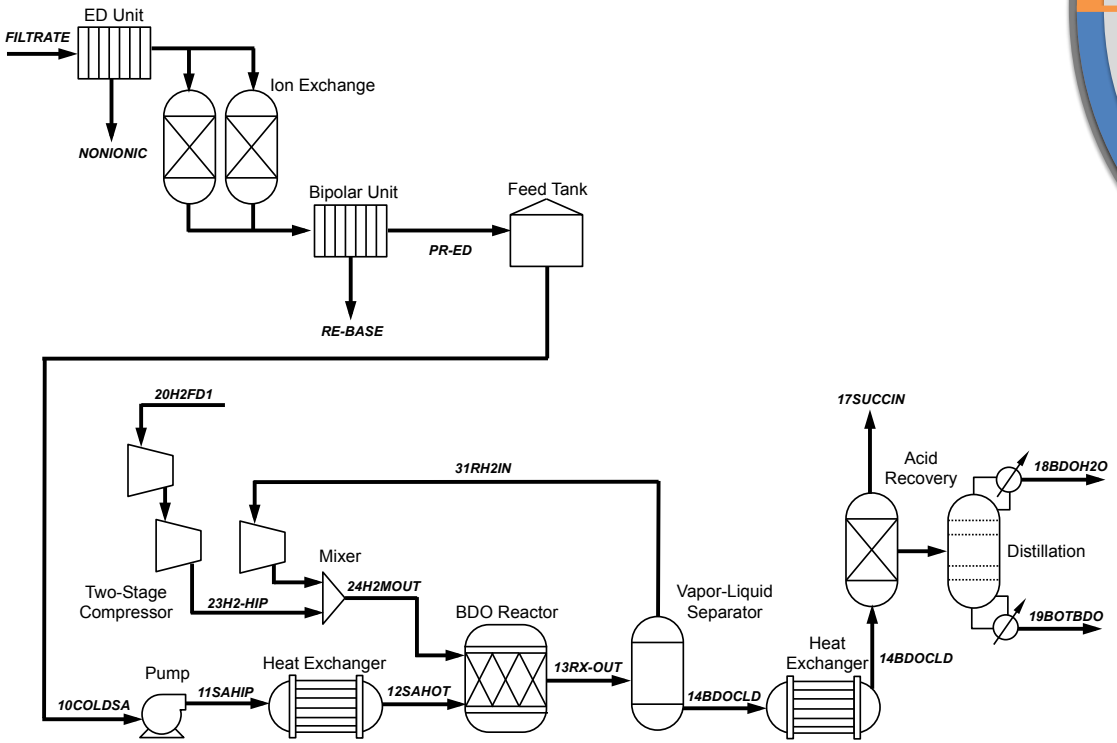


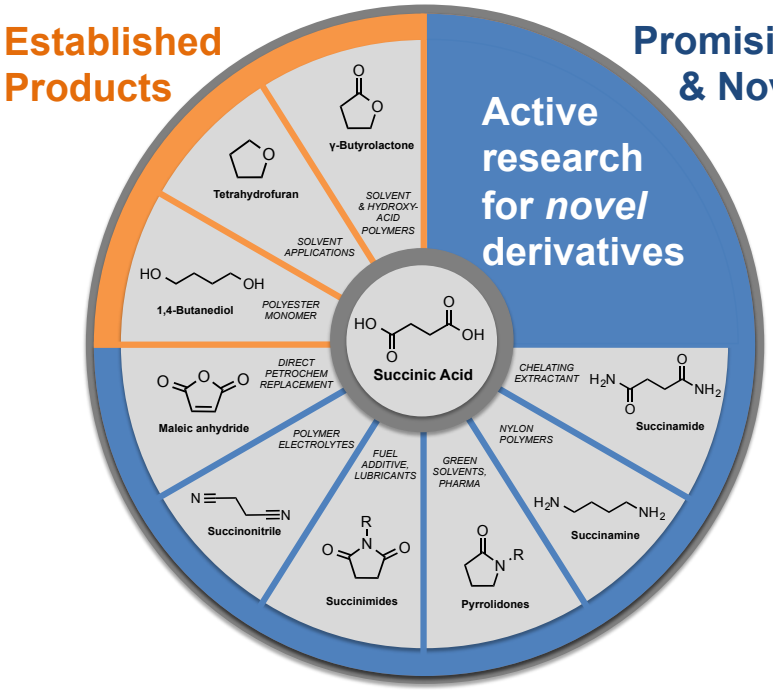


Succinic acid : Expanding the platform

Preliminary Development of TEA Models

- Developing market analysis and preliminary TEA models for established and promising targets for upgrading succinic acid
- "Base case" and integrated TEA process model in progress to evaluate reductive upgrading pathways





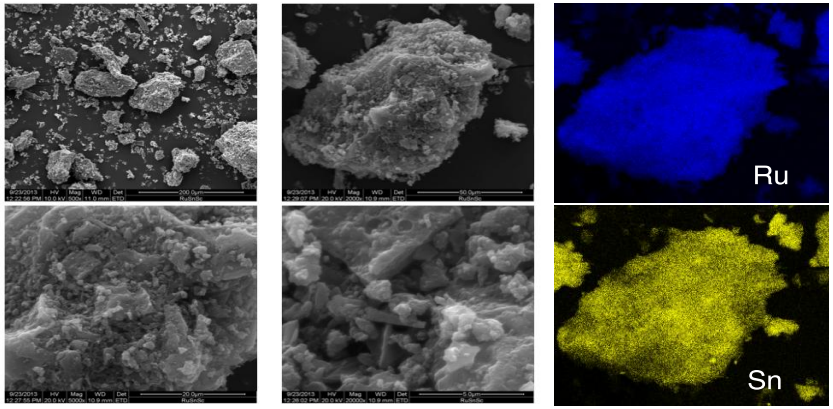
Models address the impact of target product yield, selectivity, and catalyst stability – as well as the the interface with upstream separation processes

Succinic acid : Expanding the platform

Catalyst Synthesis & Batch Reactor Screening

Catalyst	BET SA (m^2/g)	Pore vol (cc/g)	Pore Dia (Å)	Metal (wt%)
Ru-Sn	514	0.45	9.8	Ru 3% Sn 4%
Pd-Re	807	0.55	9.7	Pd 4% Re 5%

- In-house synthesis and characterization underway for promising catalyst materials. Support area and metal loading characterization will assess material stability and active site leaching.

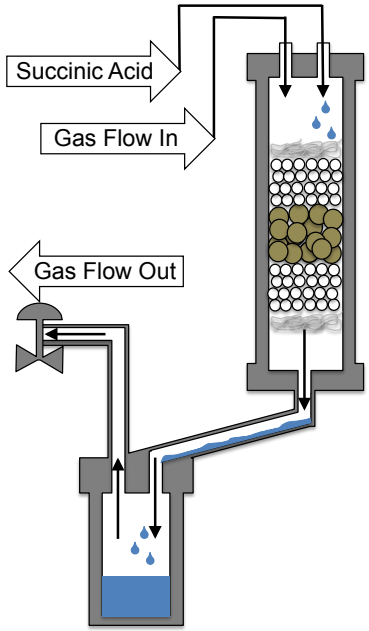


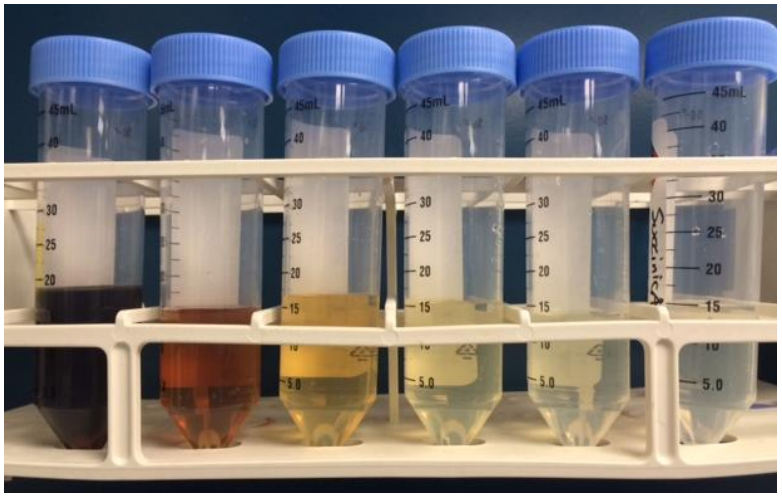
- SEM-EDS evaluates the bimetallic active site distribution to monitor for sintering post-reaction.

- Batch reactor evaluation of hydrogenolysis catalyst:
  - Ru-Sn activated carbon
  - Pd-Re activated carbon
- 220°C, 1000 psi H2
- Tracking succinic acid conversion, BDO/THF/GBL product yields, and selectivity
- Test with model and bio-derived succinic acid

Succinic acid : Expanding the platform

Separations & Continuous Catalytic Testing

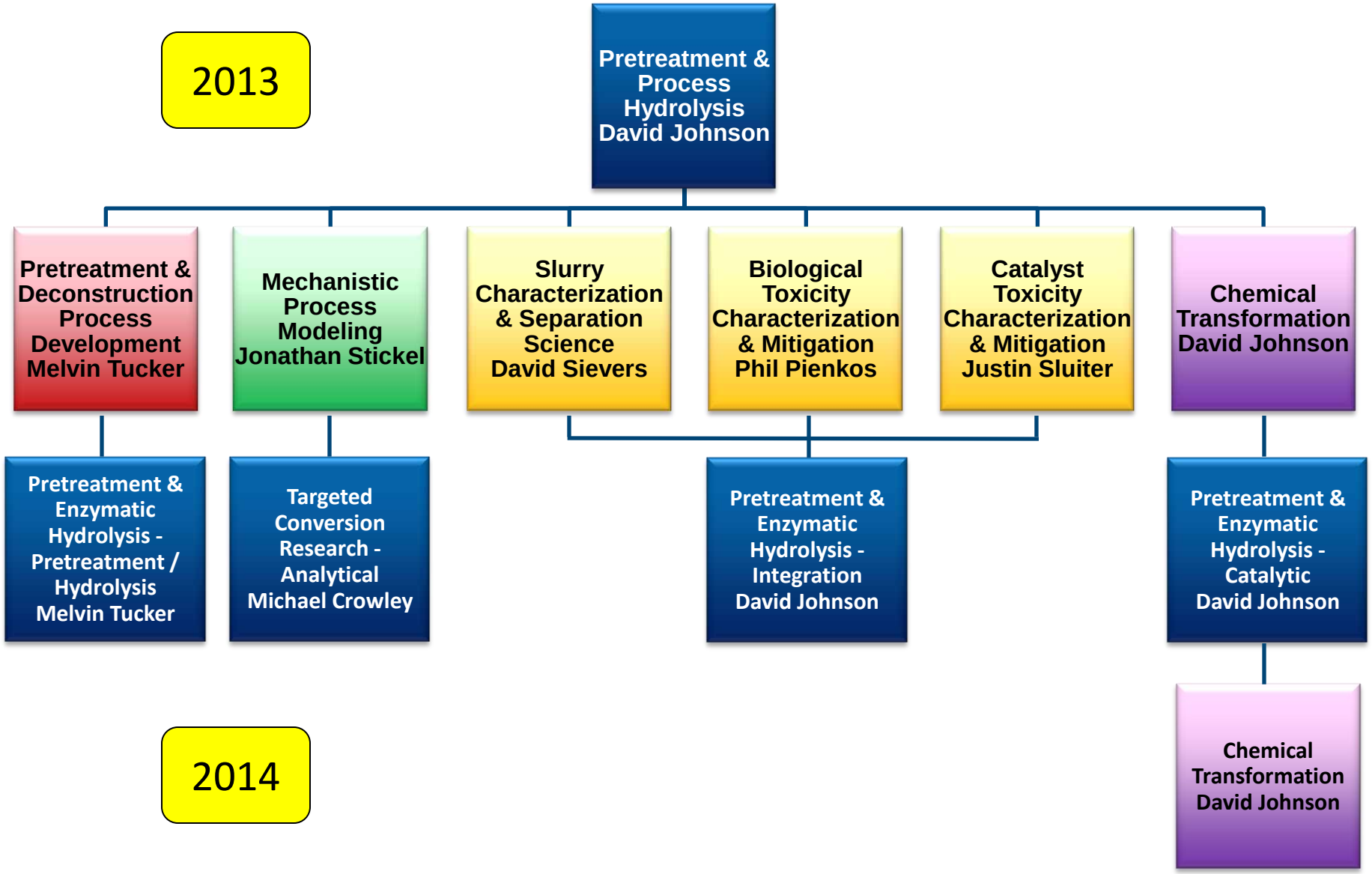




- Construction of continuous trickle-bed reactor for catalyst stability testing near complete
- Evaluate catalysts and pathways screened from batch reactor work
- Focus on catalyst activity lifetime with model and bio-derived succinic acid feedstocks

- Activated carbon treatment of hydrolyzate-derived succinate:
  - Determining influence of carbon loading on color and impurity removal
  - In progress to recover bio-derived succinic acid for catalytic upgrading

Changing Structure of Catalytic Upgrading Project



Changing Structure of Catalytic Upgrading Project