

# 2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

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



**Catalytic Conversion of  
Lignocellulosic Biomass to  
Hydrocarbon Fuels (2.3.1.12)**

**May 22, 2013     Mike Lilga**

**Technology Area  
Review: Biochemical  
Conversion**  
Organization: PNNL

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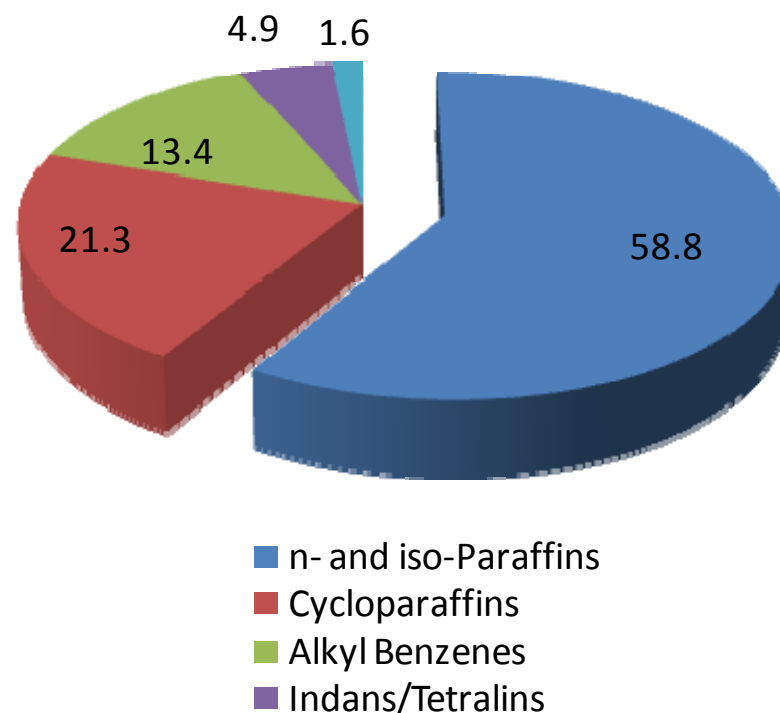
## Goals:

- There is a need to make a balanced fuel composition containing all component classes
- Current thermochemical methods, such as pyrolysis and HTL, are very good at making closed-ring classes
- There is an absence of methods that make open-chain *n*- and iso-paraffin fuel components

## Outcome/Relevance:

- Maximize whole biomass carbon utilization
- Improve economics by enabling less capital-intensive processes
- Decrease fuel production costs to help meet 2022 MYPP goals (\$3/gge [\$2011])

"Average" JP-8 Composition



## Timeline

- Project start date: 11/2/2012
- Project end date: 9/30/2015
- Percent complete: 60% FY13

## Barriers Addressed

- Bt-A. Biomass Fractionation
- Bt-D. Pretreatment Chemistry
- Bt-J. Catalyst Development

## Budget

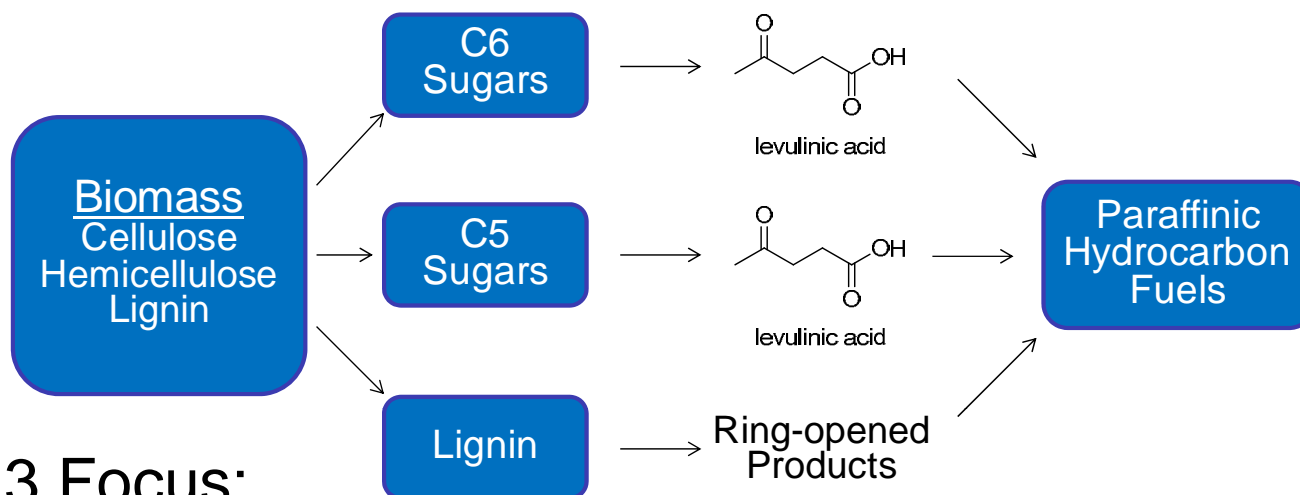
- Funding for FY11: N/A
- Funding for FY12: N/A
- Funding for FY13: \$400k (DOE)
- Years the project has been funded / average annual funding:  
1 yr / \$400k

## Partners

- Interactions: Virent, WSU
- Project management: PNNL
- Project management – communication as needed with other labs, and DOE

- This project was designed to address the need for:
  - Biomass conversion routes to linear and *iso*-paraffins as jet and diesel fuel blend stocks
  - Deconstruction methods that maximize carbon recovery in useful forms, i.e., sugars or other molecules that can be converted using catalytic or biochemical means; minimize humins
  - Deconstruction methods that minimize or do not introduce harmful impurities such as acid anions (catalyst poisons) and furans (biochemical inhibitors)
  - Low temperature and pressure, high yield conversions to fuels and chemicals
  - Lignin conversion to fuels and chemicals
  - Conversion routes that minimize H<sub>2</sub> use

# 1 - Approach



- **FY 13 Focus:**

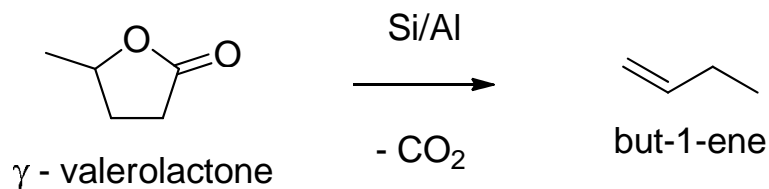
- Pretreatment and deconstruction using a novel sugar stabilization mechanism to minimize degradation, contamination, and humin formation
- Levulinic acid conversion to hydrocarbons, especially via heterogeneous ketonization catalysis and olefin intermediates

- **Out years:**

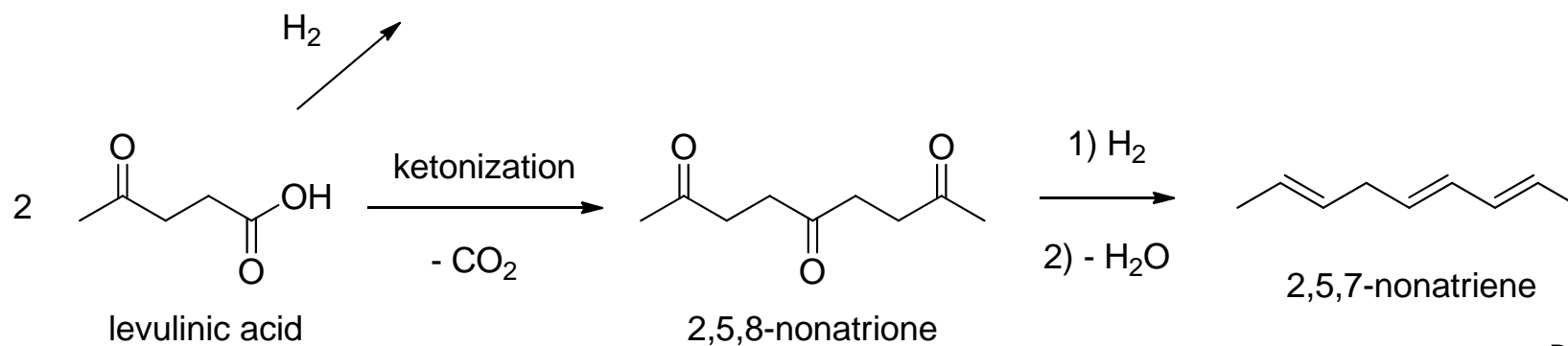
- Conversion of sugars to levulinic acid
- Conversion of lignin to fuel blend stocks and value-added products via novel ring-opened intermediates

# 1 - Approach (cont'd)

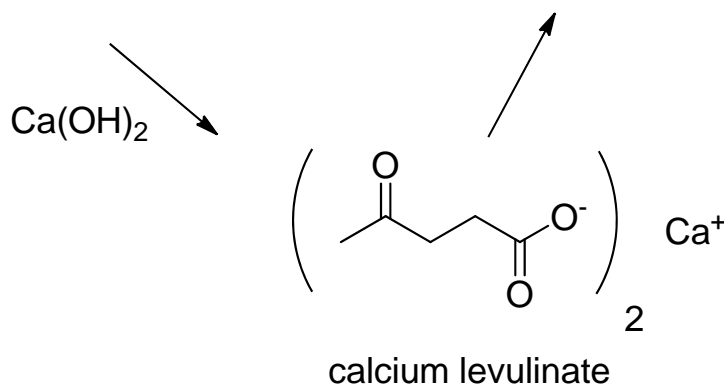
- Some possible levulinic acid upgrading approaches:



Dumesic  
J Catalysis 281 (2011) 290-299



PNNL Approach



Wheeler  
Green Chem 12 (2010) 1353-1356

- Reactors
  - Parr, 300 mL, fritted dip-tube for sampling; for deconstruction experiments
  - Glass tube reactor, 175 mL; for H<sub>2</sub>SO<sub>4</sub> digestions per NREL LAP
- Sugars Analytical
  - Shimadzu HPLC with Alltech ELSD 200 detector
  - Waters X-Bridge amide column (3.5 μm, 250 mm × 4.6 mm)
  - Eluent is acetonitrile (40%), acetone (40%), water (20%) and ammonium hydroxide (0.1%); flow rate is 0.6 mL/min
- Feed
  - American Wood Fibers (AWF) 2020 yellow pine (low ash)
  - water and ethanol washed (extractives removed)
- Typical Experiment
  - 7.5 g biomass with 100 mL water, catalyst, stabilization medium
  - 3 h reaction time, 0.5 h samples, temp. 120 °C to 200 °C

## 2 – Technical Progress (cont'd)

### Task 1 - Deconstruction

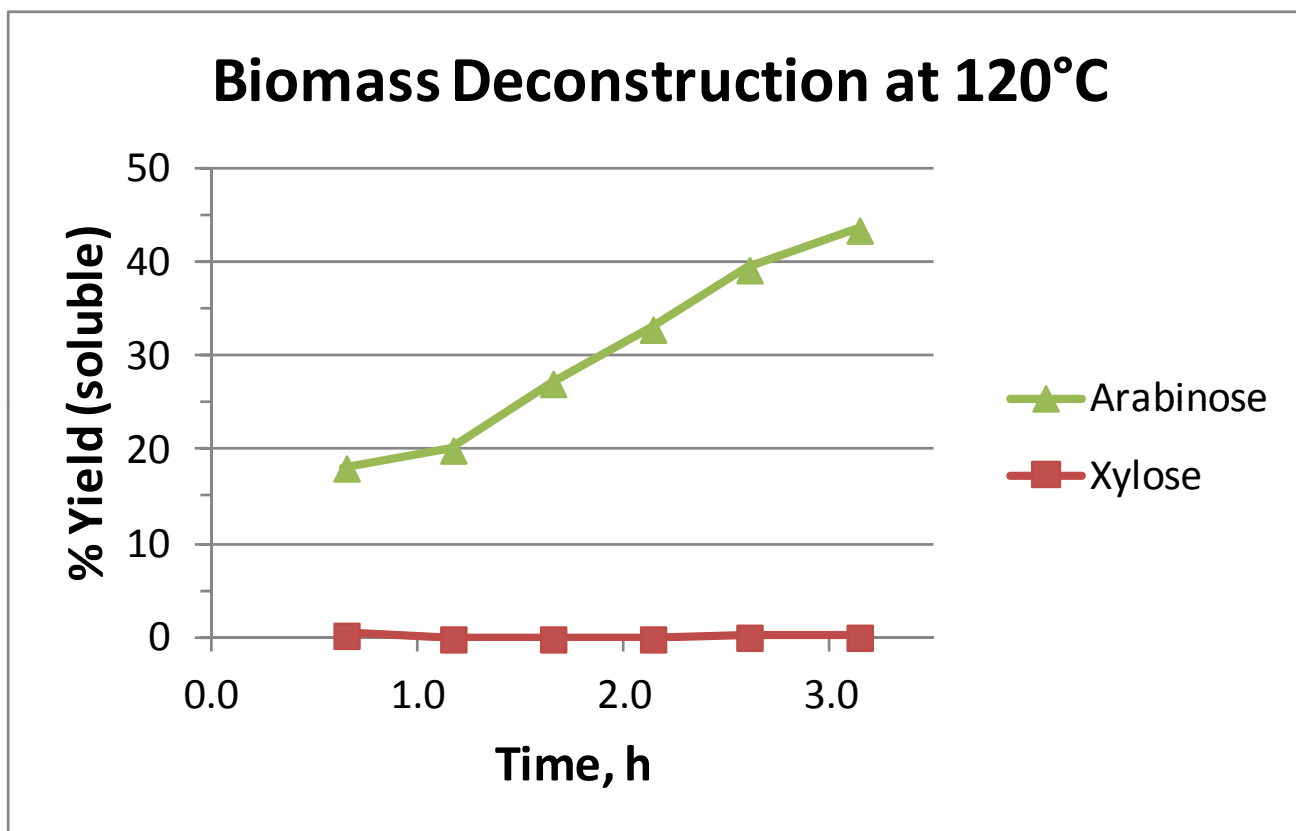
- To date, preliminary deconstruction/pretreatment experiments have been run from 120°C to 200°C to test concept
- Important control experiment: test the sugar stabilization method for sugars under reaction conditions

Results for monomeric sugars after 3 h at 160 °C under deconstruction conditions:

	wt% Before	wt% After	% Change
Xylose	0.016	0.015	-5.6
Arabinose	0.004	0.004	0.0
Mannose	0.030	0.027	-9.1
Glucose	0.160	0.166	3.4
Galactose	0.007	0.007	0.0

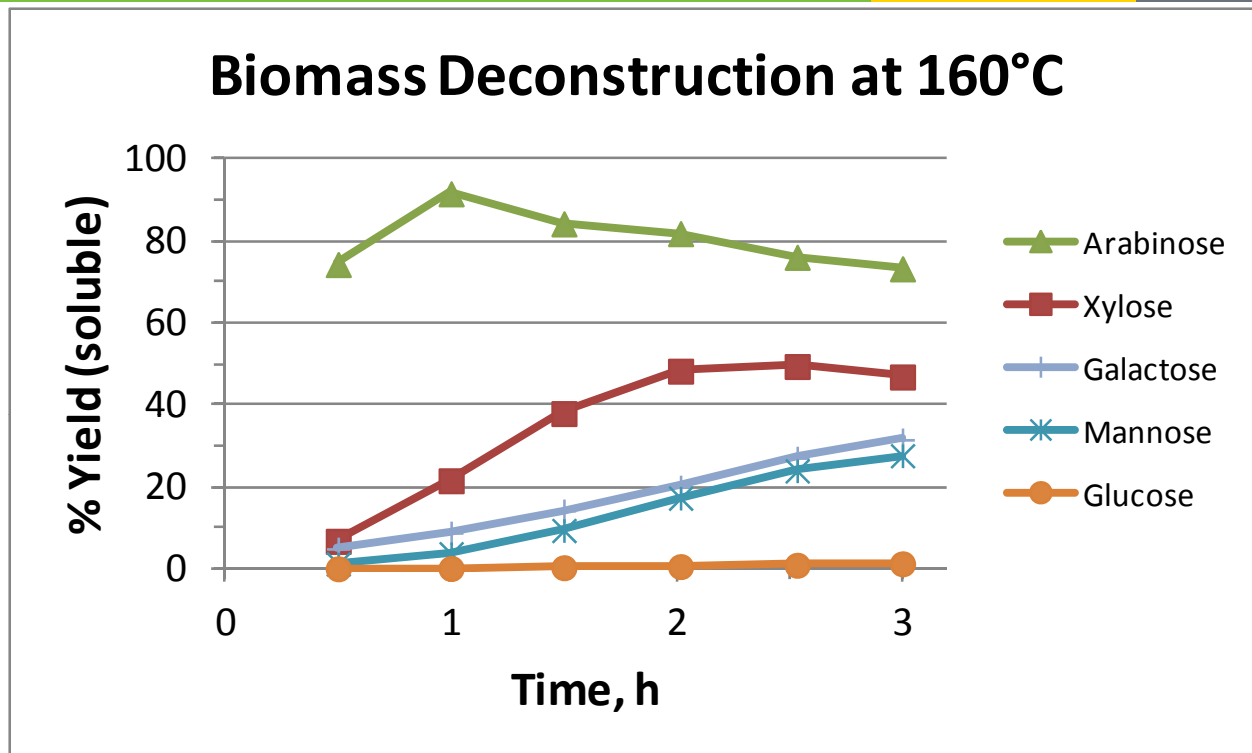
- Sugar stabilization appears to work well at 160 °C





- Arabinose cleaved selectively at 120 °C
- White insoluble solids also observed in the samples
- Exploring whether acetyl groups can also be selectively removed

## 2 – Technical Progress (cont'd)

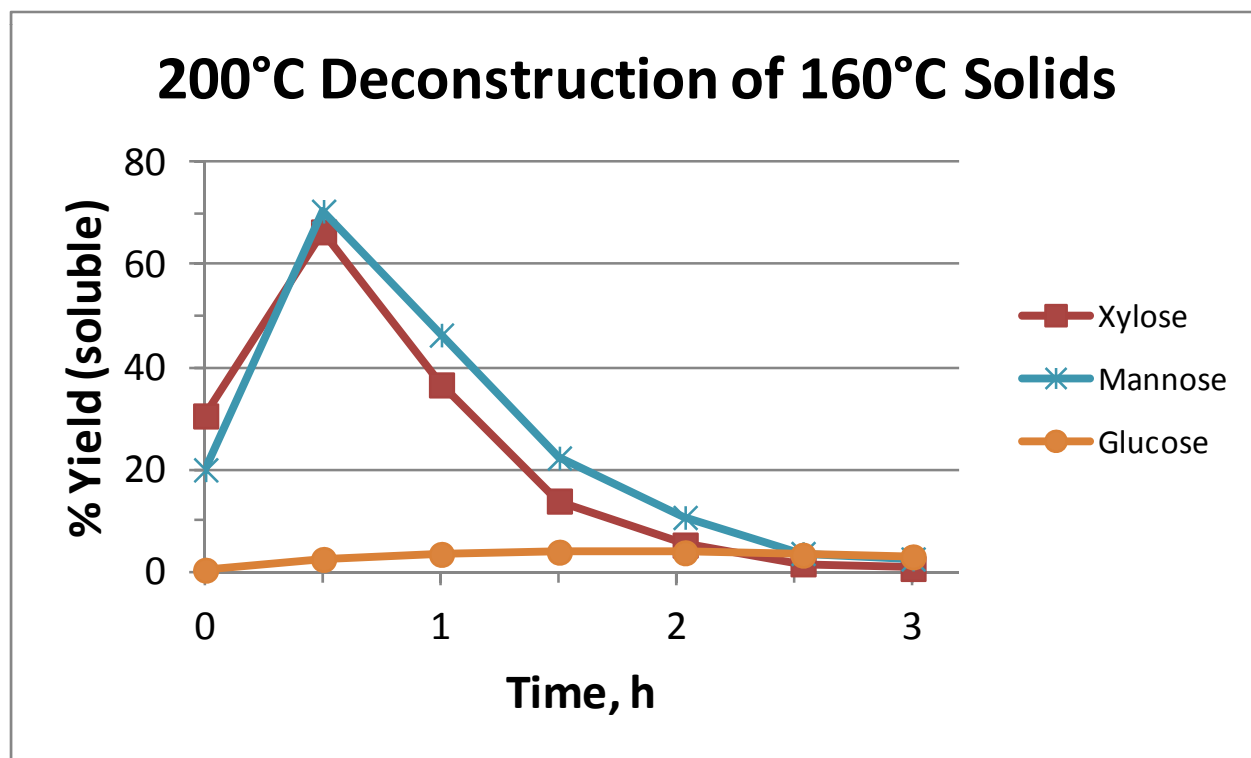


Recovered  
Unreacted Feed

- Hemicellulose-derived sugars obtained at temperatures up to 160 °C
- Product also present as insoluble white solid and water soluble oligomers
- No indication of humin or tar formation
- Recovered biomass: 1.7% xylan, 1.6% mannan, and 51.7% glucan

## 2 – Technical Progress (cont'd)

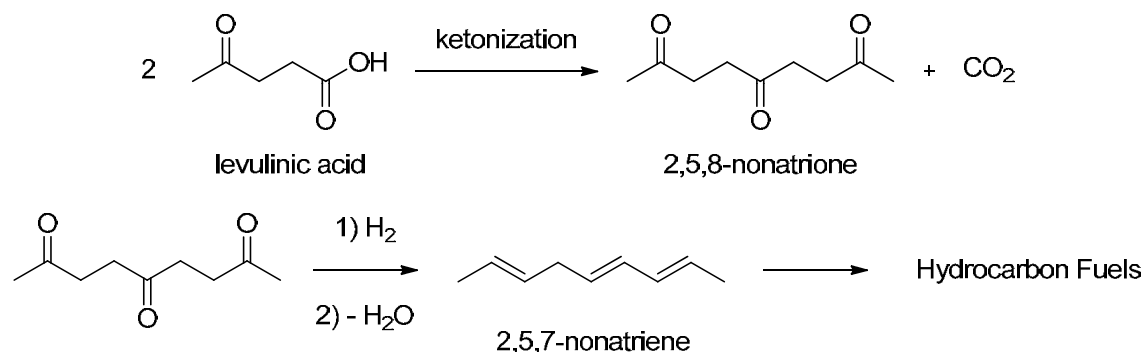
- Solids from the 160 °C experiment re-processed at 200 °C
- 30% of the feed converted; remaining hemicellulose sugars released; glucose oligomers, but little soluble glucose monomer formed
- White insoluble solids are formed, presumably polysaccharides
- % Yield glucose if white solids and oligomers are cellulosic = ~48%
- Sugar stabilization apparently not as effective at 200°C; improvements will be explored
- No indication of humin or tar formation



### Task 2 – Levulinic Acid Upgrading

- Conversion of levulinic acid to distillate hydrocarbon fuels

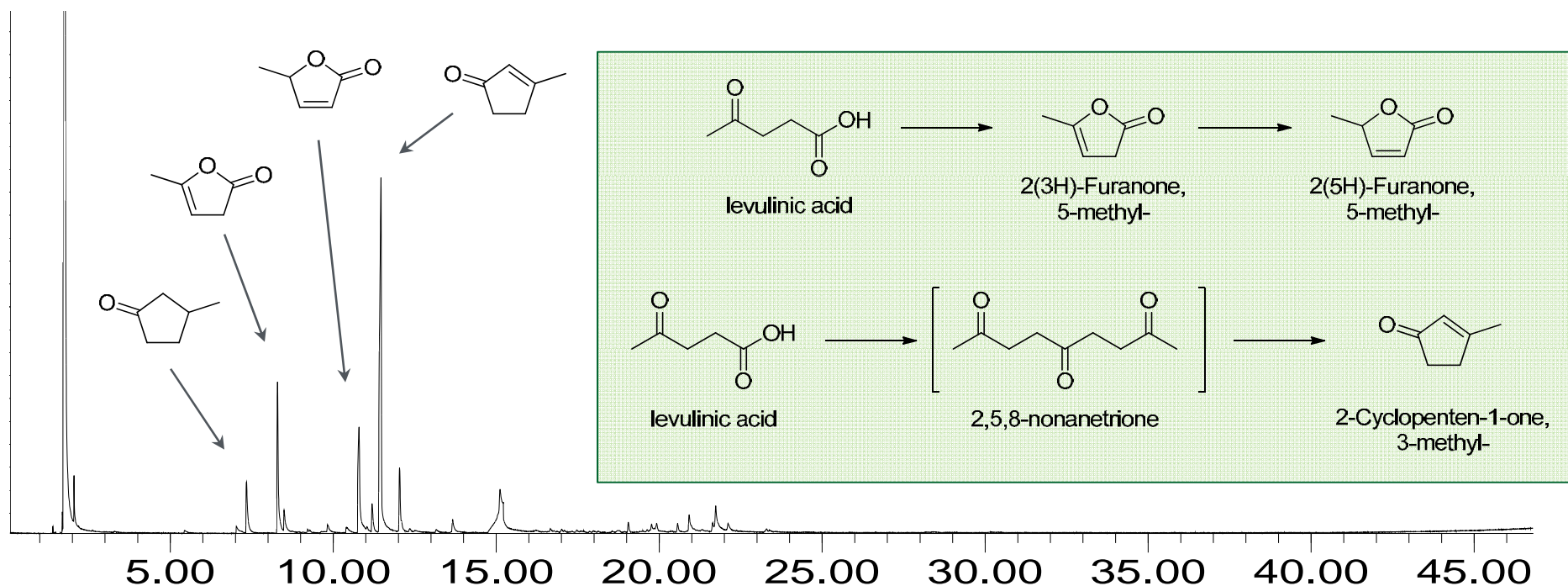
- Approach is to use ketonization to increase carbon chain length, followed by hydrogenation, dehydration, and oligomerization:



- Previous work by Wheeler, et al. suggests ketonization occurs, but the very basic Ca(OH)<sub>2</sub> “catalyst” used caused internal aldol condensation of the trione to form cyclic ketones. This approach requires significant catalyst processing and potentially adds ash
- Prior PNNL work identified heterogeneous ketonization catalysts which were highly active and much less basic than Ca(OH)<sub>2</sub>
- Believed the less basic catalysts would be less active for aldol condensation

## 2 – Technical Progress (cont'd)



- Products from 360 °C reaction of LA consistent with:
  - Known ring closure of LA to angelica lactones
  - Previously proposed follow-on reactions of nonanetrione intermediate to methyl cyclopentenone (Schwartz, Wheeler, et al. *Green Chem.* 12 (2010) 1353-1356)



### Screening Results to Date

- Ketonization appears to occur over the heterogeneous catalysts tested
- Aldol condensation to ring-closed products remains facile
- Methyl cyclopentenone could be easily deoxygenated and oligomerized to fuel products, but ...
- Because the focus is on linear hydrocarbons, strategies to minimize aldol condensation have been devised and are being explored
  - Protection of the ketone as a ketal is expected to prevent aldol condensation and ring closure; ketal formation is very easy (similar to Segetis ketal preparations)

## 2 – Technical Progress (cont'd)

Title/Description	Due Date	Completed
Identify best catalysts discovered in micro screening experiments for further ketonization testing	Dec-12	
Identify best catalysts for ketone hydrogenation discovered in screening experiments	Mar-13	 *
Identify the best catalysts for dehydration discovered in screening experiments	June-13	In Progress
Determine the feasibility of deconstruction process	Sept-13	70%
Prepare a draft manuscript for publication of results	Sept-13	On Track

\* Anticipated ketone intermediate was more reactive than expected and converted to other products.

- The deconstruction methodology, in early testing, appears to provide a beneficial path to:
  - Extract hemicellulose and cellulose oligomers from biomass in a form expected to be easily converted by enzymes to monomeric sugars or for direct thermochemical conversion (Bt-D. Pretreatment Chemistry; Bt-A. Biomass Fractionation)
  - Maximize carbon yield to useful products
  - Minimize carbon loss to humins (and therefore minimize separations to remove humins before further processing)
- Catalytic conversion of levulinic acid
  - Requires more work to assess the technical and economic feasibility of using it as a platform for fuels production (Bt-J. Catalyst Development)
- Alignment with BETO (from MYPP)
  - “Focused at improving overall cost effectiveness and productivity to enable larger sources of feedstocks to be used in producing fuels and chemicals via biological, chemical, or hybrid routes.”
  - This research enables the Biochemical Conversion Area’s strategic goal “*to develop commercially viable technologies for converting biomass feedstocks via biochemical routes into energy dense, fungible liquid transportation fuels, as well as bioproducts or chemical intermediates, and bioenergy.*”



## 4 – Critical Success Factors

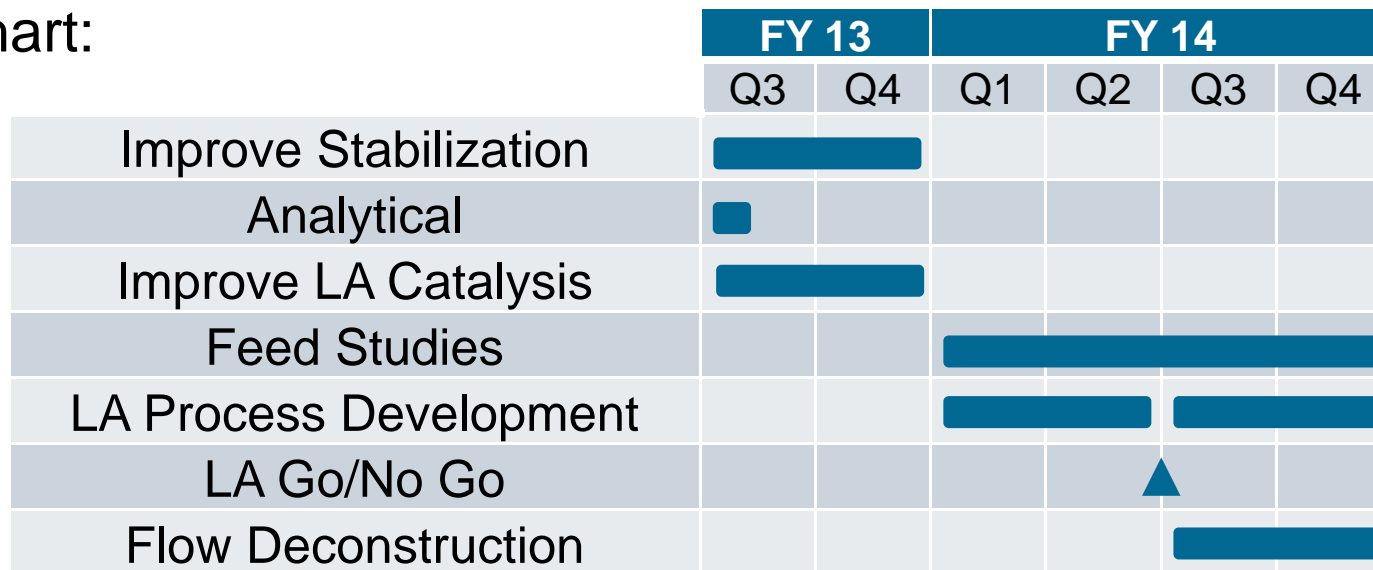
- Establish Viability:
  - Demonstrate technical feasibility of processes
  - Minimize process steps, possibly by combining compatible steps into fewer unit operations, or integrate to the extent possible
  - Identify the best commercial fit for developed technologies
- Challenges:
  - Maximize product selectivities and yields. Strategies to desired products are being explored
  - Close mass and carbon balances
  - Gain a better understanding of effects of process parameters
- Successful Outcomes:
  - Improve economics by maximizing whole biomass carbon utilization
  - Decrease capital expenses by reducing severity of process conditions
  - Produce linear and *iso*-paraffinic hydrocarbon fuels that complement aromatic fuels from pyrolysis or HTL of woody feedstocks

# 5 – Future Work

## Work Plan:

- FY13 – Continue to improve stabilization effectiveness in deconstruction
- FY13 – Establish analytical for determining furans, acids, and oligomers
- FY13 – Determine effectiveness of approach to minimize aldol condensation in catalytic LA upgrading
- FY14 – Investigate other feeds, esp. with higher ash
- FY14 – Explore possibility of a continuous deconstruction process
- FY14 – Continue LA upgrading process development (Go/No Go)

## Gantt Chart:



- Approach
  - Unique approaches are being taken to deconstruct biomass and convert levulinic acid to linear and *iso*-paraffinic fuels
- Technical accomplishments
  - The deconstruction methodology appears sound. A strategy for converting LA to desired products is being pursued. More work is needed to better define issues and opportunities.
- Relevance
  - Pretreatment, fractionation, and catalyst chemistry barriers are being addressed
- Critical Success factors and challenges
  - Technical feasibility needs to be confirmed
- Future Work
  - Future work will resolve technical issues and lead to an economic analysis
- Technology transfer
  - Better definition of products and process parameters is needed

# Additional Slides

- This is a new project and has not been reviewed previously.

- No publications or presentations to date.
- Brief discussions have been had with Virent, but they cannot be described as commercialization efforts at this early date.