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# DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review

## New Catalytic Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels

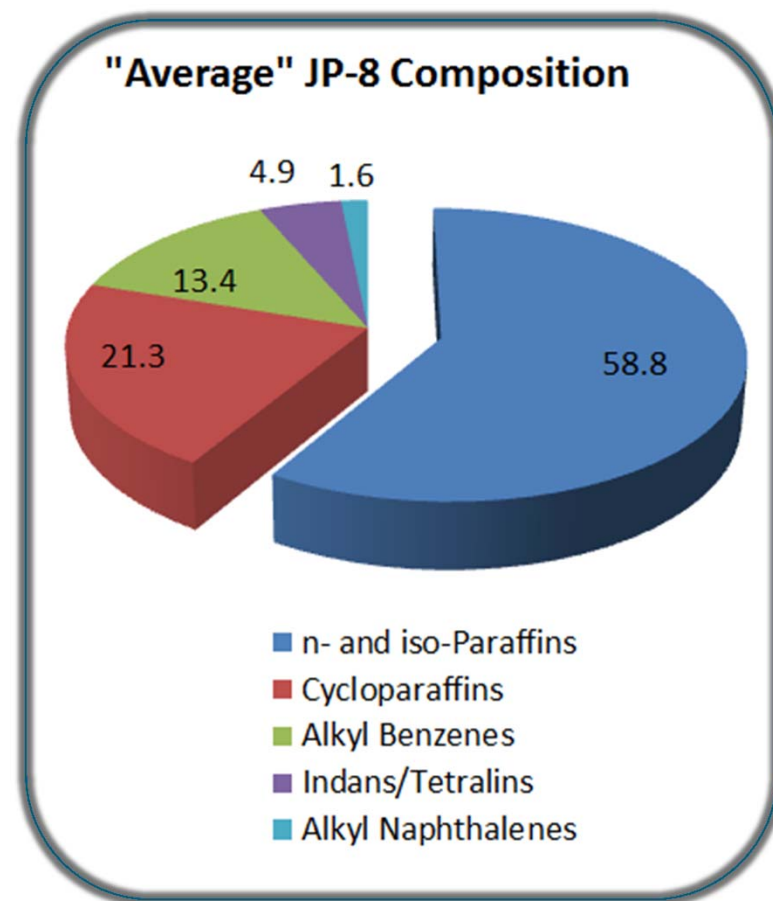
March 24, 2015  
Conversion R&D Review

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PNNL

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# Goal Statement

- ▶ Problem #1: Current thermal methods to biorenewable hydrocarbon fuels suffer from limited feedstocks (lipids) or result in primarily aromatic products (FP, HTL)
- ▶ Problem #2: Ash fouls catalysts and scales reactors in catalytic processing
- ▶ Goal: Develop catalytic routes to hydrocarbon fuels from lignocellulosic feeds
  - Develop catalytic methods that make open-chain *n*- and iso-paraffin fuel components
  - Maximize carbon utilization
  - Minimize H<sub>2</sub> utilization
- ▶ Benefits to BETO and the US
  - Enables the development of technically and commercially viable biorefineries to produce liquid transportation fuels and chemicals
  - Contributes to attaining the fuel production cost target (\$3/gge [\$2011])
  - Increase energy security and minimize reliance on foreign petroleum
  - Robust biorefineries create jobs, lower GHG, and support a domestic bio-economy



# Quad Chart Overview

## Timeline

- ▶ Project start date: FY 2013
- ▶ Project end date: FY 2017
- ▶ Percent complete: 66%

## Barriers

- ▶ Barriers addressed
  - Bt-A Biomass Fractionation;
  - Bt-D Pretreatment Chemistry;
  - Bt-J Catalyst Development

## Budget

	Total Costs FY 10 –FY 12	FY 13 Costs	FY 14 Costs	Total Planned Funding (FY 15-Project End Date)
DOE Funded	\$0	\$397,705	\$329,220	\$1,223,075
Project Cost Share (Comp.)				

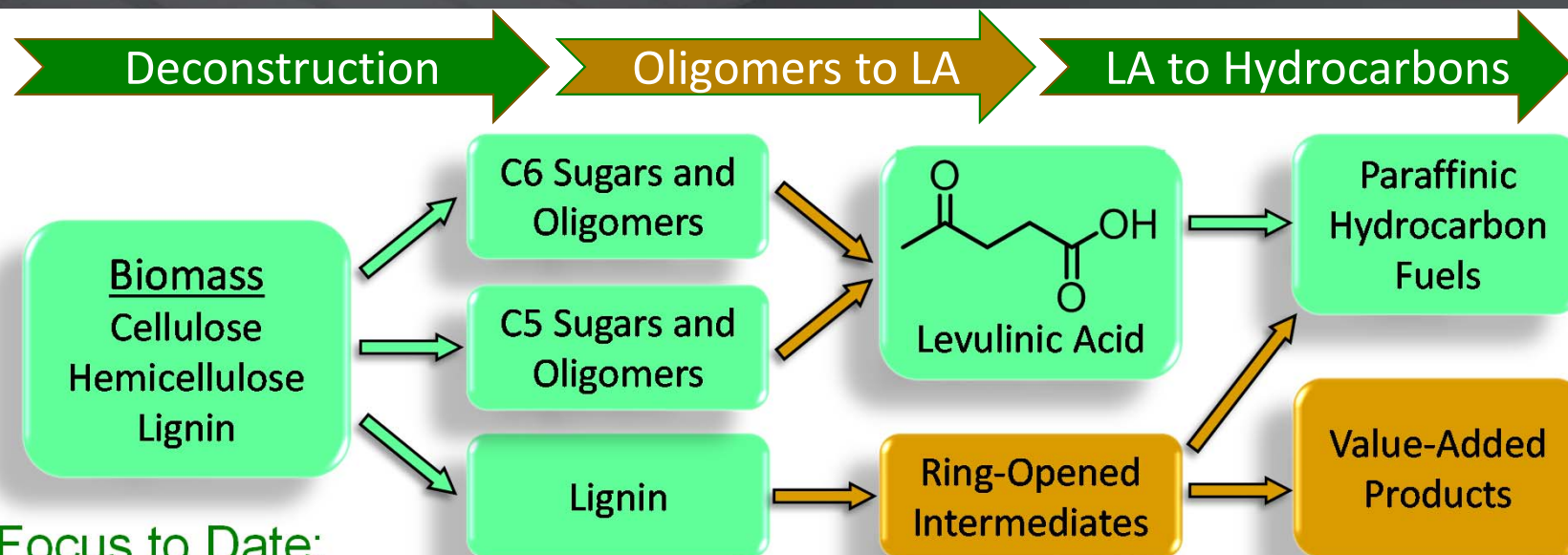
## Partners

- INL – feedstocks
- NABC – feedstocks
- Discussions about processing needs - Virent
- Possible future partnership – WSU, lignin conversions

# 1 - Project Overview

- ▶ Thermal biomass processing has its **problems**:
  - Conducted at **high temperatures and pressures** – capital expense
  - **Limited control** over products – mostly aromatics and cyclics, carbon loss
  - **Upgrading can be difficult** – reactivity, poor thermal stability, coking, carbon loss
- ▶ Catalytic biomass processing offers:
  - Opportunities for **lower temperature and/or pressure** processing
  - Opportunities to **control classes of hydrocarbons** produced – open chain
  - **Challenges by ash contamination** (from biomass and standard deconstruction methods) scales reactors and deactivates catalysts
- ▶ This project addresses opportunities and challenges facing viable industrial catalytic processing:
  - Deconstruction that **maximizes carbon recovery**
  - Deconstruction that **minimizes ash** contamination of sugar feeds
  - **High-yield conversions** of sugars to hydrocarbons
  - Control of **hydrocarbon structure** – open-chain hydrocarbons desired
  - Minimize process steps and **integrate** to an overall process

## 2 – Approach (Technical)



### ► Focus to Date:

- Novel pretreatment and deconstruction
  - New deconstruction medium (inexpensive, green)
  - Minimize ash contamination, degradation, and humin formation
- Levulinic acid (LA) conversion to hydrocarbons
  - Heterogeneous catalysis

### ► Future:

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

# 2 – Approach (Management)

## ▶ *Critical success factors*

- Transition from **batch to continuous** deconstruction
- Demonstrate technical and economic **viability** of processes
- Process **integration** and intensification
- Gain a better understanding of effects of **process parameters**
- Identify the best **commercial fit** for developed technologies; **transfer technology**

## ▶ *Potential Challenges*

- Product selectivities and **yields**.
- Accurate mass and **carbon balances**
- Limited existing foundational **science base**

## ▶ *Structure of the approach*

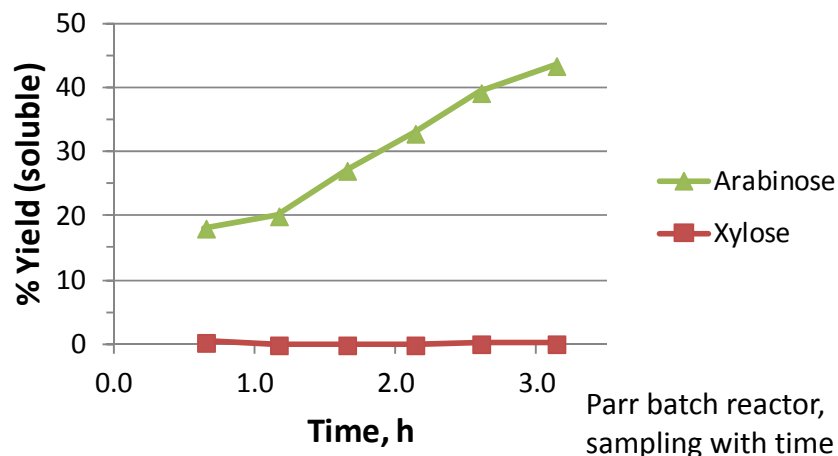
- **AOP, milestones, regular quarterly reporting, deep dive**
- **Go/No-Go** decision points used to verify or modify strategy
- **TEA & LCA** to guide technology development
- Frequent **team meetings**

# 3 – Technical Progress – Deconstruction

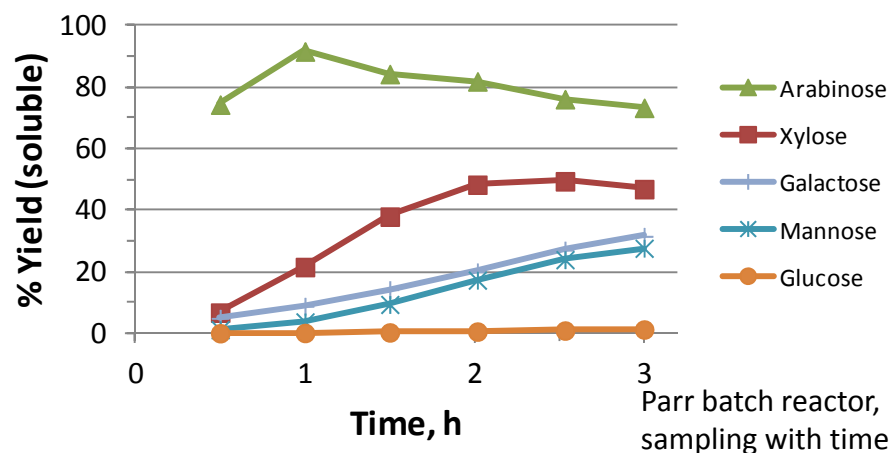
- ▶ Deconstruction Reactors
  - Batch – Parr, 300 mL, fritted dip-tube for sampling with time
    - 7.5 g biomass, 3 h reaction time, 0.5 h samples, 120 °C to 200 °C
  - Flow – custom reactor
    - 1.25 g biomass, about 0.5 h contact time, 120 to 220 °C
- ▶ Feeds
  - Yellow Pine
  - Corn Stover
  - Water and ethanol washed (extractives removed)
- ▶ Sugars Analytical
  - Agilent HPLC with Agilent 1260 Infinity ELSD detector
  - Waters X-Bridge amide column (3.5  $\mu$ m, 250 mm  $\times$  4.6 mm)
  - Eluent is acetonitrile (40%), acetone (40%), water (20%) and ammonium hydroxide (0.1%); flow rate is 0.6 mL/min

# Batch Deconstruction - Pine

## Biomass Deconstruction at 120°C



## Biomass Deconstruction at 160°C



- Arabinose cleaved selectively at 120 °C
- Hemicellulose-derived sugars obtained at temperatures up to 160 °C
- Oligomeric solids (at early reaction times) and water soluble oligomers formed
- No indication of humin or tar formation



Remaining  
Biomass



# Batch Deconstruction – Corn Stover

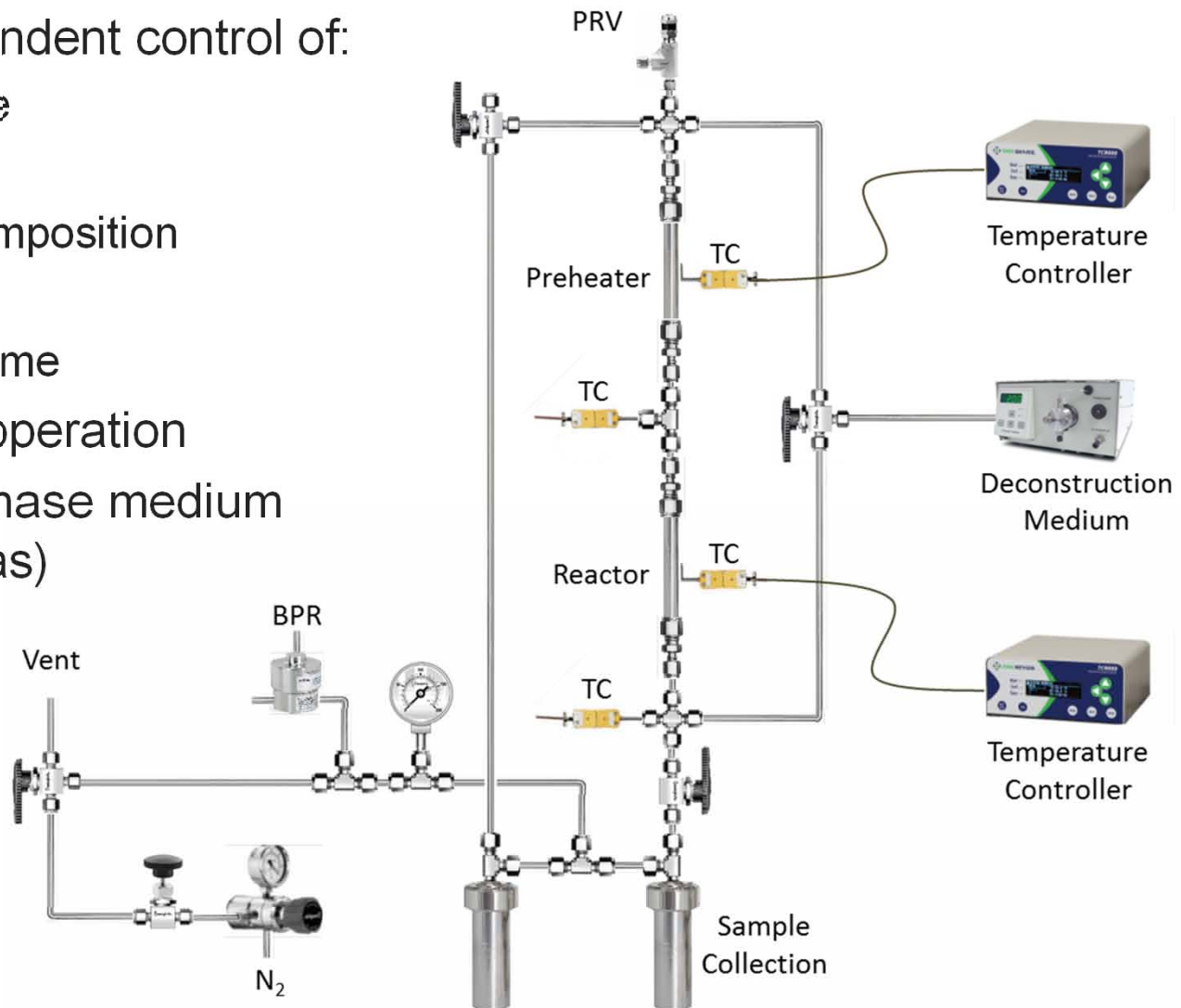
- ▶ Corn stover deconstruction gave about the same carbohydrate recovery as pine:
  - 100% hemicellulose could be recovered at 160 °C
  - 100% hemicellulose and 50% cellulose recovered at 200 °C
- ▶ Polysaccharide removal leaves the ash behind
  - After deconstruction, *most ash is found in the remaining biomass solids, not in the deconstruction medium where the polysaccharides are*
  - *Low ash polysaccharide solution may be a good feed for catalytic reactors*

Ash Distribution After Deconstruction:

Run	% Ash in Medium	% Ash in Solids
3	0.5	99.5
5	1.3	98.7
8	0.6	99.4
11	0.2	99.8

# Deconstruction Flow Reactor

- ▶ Allows independent control of:
  - temperature
  - pressure
  - medium composition
  - flow rate
  - residence time
- ▶ Flooded bed operation
- ▶ Condensed phase medium desired (no gas)



# Flow Deconstruction – Preliminary Results

Feed	°C	Run Time (h)	% Wt Loss	Mole % Soluble Sugar	% Recovery (by solids digestion)				
					Xyl	Arab	Man	Gal	Glu
Pine	120	3	11.0	0.9	39	100	0	0	17
	160	3	35.1	4.1	87	100	89	100	4
	~220	4	50.0	0.0	100	100	100	100	46 <sup>a</sup>
Corn Stover	160	3	55.8	1.9	96	100	100	100	35
	220	3	65.3	0.0	100	100	100	100	74

Arabinose selectivity at 120 °C

Hemicellulose recovered at 160 °C

Potential for high levels of deconstruction

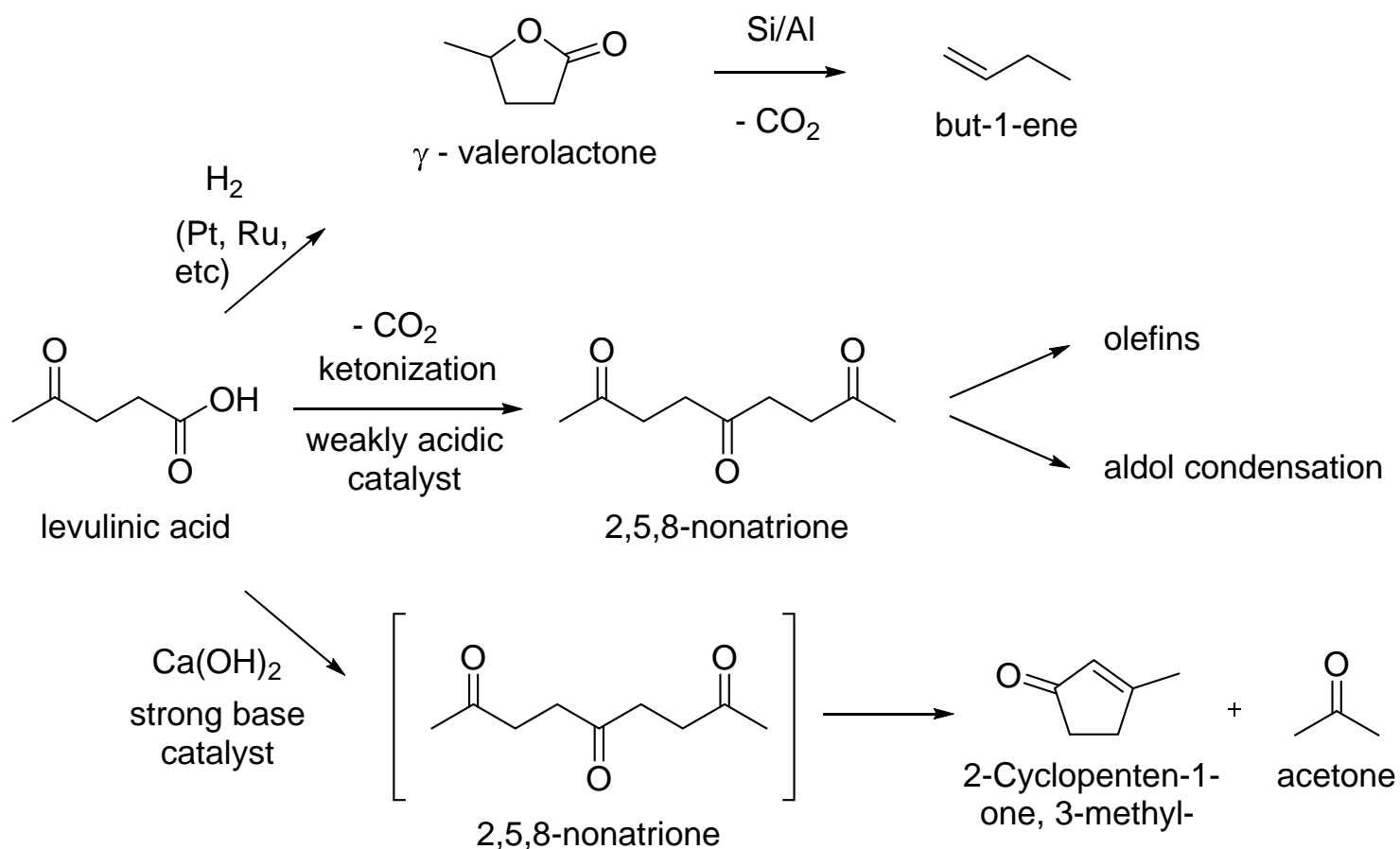
a) material at the top of the reactor

b) material at the bottom of the reactor

- ▶ 160 °C effective at hemicellulose recovery; > 200 °C recovers cellulose
- ▶ Most of the carbohydrate product is oligomeric; little soluble sugar
  - About 91 mole % carbon balance overall
- ▶ Several more process options available to improve performance
- ▶ New IP

# 3 – Technical Progress – Levulinic Acid Conversion

- Some possible levulinic acid conversion approaches to *iso*-paraffinic hydrocarbons:



Dumesic  
J Catalysis 281  
(2011) 290-299

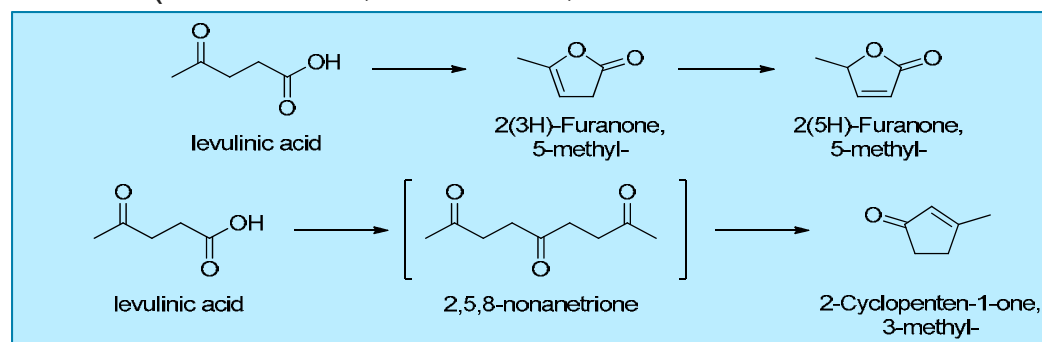
PNNL  
Initial Approach

Wheeler  
Green Chem 12  
(2010) 1353-1356

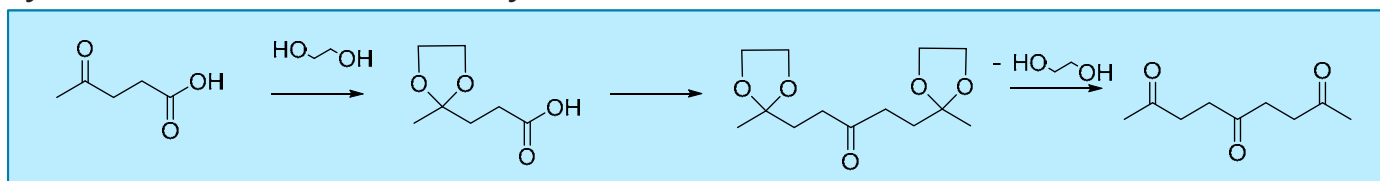


# Levulinic Acid Ketonization

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

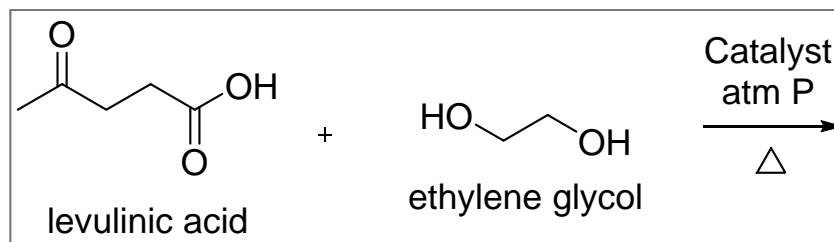


- ▶ New strategy – protect the ketone as a ketal of ethylene glycol (EG)
  - Prevent ring closure to the lactones
  - Prevent internal aldol condensation of the ketonization product
  - Ketal formation is very easy (similar to Segetis ketal preparations)
  - Easy to remove EG for recycle



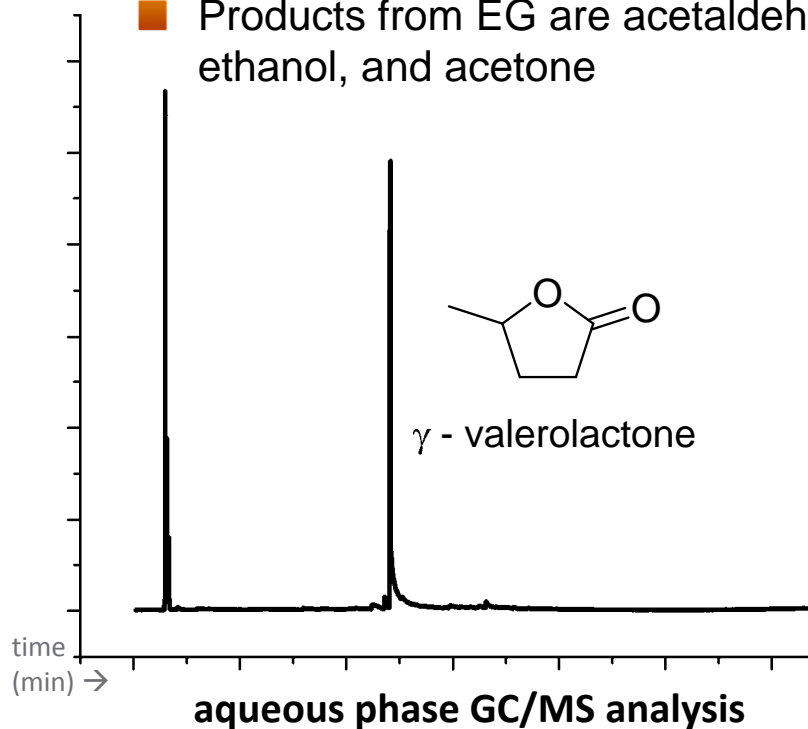
- ▶ Results were surprising ...

# Levulinic Acid Conversion to GVL and Polyunsaturated Hydrocarbons



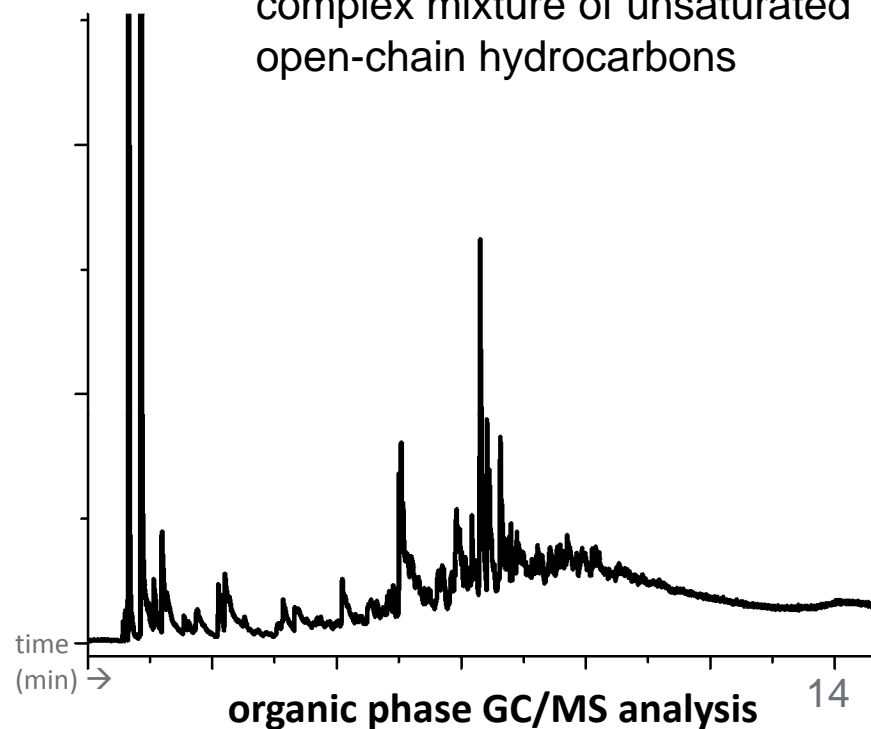
## ▶ 330 °C, atm. P

- A single aqueous phase product
- LA is hydrogenated by EG to GVL
- Products from EG are acetaldehyde, ethanol, and acetone



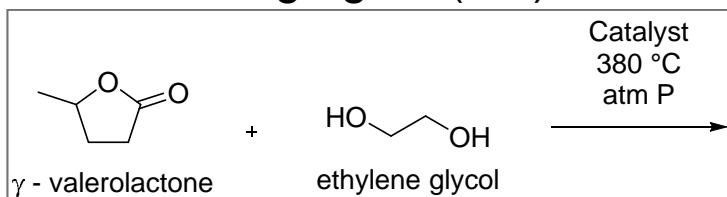
## ▶ 380 °C, atm. P

- An organic phase forms
- LA is converted via GVL to a complex mixture of unsaturated open-chain hydrocarbons

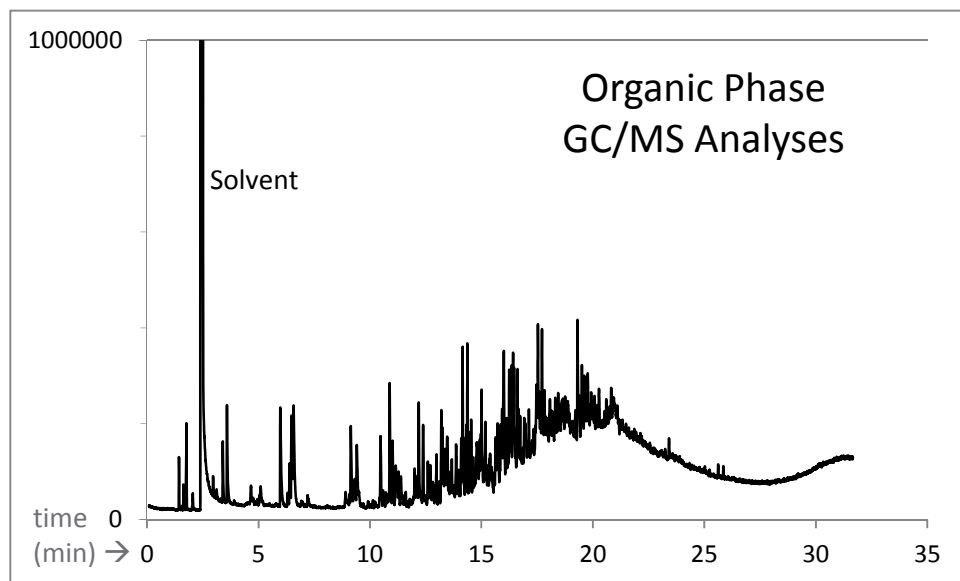


# GVL Conversion With and Without EG at 380 C, atm. P

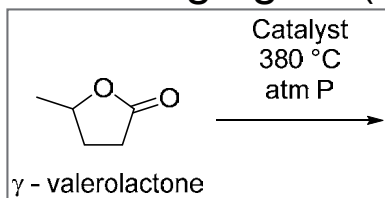
## ▶ With reducing agent (EG)



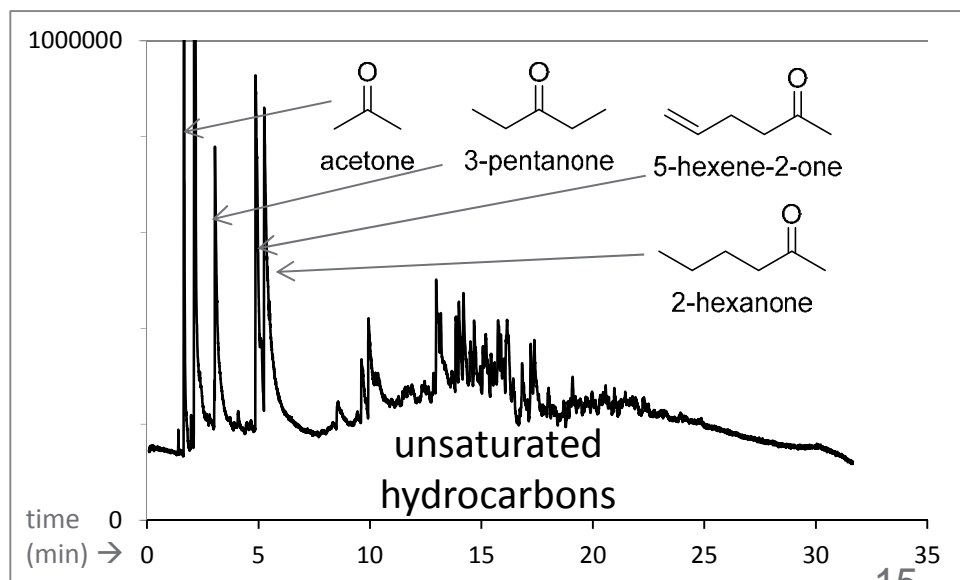
- main product is unsaturated hydrocarbons that are largely deoxygenated
- ketone products greatly decreased
- higher boiling products are formed



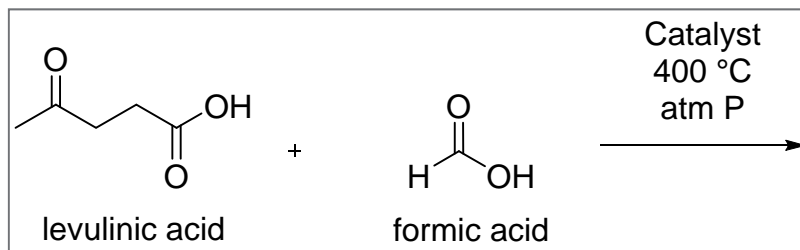
## ▶ Without reducing agent (EG)



- ketone products prevalent
- the ketones are consistent with ketonization of intermediates from GVL ring opening
- the aqueous phase contains MEK, EtOH, and 1-PrOH

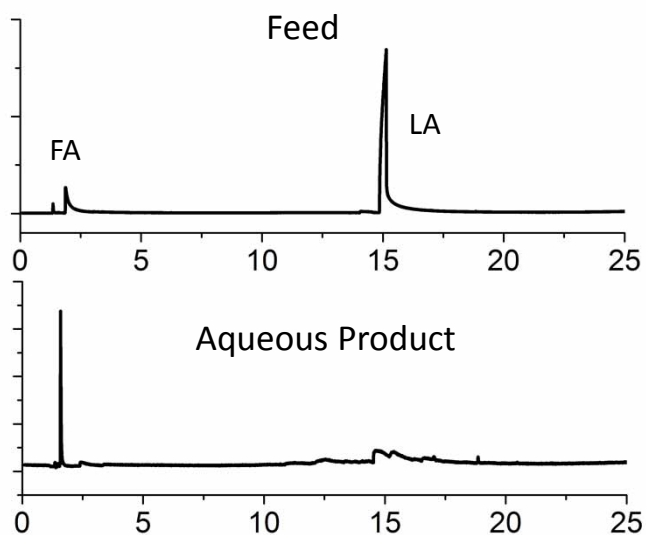


# LA Catalytic Conversion to Hydrocarbons with Formic Acid



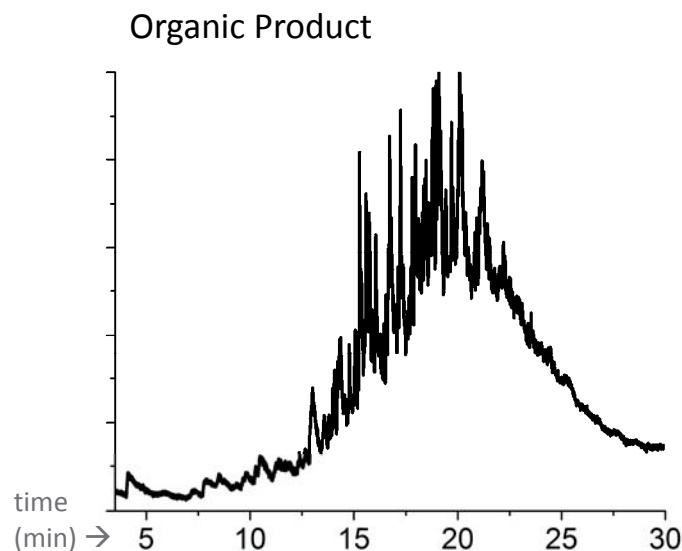
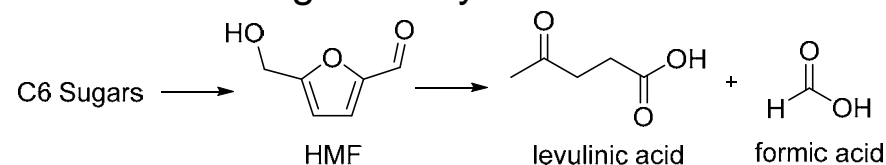
## ► 1:1 LA : Formic Acid

- Unsaturated hydrocarbons produced
- Open-chain products predominate
- Product is partly deoxygenated
- Very little light ketone products
- Complete LA and FA conversion



## ► Significance

- C6 sugars dehydrate to 1:1 LA:FA





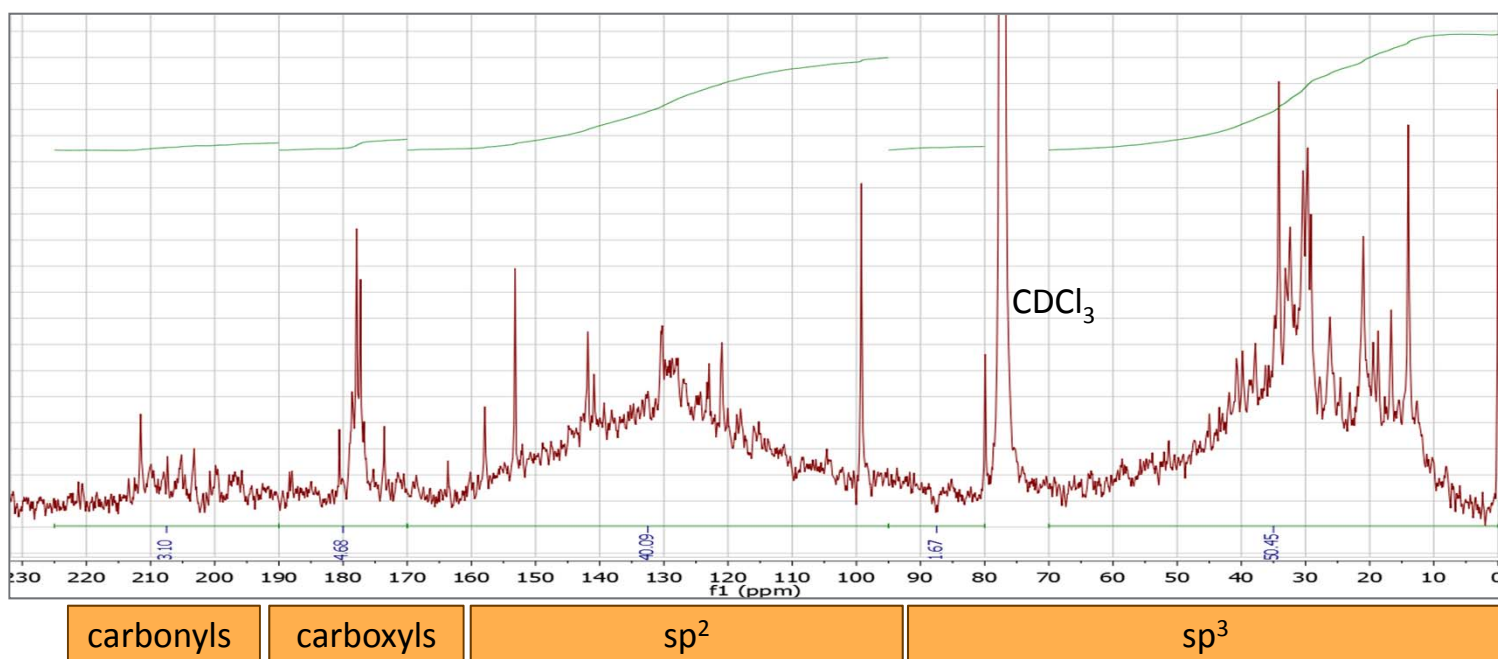
# $^{13}\text{C}$ NMR Spectrum of LA + FA Organic Product

## ► NMR Results

- Mostly alkanes
- Contains olefins
- Either aromatics or angelica lactones are present
- No aldehydes
- Low ketones

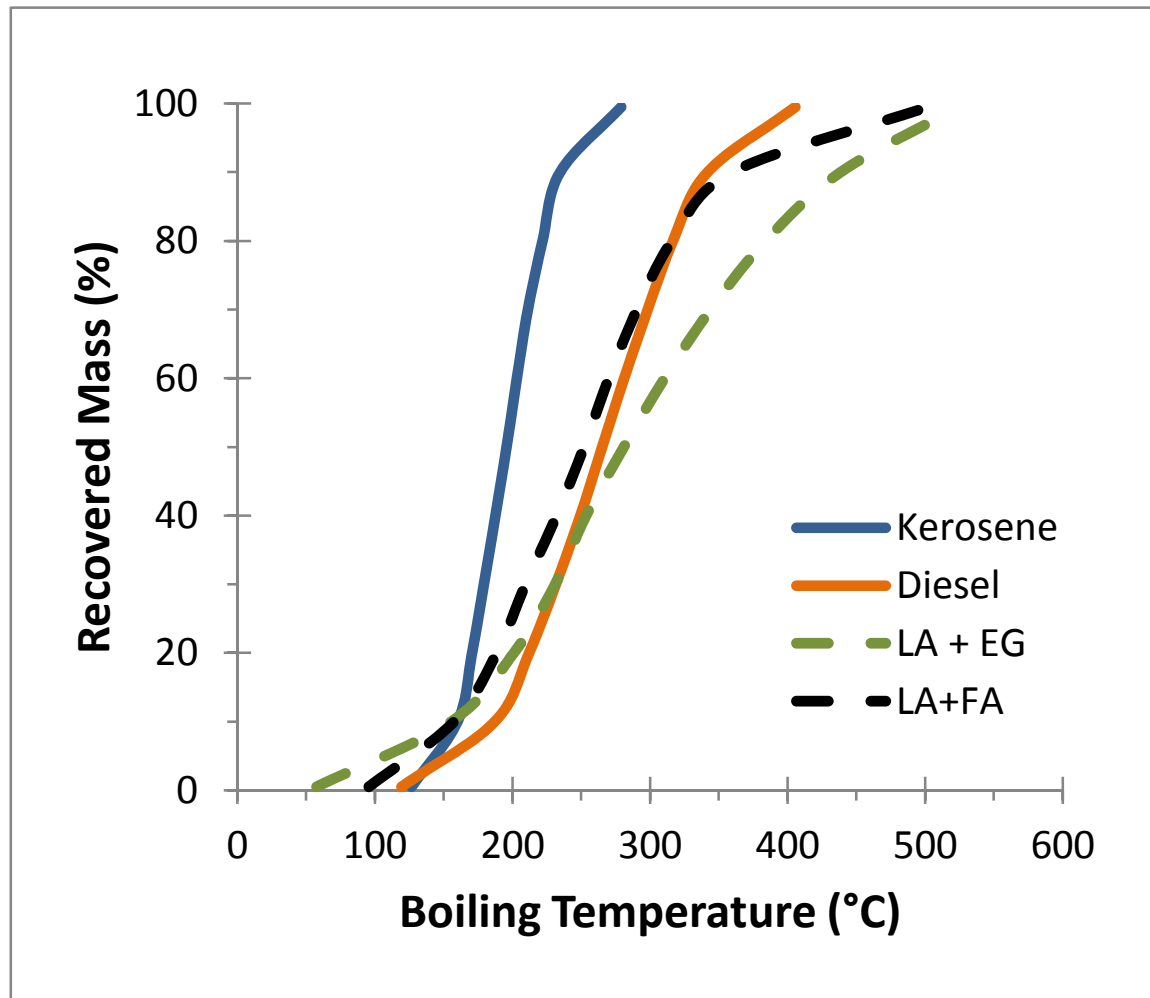
Functional Group	Content by $^{13}\text{C}$ NMR
Carbonyls (ketones, aldehydes)	3%
Carboxyls (acids, lactones)	5%
$\text{sp}^2$ Carbon (olefins, aromatics)	40%
$\text{sp}^3$ Carbon (saturated alkanes)	52%

$^{13}\text{C}$  NMR



# Simulated Distillation of LA + FA and LA + EG Organic Products

- Organic product has a boiling distribution similar to diesel
- New IP

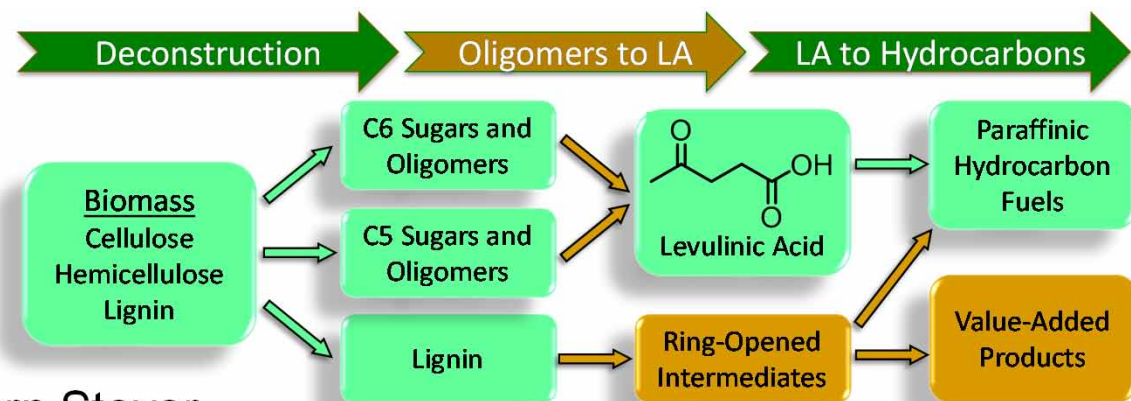


# 4 – Relevance

- ▶ This project addresses the strategic goal of Conversion R&D, which is *“to develop commercially viable technologies for converting biomass feedstocks into energy-dense, fungible, liquid transportation fuels, as well as bioproducts or chemical intermediates and biopower”*
- ▶ It also addresses the strategic goal of the Biochemical Conversion Technology Area, which is *“to develop commercially viable technologies for converting feedstocks via biological and chemical routes into energy-dense, fungible, liquid transportation fuels and chemicals”*
- ▶ These goals are addressed in this project by:
  - Directly converting levulinic acid to **distillate range hydrocarbons**
  - **Maximizing carbon utilization** through a new deconstruction technology
  - Creating a **low-ash feedstock** of sugar oligomers for chemical conversions
  - A **variety of feeds** appear to be viable using the deconstruction technology
- ▶ The need for bio-renewable **open-chain** hydrocarbon fuel blend stocks is addressed by this project
- ▶ The technology being developed **complements other conversion technologies** and produces a different fuel product

# 5 – Future Work

- ▶ Deconstruction
  - Continue parameter testing to maximize deconstruction
  - Scale up reactor – make material for Oligomer → LA process development
- ▶ Levulinic Acid Conversion to Hydrocarbons
  - Determine the optimal ratio of formic acid/LA to maximize deoxygenation
  - Scale up reactor – make enough sample to hydrotreat (< 50 mL)
  - Test other catalysts
  - Determine catalyst lifetime
- ▶ Oligomer → LA Process Development
  - Integrate Deconstruction with LA Conversion
- ▶ Tech Transfer
  - IP development
  - Industrial partners
- ▶ Key milestones
  - Q3 – TEA
  - Q4 – Go/No-Go (Corn Stover – recover 100% hemicellulose, 75% cellulose)



# Summary

- ▶ A novel deconstruction process has been demonstrated for pine and corn stover feeds. FY15 stretch milestone target was easily attained and the target in the Go/No-Go nearly attained already
- ▶ Flow deconstruction allows process improvements and independent control of deconstruction process parameters
- ▶ Deconstruction separates carbohydrates from the ash
- ▶ LA is converted to deoxygenated hydrocarbons in the distillate range in a single process step at ambient pressure without added hydrogen
- ▶ The catalyst ketonizes, hydrogenates ketones and aldehydes, dehydrates alcohols, carries out aldol condensations, and oligomerizes simultaneously
- ▶ The catalyst does not contain platinum group metals and is made commercially
- ▶ Future work will integrate deconstruction and LA conversion processes



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# Additional Slides

# Responses to Previous Reviewers' Comments

- ▶ Overall Impressions:
- ▶ • A good addition to BETO's portfolio of projects. This is fundamental research that should continue.
- ▶ • In my opinion, it sounds like the deconstruction process will be expensive, so the TEA on the products will be important. Production of fuels may not be viable using these methods.
- ▶ • Project seems to be a 'one-off' from some previous work in the literature. Project team needs to make a better case for why project should go on.
- ▶ • The deconstruction method of biomass and the ultimate production of linear HC is a novel approach that would fill the void in this area. The project is in its very early stages and the PI has posed several questions that need to be addressed in the future work.
- ▶ • This is a scoping project to evaluate a novel biomass deconstruction method and a chemical conversion process for the conversion of LA to higher value product. The advantages of the biomass deconstruction effort should be more clearly communicated. The chemical conversion of LA seems that it would benefit from efforts to understand the fundamental chemical reaction mechanism(s) that are being explored.
- ▶ • Very early in the project cycle, but it appeared that the team has a good plan. My main concern is that it appears to be two projects in one: biomass deconstruction to sugars and levulinic acid conversion to hydrocarbon fuels. Integration appears to be missing.

## Responses to Reviewer Comments:

Thank you for your comments. The economic viability of the overall approach is yet to be determined, but is a key consideration in the design of the project and in process development. Regarding deconstruction, there are several potential economic and technological advantages over the current state of the art that I was unable to comment on at the review due to a positive breakthrough that is being utilized to seek intellectual property. After the patent application is public, there will be significantly more disclosure. Overall, the process was designed to maximize carbon efficiency, a critical need in developing an economical process. Continued experimentation will assess the process robustness and lead to the quantification of economic advantages.

Early slides in the presentation showed how individual steps in the proposed process integrate for the conversion of biomass to hydrocarbon fuels. The steps include biomass deconstruction, separate conversion of C5 and C6 sugars (or oligomers) to levulinic acid as a common intermediate, and conversion of levulinic acid to ring-opened fuel precursors. The two tasks for initial studies, deconstruction and levulinic acid upgrading, were chosen because they are key steps in the process and they are novel and untested. While they appear disconnected, they are really individual steps in an overall cohesive strategy. Conversion of oligomers or sugars to levulinic acid will be conducted later, based upon the results of earlier tasks and guided by literature precedent, to complete the process.

# Publications, Patents, Presentations, Awards, and Commercialization

- ▶ None. The project is maturing to the point where these activities will be undertaken.

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