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DOE Bioenergy Technologies Office (BETO) 2017 Project Peer Review

Catalytic Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels – Deconstruction (2.2.3.105)

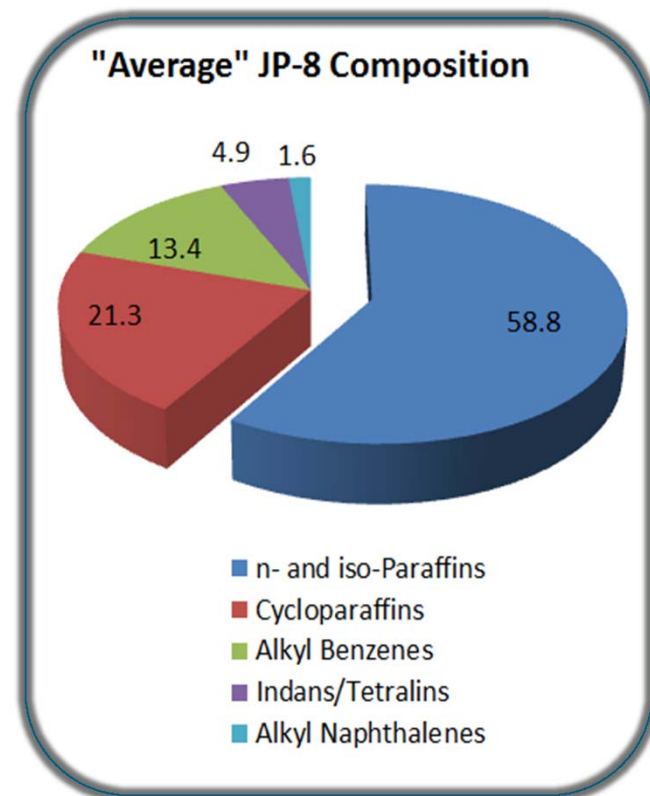
March 8, 2017
Biochemical Conversion R&D Review

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

Goal Statement

- ▶ **Need:** Catalysis and biochemical conversions of sugars and sugar-derived compounds can produce open-chain hydrocarbon fuel components not available through other methods (such as FP, HTL, APR, some ETJ)
- ▶ **Challenges:** Ash fouls catalysts and scales reactors in catalytic processing; organic and inorganic impurities inhibit catalysts and fermentations
- ▶ **Goal:** Develop a new deconstruction technology to provide low ash and low impurity sugars and sugar-derived intermediates from lignocellulosic feeds for use in catalytic and biochemical conversions
- ▶ **Outcomes (key findings to date):**
 - The deconstruction technology does not require neutralization; deconstruction media can be recovered for reuse
 - Batch or flow modes can provide sugar oligomers or furans – applicable to both bio- and thermochemical routes
 - Low ash products suitable for catalytic processing
- ▶ **Relevance:** Diverse downstream processing options are enabled, increasing the probability that new economical routes to fuels will be developed



Quad Chart Overview

Timeline

- ▶ Project start date: FY 2016
- ▶ Project end date: FY 2018
- ▶ Percent complete: 42%

Budget

	FY 16 Budget	FY 17 Budget	FY 18 Budget
DOE Funded	\$200,000	\$200,000	\$200,000
Project Cost Share (Comp.)			

Barriers

- ▶ Barriers addressed
 - Ct-A. Feedstock Variability
 - feedstock variability (wood and cornstover used)
 - physical parameters (different particle sizes used)
 - Ct-C. Efficient Preprocessing
 - removal of ash
 - removal of problematic components
 - preserve catalyst performance
 - Ct-D. Efficient Pretreatment
 - increase the availability of sugar polymers for subsequent hydrolysis
 - maximize yields as well as remove problematic components from the intermediate streams
 - new and innovative strategies for efficient low temperature pretreatment and subsequent deconstruction

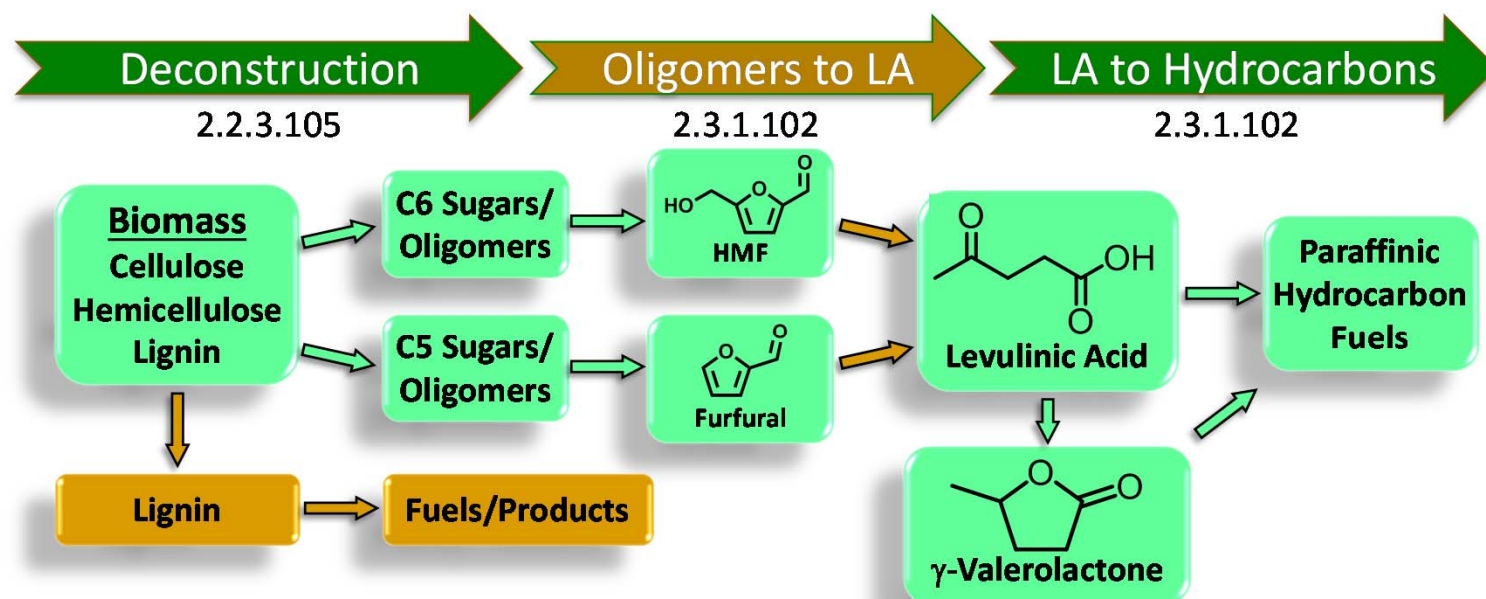
Partners

- INL – feedstocks
- NABC – feedstocks

1 - Project Overview

► Brief History

- Merit reviewed for FY16 AOP
- Prior to FY17, project was part of a combined deconstruction and upgrading effort in which levulinic acid was a key intermediate
- In FY17, two separate projects were formed
 - 2.2.3.105 Deconstruction
 - 2.3.1.102 Levulinic acid conversion to hydrocarbon fuels (CCB; see appendix for info)



1 - Project Overview (cont'd)

- ▶ Two related optional approaches to deconstruction – both use biphasic deconstruction media with organic acids
 - Approach A – sugar-derived intermediate production
 - intermediates = furfural, HMF
 - currently operated in a batch reactor
 - long residence time drives sugars and oligomers to intermediates
 - high temperature maximizes oligomer conversion (but can have other consequences)
 - Approach B – sugar and sugar oligomer production
 - currently operated in a flow reactor to control solution compositions, temperatures, residence times
 - short residence time in the heated zone to minimize sugar conversion to furans
 - lower temperatures (although high temperatures at short residence times can be ok)

2 – Approach (Management)

- ▶ *Critical success factors*
 - 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; design an industrially-relevant process**
- ▶ *Potential Challenges*
 - Product **selectivities and yields**.
 - Accurate mass and **carbon balances** require numerous analyses
 - Limited existing foundational **science base**
- ▶ *Structure of the approach*
 - **AOP, PMP, milestones, regular quarterly reporting, deep dives**
 - **Go/No-Go** decision points used to verify or modify strategy
 - **TEA & LCA** to guide technology development

2 – Approach (Technical) – Current State of the Deconstruction Art

- ▶ *State of the Art* – aqueous mineral acid solution contacts solid biomass
 - Standard aqueous acid approaches add inorganics that deactivate catalysts and scale and corrode reactors
 - Acid anions contaminate the sugar product
 - Ash in biomass not efficiently dealt with; ion exchange is required (NABC)
 - Aqueous acid catalyst degrades sugars
 - Sugars convert to HMF and furfural
 - HMF decomposes to levulinic acid
 - Need to concentrate the hydrolyzate (NABC)
 - Aqueous acids and bases need to be neutralized
 - Expensive enzymes are needed in hybrid processes

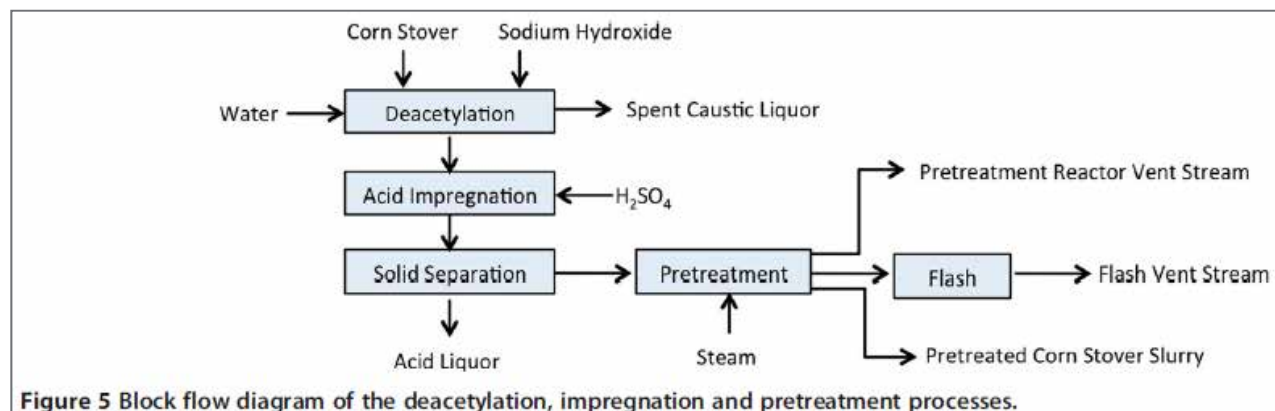
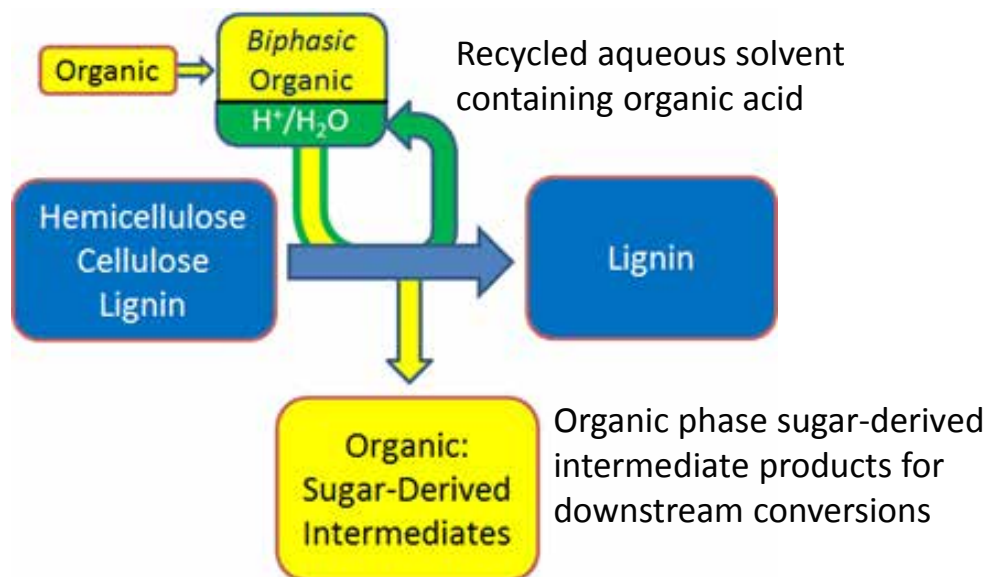


Figure 5 Block flow diagram of the deacetylation, impregnation and pretreatment processes.

2 – Approach (Technical) – A New Concept for Biomass Deconstruction: Approach A

- ▶ *New Concept* – a biphasic aqueous/organic solution with an organic acid catalyst contacts solid biomass
- ▶ **Approach A: Sugar-derived intermediate production**
 - biphasic solution: organic solvent and hydrophilic organic acid dissolved in water
 - aqueous acid converts sugars to furans which extract to the organic phase
 - aqueous solution can be recycled and organic phase further processed

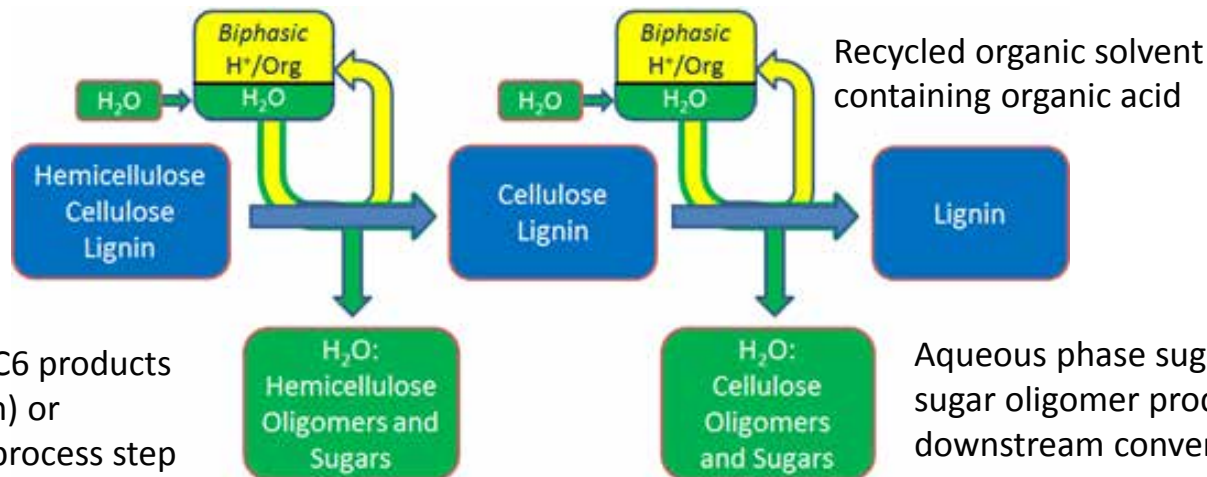


Similar to:

- Y Roman-Leshkov, JA Dumesic “Solvent Effects on Fructose Dehydration to 5-Hydroxymethylfurfural in Biphasic Systems Saturated with Inorganic Salts” *Top Catal* (2009) 52:297–303;
- P Zhou, Z Zhang, “One-pot catalytic conversion of carbohydrates into furfural and 5-hydroxymethylfurfural”, *Catal. Sci. Technol.*, 2016, 6, 3694–3712

2 – Approach (Technical) – A New Concept for Biomass Deconstruction: Approach B

- ▶ *New Concept* – a biphasic aqueous/organic solution with an organic acid catalyst contacts solid biomass
- ▶ **Approach B: Sugar and sugar oligomer production**
 - biphasic solution: water and a hydrophobic organic acid dissolved in an organic solvent
 - released sugars extract into the aqueous phase and away from the acid
 - deconstructing acid remains in the organic phase and does not contaminate the sugar product
 - organic solvent and organic acid catalyst can be recycled and do not need to be neutralized
 - acid does not appear to be corrosive under reaction conditions



Can recover C5 and C6 products separately (as shown) or together in a single process step

Aqueous phase sugar and sugar oligomer products for downstream conversions

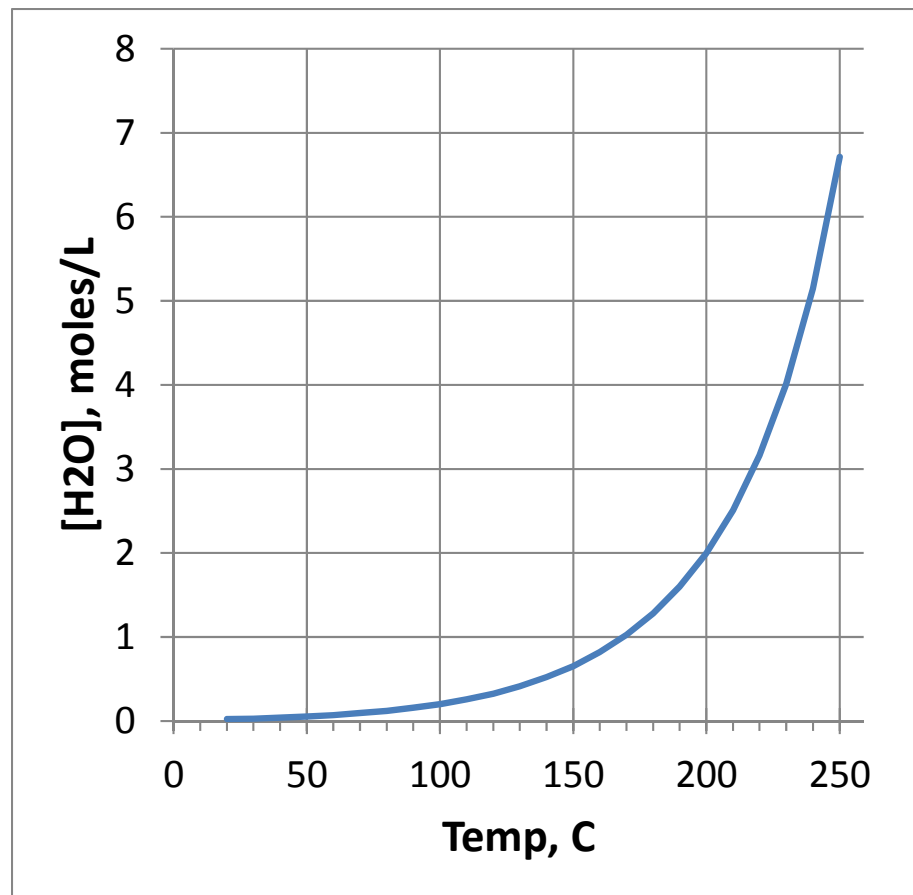
2 – Approach (Technical) – Approach B: Organic Phase of the Biphasic Deconstruction Media

- ▶ Toluene
 - nonanoic (C9) and undecanoic (C11) acid catalysts completely miscible
 - water solubility in toluene about:
0.8 M (1.7 wt%) at 160 °C,
2.0 M (4.1 wt%) at 200 °C
- ▶ Xylene has also been used
- ▶ Dibutyl diglyme has also been used
 - acid stable solvent
 - water solubility is about 1.4 wt% at ambient temperature

Significance:

- Hydrolysis occurs at higher temperatures where organic solvent, water, and acid are miscible and all can contact biomass.
- Upon cooling, phase separation enables separate recovery of products and deconstruction medium

Water Solubility in Toluene



Neely et al., J. Chem. Eng. Data 53 (2008) 165–174

3 – Technical Progress – Deconstruction Experimental

▶ Deconstruction Reactors

- Batch – Parr, 300 mL, fritted dip-tube for sampling with time
 - 7.5-15 g biomass, 3-6 h reaction time, 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 (fine and course)
- Water and ethanol washed
(extractives removed)



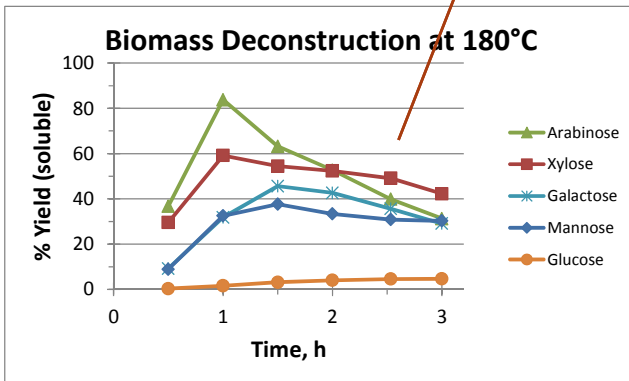
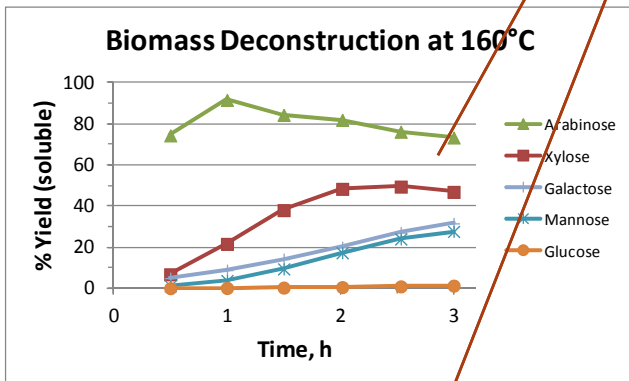
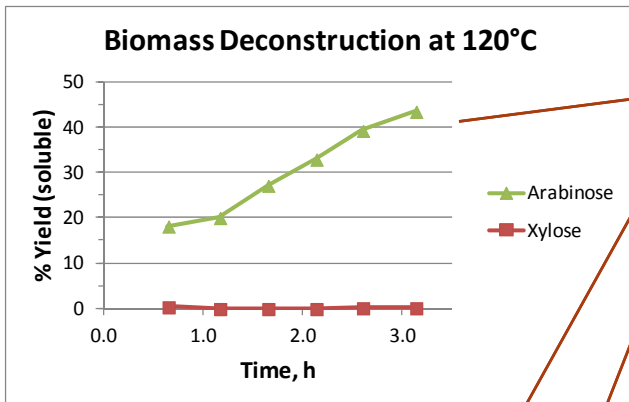
▶ Analytical

- Sugars
- Furans
- Acids
- Ash

Significance:

- Batch and flow configurations used
- Variety of feeds and particle sizes used
- Analyses of sugars, sugar decomposition products, and ash are conducted

3 – Technical Progress – Batch Deconstruction – Monomeric and Oligomeric Sugars from Pine



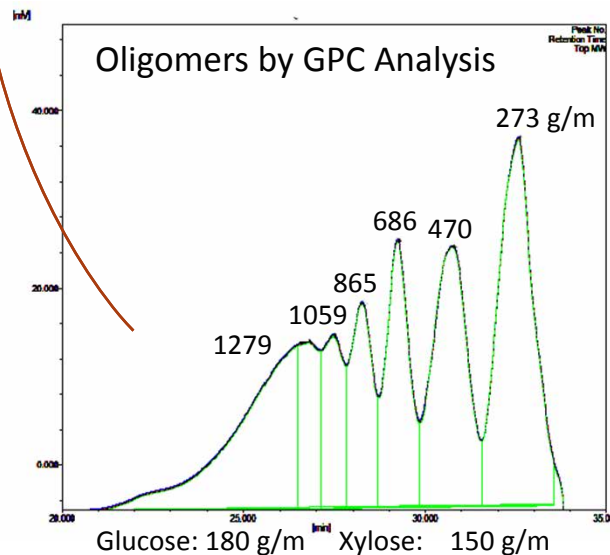
Parr batch reactor, DBDG, nonanoic acid

Monomeric Sugars:

- Arabinose cleaved selectively at 120 °C
- Hemicellulose-derived sugars obtained at temperatures up to 160 °C
- High temperatures and long residence times cause sugar degradation to furans
- No indication of humin or tar formation

Sugar Oligomers:

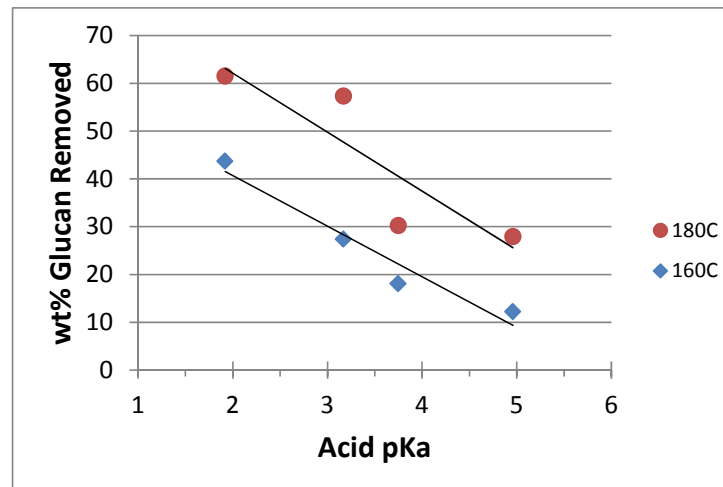
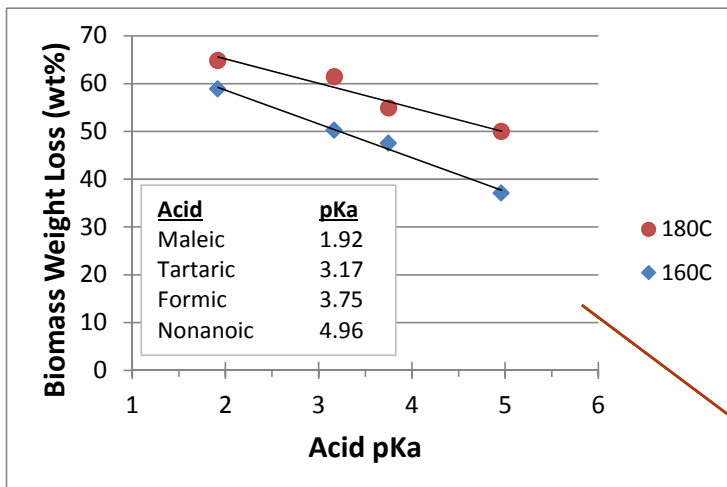
- Oligomeric solids observed, especially at early reaction times
- About 48% of the cellulose removed as oligomers at 200 °C



Significance:

- Batch reactor residence times more favorable for furan formation
- Residence times less than 30 min in a flow reactor can recover sugar oligomers

3 – Technical Progress – Batch Deconstruction – Acid Strength and Furfural Production (Corn Stover)



Run	Temp (°C)	Acid	% Wt Loss	Furfural Yield, %	C5 Mole bal, %
140	160	Maleic	59	55	76
24	180	Maleic	65	51	53
157	160	Tartaric	50	60	94
25	180	Tartaric	61	54	54
144	160	Formic	48	59	98
27	180	Formic	55	63	75
145	160	Nonanoic	37	25	99
28	180	Nonanoic	50	40	66

7.5 g extracted corn stover except for Run 157 which had 9.5 g; toluene; 3h runs

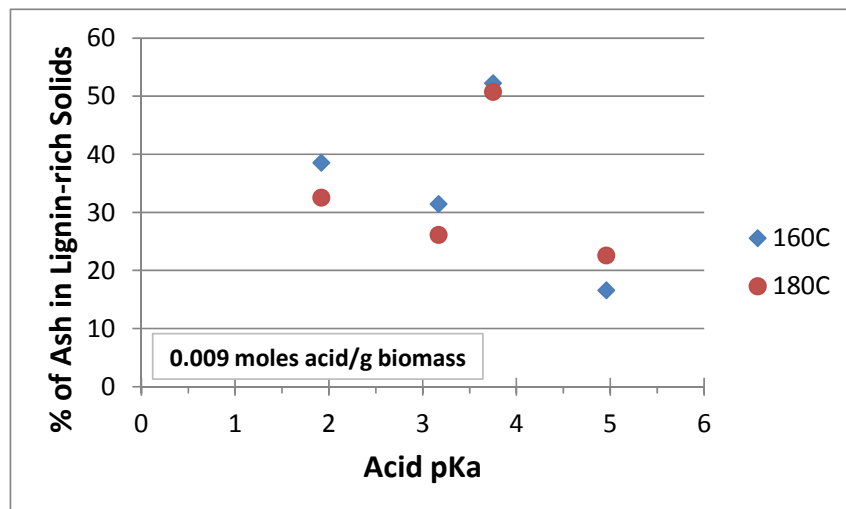
Acid Strength:

- Extent of deconstruction and glucan removal **increases with acid strength**
- Stronger acids **decrease process temperature** 40-50 °C for the same extent of deconstruction as weaker acids
- C5 sugars **convert directly to furfural** – 60% yield better than most in the literature for thermal conversions
- C5 mole balance is excellent at 160 °C, but decreases at 180 °C, probably because of humin formation
- HMF analysis underway

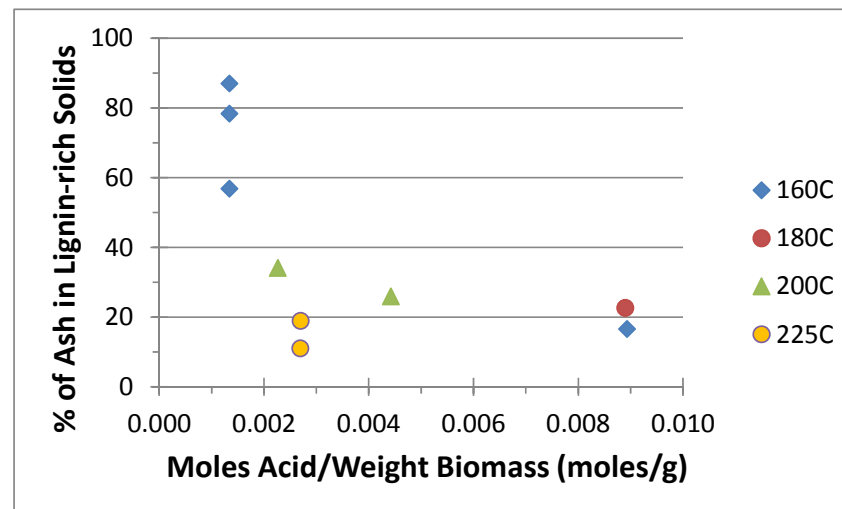
Significance: Furans can be obtained directly from biomass without sugar isolation; stronger acids decrease processing temperature

3 – Technical Progress – Batch Deconstruction – Ash Distribution (Corn Stover)

Ash in solids as a function of acid strength (pKa)



Ash in solids as a function of nonanoic acid content



Ash Distribution:

- Ash content in solids remaining after deconstruction a function of both acid strength and acid content in the medium
- pKa not the only factor; anion appears to play a role (Ksp?)
- Lower acid content and lower temperature generally give more ash in the solids.
- Lower acid content does not significantly change the extent of deconstruction at 160 °C

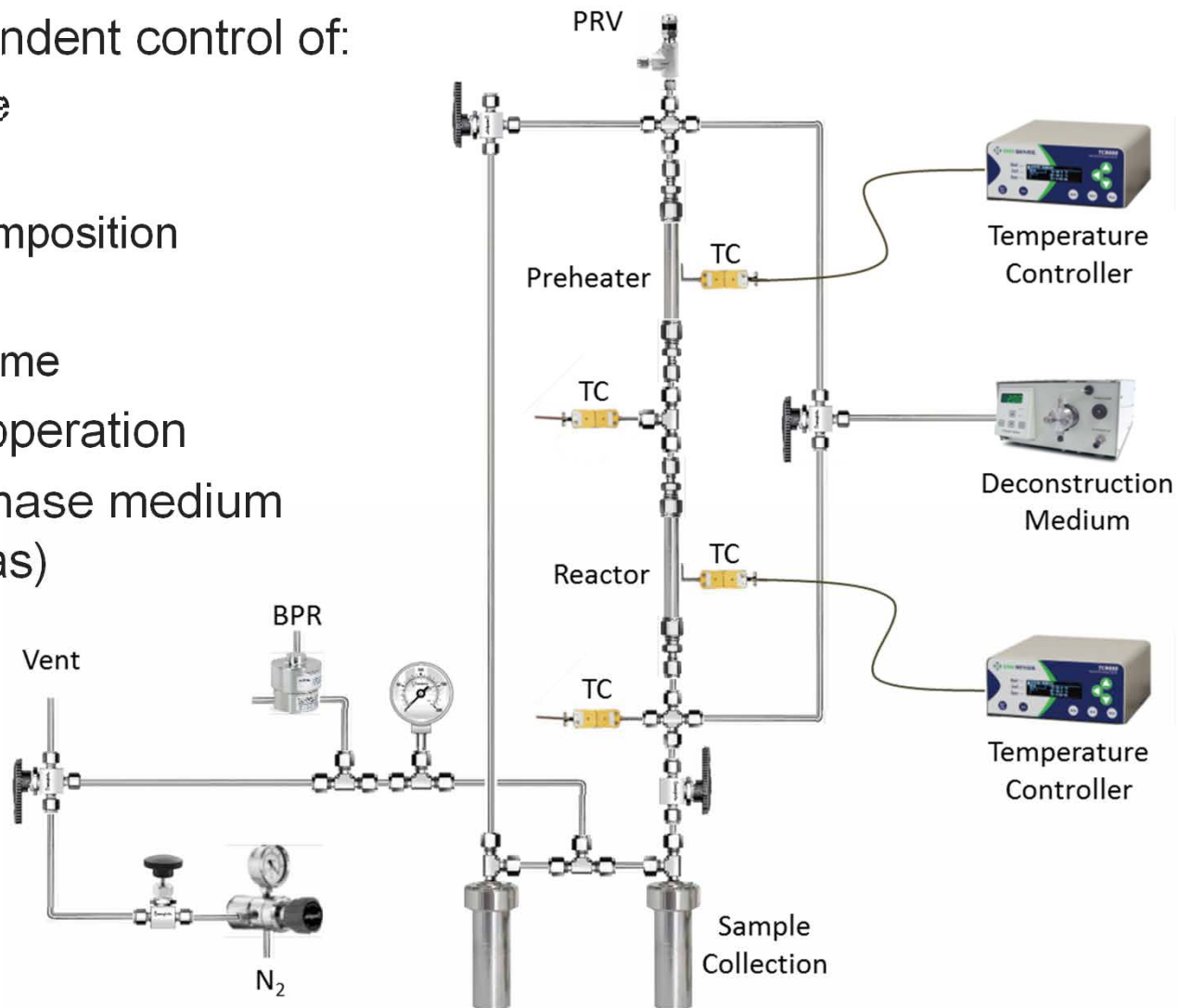


Remaining Biomass Solids

Significance: Organic acids can help keep ash in the solid phase rather than solubilizing it. This would be a benefit to downstream processing in fixed bed reactors.

3 – Technical Progress – Deconstruction Flow Reactor

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



3 – Technical Progress – Flow Deconstruction – Results for Xylene/Nonanoic Acid

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 ^a
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 % balance overall
- ▶ Furfural yield: 0.5% at 160 °C with 30 min residence time

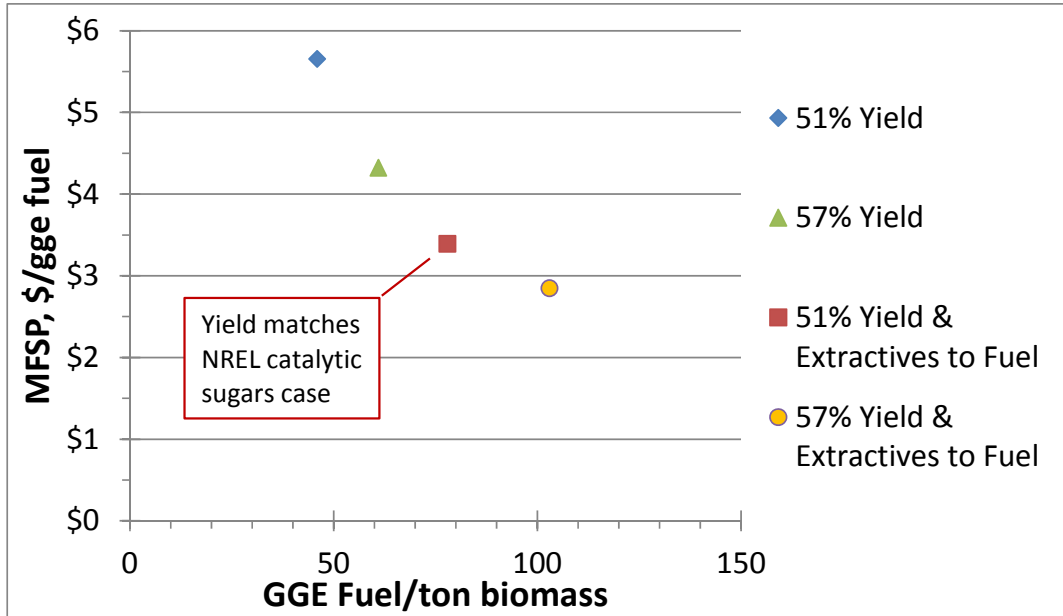
Significance:

- Flow reactor gives little monomeric sugars and less decomposition to furans
- Oligomers can be subsequently hydrolyzed to monomeric sugars if desired

3 – Technical Progress – Techno-Economic Analysis

TEA was conducted for the overall process, i.e., yield is for biomass to fuel precursor

Conclusions suggest how the MFSP can be reduced through the following research improvements:



- ▶ **Reduce water-solvent addition** in the biomass deconstruction step
 - Lower capital costs in each conversion step and in wastewater treatment
 - Reduce operating costs through lower water and solvent consumption.
- ▶ **Increase conversion** in the following steps: deconstruction, sugar-to-GVL production and GVL-to-fuel precursor.
- ▶ **Improve yield** by recovering more sugars, recovering carbon in aqueous phases, or demonstrating conversion of extractives to fuel precursors.

4 – Relevance

Develop a new deconstruction technology to provide low ash and low impurity sugars and sugar-derived intermediates for use in catalytic and biochemical conversions

Directly Supports BETO’s Mission: “Develop and demonstrate transformative and revolutionary bioenergy technologies for a sustainable nation.”

Supports the Industry: The future of all biochemical routes to fuels and chemicals hinges on the ability to access clean sugars. Access to clean sugars from a variety of feedstocks is a critical barrier to the whole industry.

Barrier:	Issue or Need:	Addressed in this project by:
Ct-A. Feedstock Variability	Variability in feedstocks reduces conversion rates and product yields	Both wood (pine) and corn stover give comparable results
	Physical parameters a challenge to consistency and quality	Fine and course particle sizes give comparable results
Ct-C. Efficient Preprocessing	Removal of ash important	Up to 90% ash prevented from entering process streams
	Preserve catalyst performance	Clean streams will minimize catalyst deactivation and reactor scaling
Ct-D. Efficient Pretreatment	Increase the availability of sugar polymers for subsequent hydrolysis	Sugar polymers are the primary product in one deconstruction approach
	Develop innovative strategies for efficient deconstruction	This is a new technology that does not require neutralization and can provide either sugars or intermediates for upgrading

5 – Future Work

- ▶ Batch Deconstruction
 - Continue deconstruction and direct conversion to furan intermediates
 - Q4 Milestone: scale up reactor – make material for downstream process development
- ▶ Flow Deconstruction
 - Parameter testing for deconstruction to sugar oligomers
 - Q2 Milestone: acid dependence of oligomer production yield and selectivity
- ▶ Tech Transfer
 - T2M: Q3 Milestone to deconstruct commercially-relevant materials
 - Industrial partners
 - IP development – Provisional patent application has been filed
- ▶ Go/No-Go
 - Design a conceptual pilot-scale flow reactor
 - 6-30-2018

Summary

- ▶ A novel deconstruction process has been demonstrated for **different feeds** – pine and corn stover feeds are comparable.
- ▶ **Particle size** does not affect deconstruction
- ▶ Batch deconstruction provides a **direct route to furans** without isolation of intermediate sugars and sugar oligomers
- ▶ Flow deconstruction **provides sugar oligomers**
- ▶ Deconstruction **separates ash** from carbohydrates
- ▶ Deconstruction medium **does not need neutralization** (minimizing waste generation) and may be recycled to the process
- ▶ Deconstruction **process options** to either sugars or furans may enable a variety of downstream conversion technologies



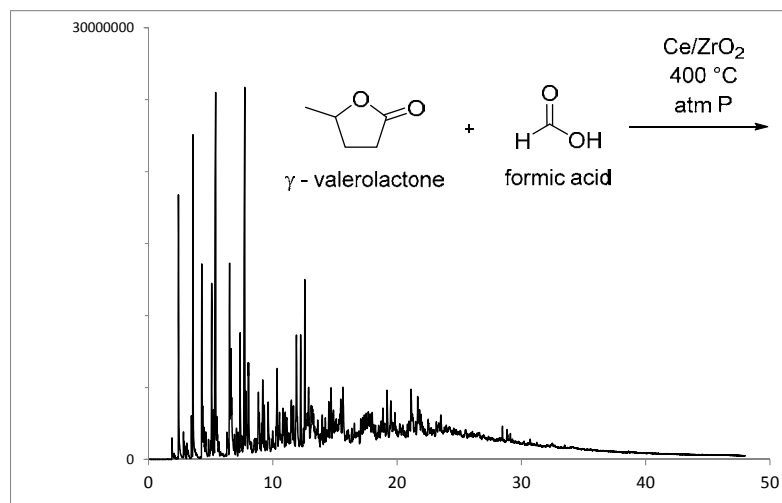
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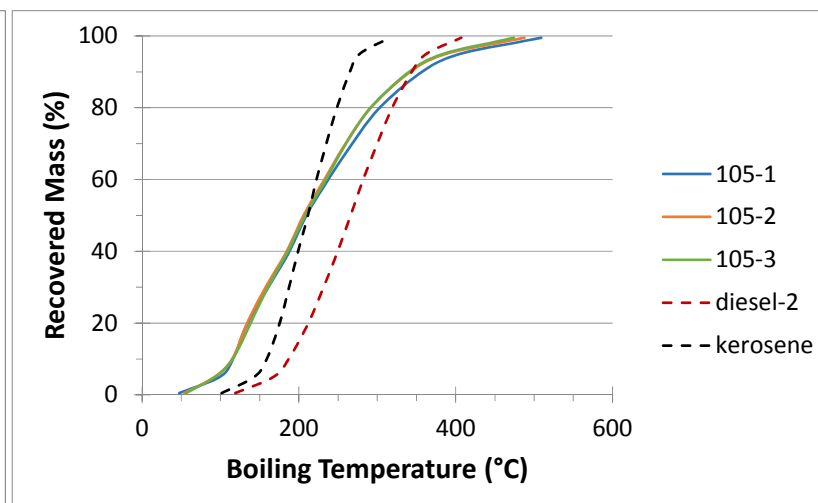
Additional Slides

Deconstruction Strategy Shaped by Levulinic Acid and γ -Valerolactone Process to Hydrocarbons

Organic Phase GC/MS Analyses



Organic Phase Simulated Distillation






- ▶ **Atmospheric processing** gives deoxygenated and oligomerized oil product **in the distillate range**
- ▶ Simple reprocessing of the aqueous phase produces additional oil product for a **higher C yield**
- ▶ Light ketone products identified by Co-Optima as **high octane components** for gasoline
- ▶ GVL and LA can be obtained from C6 and C5 sugars
- ▶ Excellent mass balance
- ▶ Lower GVL WHSV produces a more **deoxygenated oil product** with less C in the aqueous phase, but mole balance is low (because less material was processed?)

Run	mL/min	GVL WHSV, h ⁻¹	Collected Product, g	Oil Molar Yield, % C	Aqueous Molar Yield, % C	Mole Balance, % C #	Mass Balance, wt % #
105-1	0.08	0.123	28.09	37	35	101	99
105-2	0.05	0.077	26.87	43	22	95	99
105-3	0.03	0.042	10.11	37	17	83	99
# using theoretical values for CO ₂							

Run	Moles C				Oil Elemental Analysis, wt%		
	Feed	Oil	Aqueous	CO ₂	C	H	O
105-1	5.04	1.84	1.74	1.51	78.88	10.43	10.54
105-2	4.16	1.79	0.89	1.25	80.13	10.42	7.83
105-3	1.87	0.69	0.31	0.56	81.79	10.46	7.26
GVL (feed)	-	-	-	-	59.98	8.05	31.96

2 – Approach (Management)

Deconstruction-relevant milestones attained in FY15 and FY16:

Milestone	Date	Type	Outcome
In a continuous process, remove >95% of the hemicellulose fraction and > 50% of the cellulose fraction of corn stover as usable carbohydrate products. This would reproduce results obtained during batch processing and establish a baseline for the more industrially relevant flow configuration.	12/31/2014	QPM (stretch)	Extent of deconstruction was attained 
Remove >95% of the hemicellulose fraction and > 75% of the cellulose fraction of corn stover as usable carbohydrate products.	9/30/2015	Go/No-Go	A go decision continued planned activities for overall process development 
Scale up and demonstrate the process for deconstruction of corn stover from the current 1.25 g scale to 12.5 g scale to produce oligomer feeds for developing downstream processes.	3/31/2016	Regular	Several batch runs at the larger scale produced 1.5 L of product for process testing 

Responses to Previous Reviewers' Comments

▶ Selected Comments:

- This is a good generic platform for research to produce sugars that can be utilized in most biochemical/catalytic processes
- This is differentiated work to make products of open chain hydrocarbon molecules. There has been good progress toward demonstrating new reaction pathways. It would be good to see the use of techno-economic analysis and more relevant sugar feedstocks earlier in the experimental work.
- This project may have great potential, but it is disconcerting that so little economic analysis has been done. On first glance, there are several items that could significantly impact commercialization potential that should be evaluated. Given that much of the process is novel, techno-economic analyses should have been performed to help direct the R&D effort. It is strongly recommended that this be completed immediately.
- No economics have been analyzed yet; not even a cost analysis of the liquid being used in the process. It seems more like a technical feasibility assessment. From a high level, it appears this will be a costly process.

▶ Selected Responses:

- Techno-economic analysis is to be conducted in FY15. The technical challenges we have overcome to bring the technology to the current level have been large. In fact, our course has changed significantly on both the deconstruction and levulinic acid conversion tasks. The levulinic acid conversion work was surprising and could not have been predicted.
- Significant progress has been made since the last review. Flow deconstruction is new and has demonstrated improved performance over earlier batch studies. Discovery that ash components do not transfer to the sugar phase in batch experiments is remarkably significant and is new information. The levulinic acid conversion data is totally new and also remarkably significant. Clearly, there is more to do.
- The chemistries and processes are totally different than most are familiar with. The deconstruction, in particular, is unique, yielding low-to-no ash sugar streams. Ash content associated with current biomass deconstruction methods presents tremendous challenge to catalytic sugar upgrading. The role of the national laboratories is to do everything we can to ensure opportunities for tech transfer, provision of licensing rights, and commercialization are secured so that the technology can be put to work to bring a return to the country. Following IP protection, results of this work will be presented at a professional society meeting to begin dissemination of information. Discussions with potential industrial partners will continue in order to move this technology toward eventual commercialization.

Publications, Patents, Presentations, Awards, and Commercialization

▶ Prior to FY17:

- Lilga, Padmaperuma, et al., “Ketonization of Levulinic Acid and γ -Valerolactone to Hydrocarbon Fuel Precursors”, submitted as invited paper to Catalysis Today
- “Process for Conversion of Selected Feedstock Compounds to Distillate Range Hydrocarbons”, Michael A. Lilga, Asanga B. Padmaperuma, Provisional Patent Application No. 62/253,007 filed 11/9/2015.
- Lilga MA, AB Padmaperuma, D Auberry. 2016. "Conversion of lignocellulosic biomass to hydrocarbon fuels." (invited Talk) 252nd ACS National Meeting, Philadelphia, PA. August 21, 2016
- Catalytic Conversion of Lignocellulosic Feedstocks to Hydrocarbon Fuels
- Lilga MA, AB Padmaperuma, and HM Job. 2015. "Catalytic Conversion of Lignocellulosic Feedstocks to Hydrocarbon Fuels." Presented by Asanga B Padmaperuma (Invited Speaker) at 2015 AIChE Annual meeting on November 9, 2015.

▶ FY17:

- Lilga, et al., “Novel Bi-Phasic Deconstruction of Biomass to Sugars and Sugar-Derived Intermediates”, in preparation
- “Bi-Phasic Deconstruction of Biomass to Sugars and Sugar-Derived Intermediates”, Michael A. Lilga, Provisional Patent Application, filed 2/2017.