DOE Bioenergy Technologies Office (BETO) 2019 Project Peer Review

Condensed Phase Catalysis Technology for Fuels and Carbon Products

March 4 – 8, 2019
Catalytic Upgrading

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Organization: The University of Tennessee

Goal Statement

Goal: The goal is to separate biomass into high purity streams of its three main components, cellulose, hemicellulose and lignin in an integrated process to enable efficient and cost effective downstream conversion processes.

- *Meet BETO cost targets of $3/GGE for hydrocarbon fuel production*
- *Focus on high value carbon markets for lignin, jet-fuel and chemical production from polysaccharides*

Project outcomes:

- *Use biomass derived solvent (GVL) to fractionate diverse biomass feedstocks into high purity cellulose, hemicelluloses, and lignin fractions*
- *Produce high value carbon products from lignin fractions*
- *Produce an established intermediate chemical (furfural) from hemicelluloses*
- *Convert hemicelluloses and cellulose to aviation fuels (alkanes)*
- *Demonstrate the techno-economic viability of the integrated process*

Relevance: economically fractionating and upgrading each major biomass component into high value products enables meeting DOE fuel cost targets.

Quad Chart Overview

Timeline

- Start date: 8/2018
- End date: 7/2020
- Percent complete: 15%
- Funded by 2017 BRDI FOA - DE-FOA-0001637
- Award Number: DE-EE0008353

	FY 19	FY 20	Total
DOE-funded	$678k	$722k	$1,400k
Cost share	$167k	$184k	$351k
UT (35%) : UW (35%) : GB (30%)			

Barriers

- Ot-B. Cost of Production
  - Cleanly fractions of biomass at high yields, concentrations, and purity under mild conditions
- Ct-C. Process Development for the Conversion of Lignin
  - Lignin converted to activated carbon, foam cores, and graphitic carbon
- CT-F: Increasing the Yield from Catalytic Processes:
  - High yield, low loss, mild conditions, bio-derived solvent

Objectives: Separate biomass into high purity streams of cellulose, hemicellulose and lignin in an integrated process to enable efficient and cost effective downstream conversion processes.

End of Project Goal:

- Produce high value carbon products from lignin
- Produce intermediate chemicals from hemicelluloses
- Bioderived alkane jet fuel at <$3.00 GGE

*Only fill out if applicable. If there are multiple cost-share partners, separate rows should be used.

**Only fill out if applicable.

Project Overview

History and Context: Biomass needs efficient fractionation to maximize value

- *BETO focus on hydrocarbon fuel*
- *Demonstrated ability to produce hydrocarbon fuel*
- *Using proven technology to fractionate biomass at high solids, mild conditions, with high yields*
- *Demonstrated ability to produce carbon foams from lignin with controlled structure*

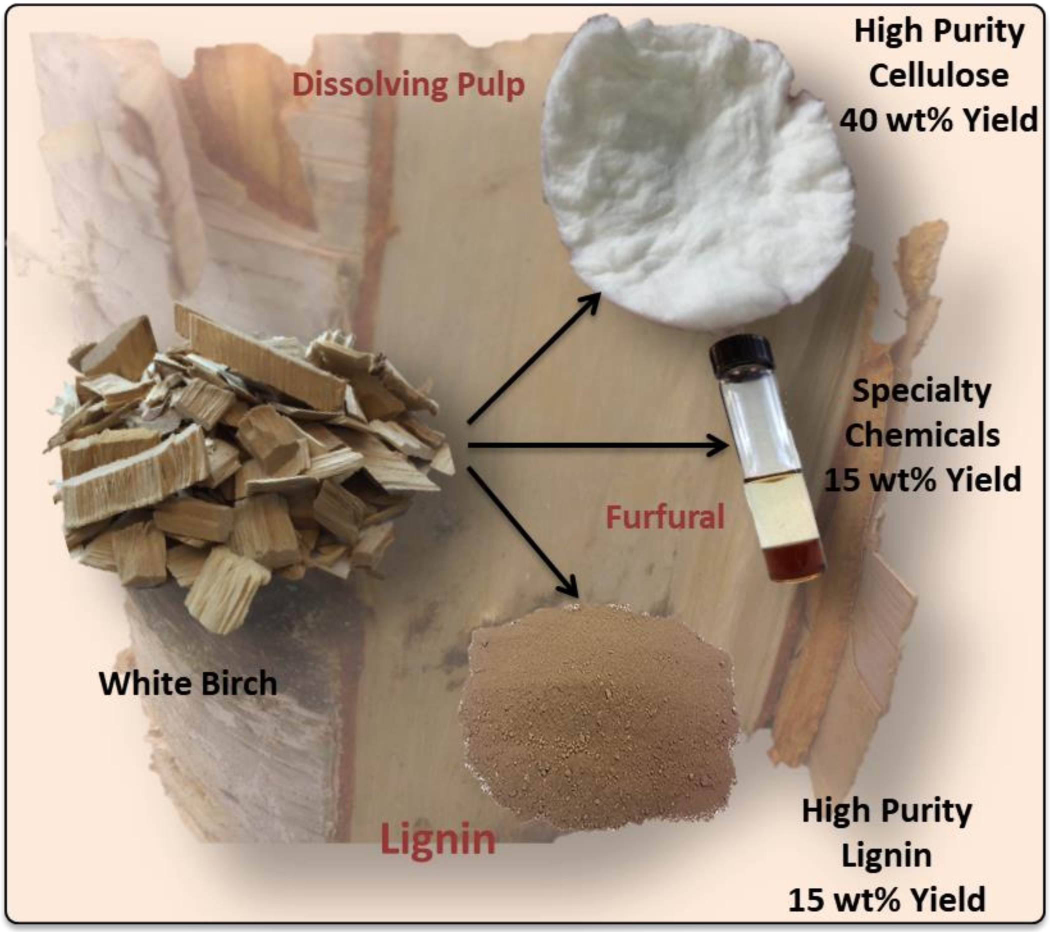
Project Objectives:

- Fractionate multiple bioenergy crops to produce high purity fractions of cellulose, hemicellulose, and lignin at low cost and high concentration using a biomass-derived solvent gamma-valerolactone (GVL).
- Produce high-value carbon products from unique, high purity GVL-derived lignin that will reduce the cost of the biofuels.
- Produce an established intermediate chemical from the hemicellulose (furfural) to reduce the cost of cellulosic ethanol <$3 GGE.
- Convert hemicellulose and cellulose to aviation fuel (alkanes) via intermediate chemicals derived from biomass polysaccharides (i.e., furfural, levulinic acid).
- Demonstrate techno-economic viability of the integrated processes and produce aviation fuel <$3 GGE.

Management

- *Overall project management: David Harper (UT)*
- *Task 1: Feedstock selection and analysis – David Harper (UT)*
  - *Feedstocks delivered to GB and chemical analysis conducted*
- *Task 2: Fractionation of Biomass – David Alonso (GB)*
  - *Biomass fractionated, sugars streams handed off to UW, lignin to UT*
- *Task 3: Carbon Products – David Harper (UT)*
  - *UT will produce activated carbon foams to be evaluated by industrial partners*
  - *TEA/LCA data will be employed to select products*
- *Task 4: Production of chemicals, intermediates, and liquid fuels – Jim Dumesic (UW)*
  - *Convert sugar streams into furfural, levulinic acid, GVL, and alkanes*
- *Task 5: Economic Analysis – Christos Maravelias (UW)*
  - *Collect all process and economic data for LCA and TEA analysis*

Technical Approach – Overview. Previous work



D.M. Alonso et al. Science Advances 3 (5), e1603301

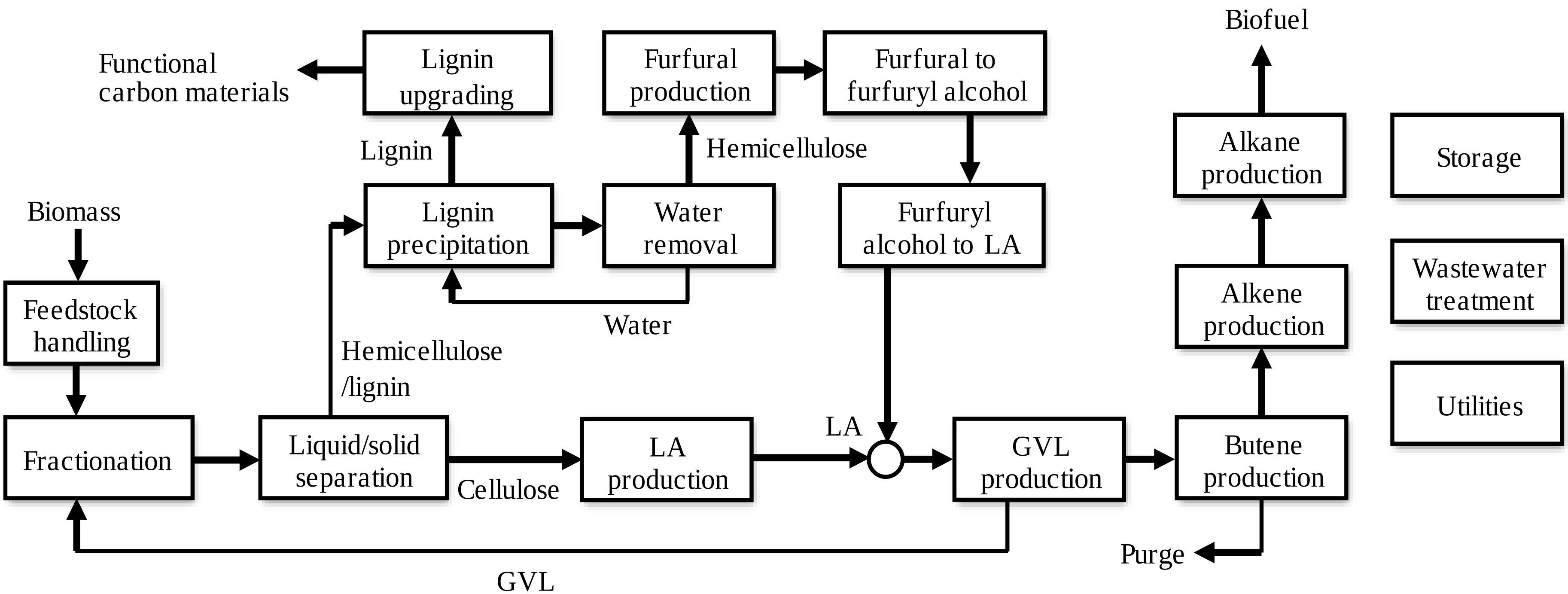
- Process combines biomass fractionation with chemical production
- >80% of the initial wood converted to products:

1. High purity cellulose
2. Furfural
3. High purity lignin
4. Acetic acid
5. Formic acid
6. Levulinic acid

- **High biomass loading 20-30 wt%**
- **>$500 revenue per MT of wood**

Technical Approach – Overview.

- Fractionate biomass into pure components using a biomass derived solvent (GVL)
- Demonstrate feedstock flexibility of the fractionation process
- Upgrade each component into higher value chemicals and materials with existing markets to produce fuels (alkanes) at <$3 GGE.



Technical Approach – Feedstock Selection

- *Use a variety of bioenergy biomass species, sizes, and combinations*
  - *Acquire switchgrass (Panicum virgantum), hybrid poplar (Populus spp.), and Southern yellow pine (Pinus spp.)*
  - *Remove bark from wood*
  - *Hammermill biomass to acquire discreet biomass size fractions*
  - *Use varying combinations of biomass for fractionation*

- *Potential challenges*
  - *Biomass species leads to variation in particle size distribution and chemical composition*
  - *Switchgrass normally contains higher extractives and ash content than wood species*
  - *Removing bark from hybrid poplar may not be realistic in future large scale operations*

Technical Approach - Fractionation

- *Use biomass derived solvent (GVL) to fractionate diverse biomass feedstocks into high purity cellulose, hemicelluloses, and lignin fractions.*
  - *Processing several feedstocks together (at least 2 types) with minimal pre-processing (wet samples)*
  - *Minimal degradation of any of the fractions (retain >85% cellulose, >90% hemicellulose, >70% lignin)*
  - *Maximize biomass loading, >20 wt% loading (hemicellulose and lignin soluble)*
  - *Minimize separation steps (GVL solvent is the intermediate to produce fuels)*
  - *Reutilize the solvent and recycle as many streams as possible*

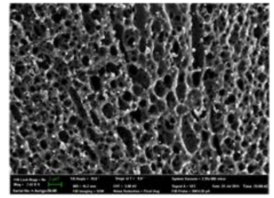
- *Potential challenges*
  - *Different lignin structure and hemicellulose composition of hard/soft wood and grasses may complicate mixed feedstock upgrading*
  - *Solvent must be recovered and recycled*
  - *Accumulation of impurities in the recycle streams*
  - *Lignin products, chemicals and fuels must meet market specifications*

Technical Approach – Lignin Products

GVL Lignin

Pyrolysis / foaming

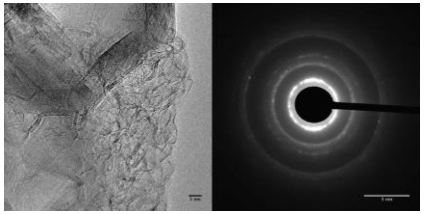
Porous carbon



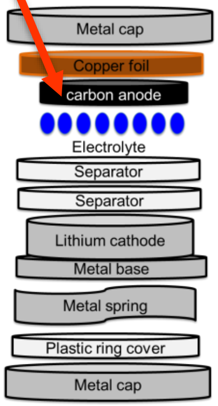
Foam cores
Activated foams

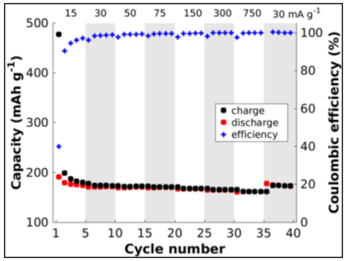
Reduction or activation

Reduced carbon



Graphitic carbon





GVL lignin-carbon battery anode

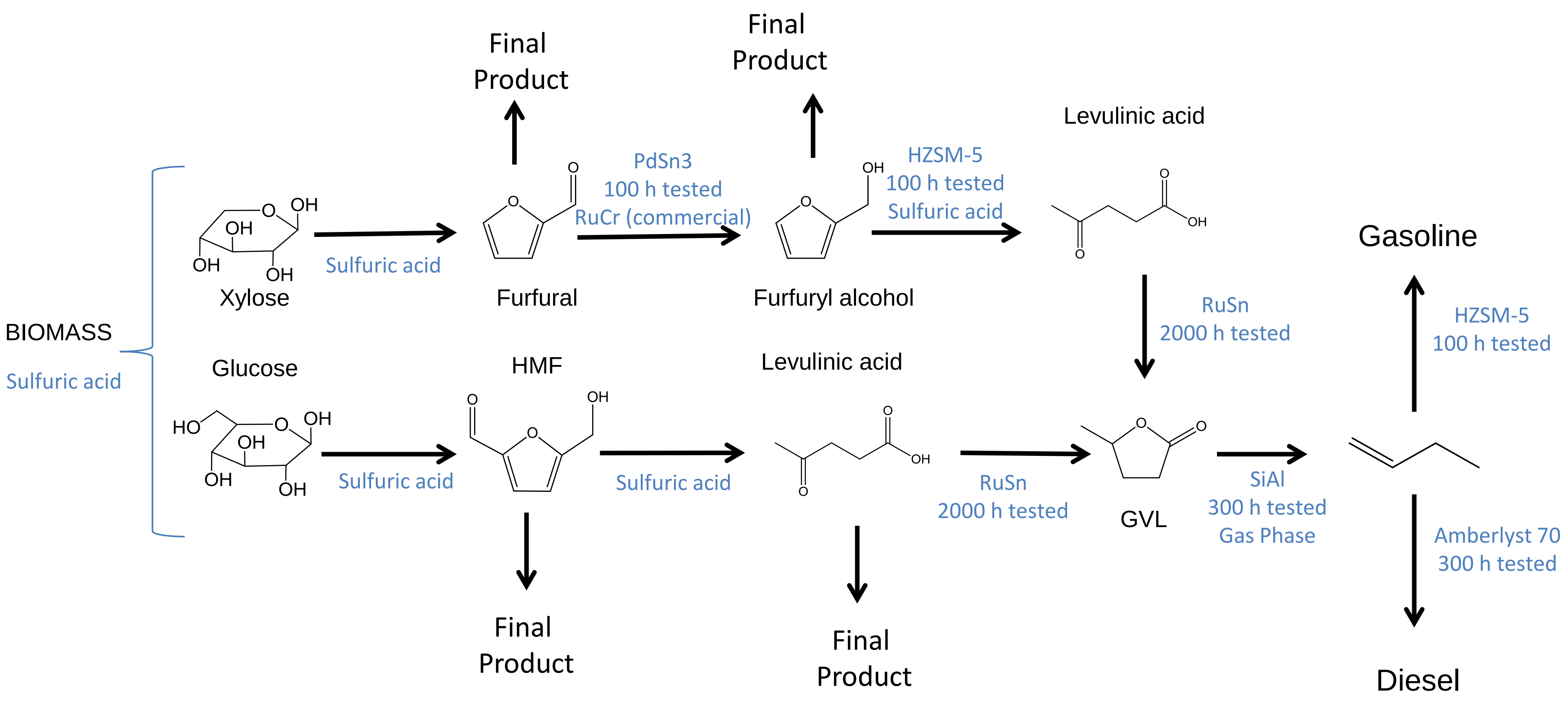
- ***Use GVL fractionated lignin to produce carbon products***
  - *Evaluate lignin streams*
  - *Porosity, surface area, thermal, and mechanical properties*
- ***Possible challenges - solutions***
  - *Pore distribution – use external blowing agents*
  - *Cracking of carbon monoliths – employ plasticizers, controlled processing, OR use in powdered form*
  - *Extra processing steps will be guided by the TEA/LCA*

Technical Approach – Chemicals, Intermediates, and Fuels

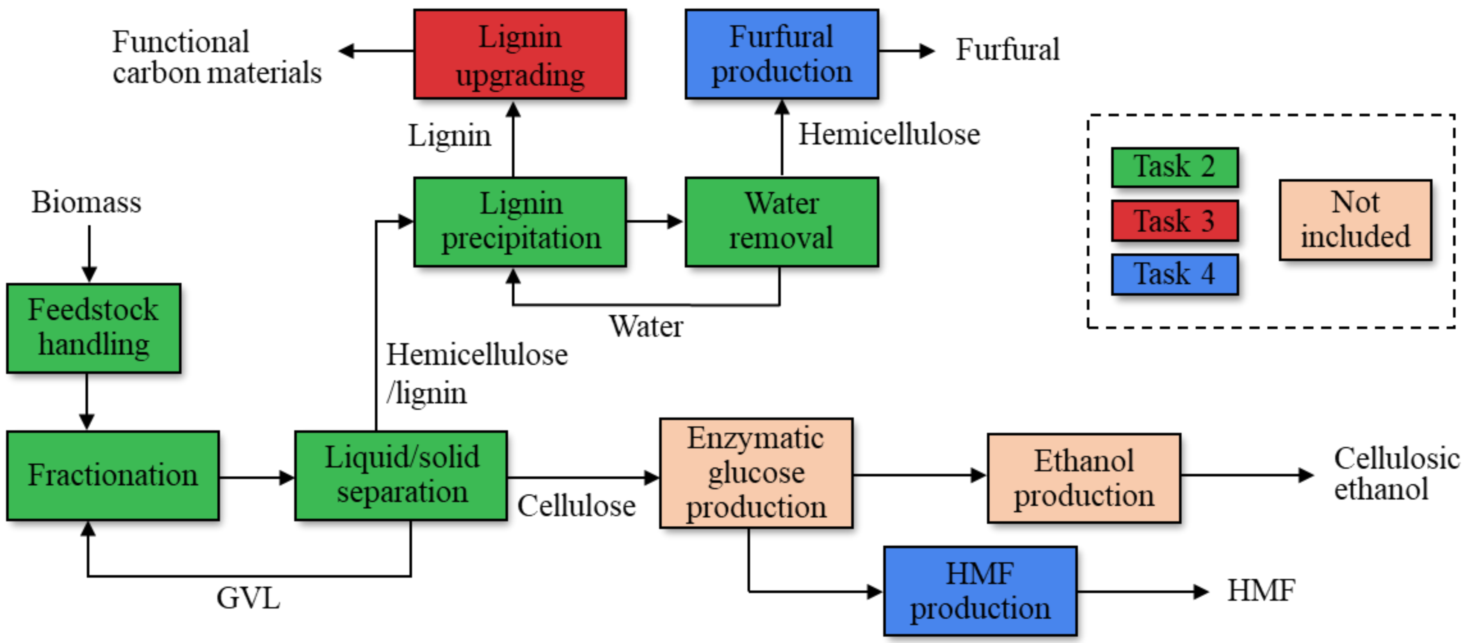
- *Use intermediate chemicals production to decrease the value of the fuels*
  - *Chemicals produced are part of the pathway to produce liquid fuels (i.e. furfural, HMF, levulinic acid, GVL, butene…)*
  - *Catalyst resistant to biomass-derived impurities and operate within the GVL solvent to minimize separations.*
  - *Combine catalytic and separation steps, process intensification, to reduce process cost (GVL intermediate to fuels is produced in GVL-solvent)*

- *Potential challenges*
  - *Catalyst stability (Metal catalyst RuSn has been stable >2000 h)*
  - *Low furfural production using feedstocks with low C5 sugars content.*
  - *Valorization of C6 sugars in the hemicellulose fraction (can be used to make-up the solvent)*

Technical Approach – Chemicals, Intermediates, and Fuels

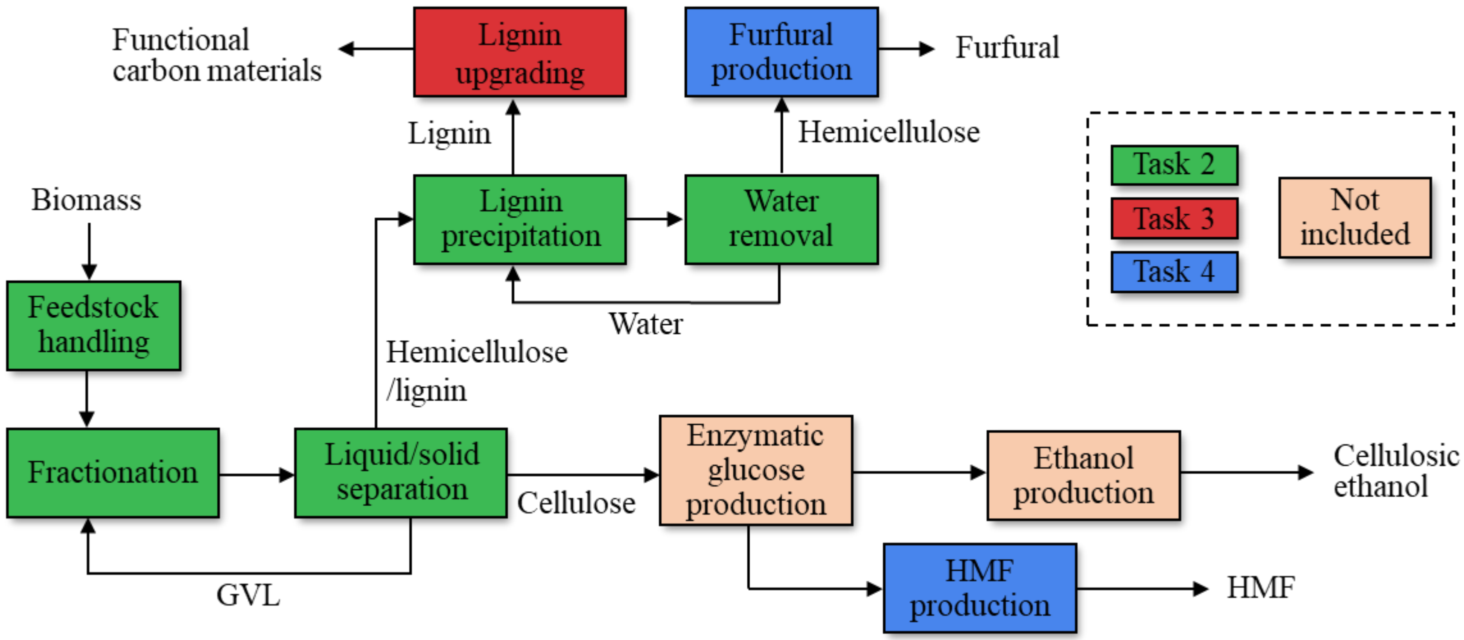


Technical Approach – Economic Analysis



- Process and economic models available for coproduction of cellulosic ethanol, lignin and furfural
  1. Alonso, D.M., et al., *Increasing the revenue from lignocellulosic biomass: Maximizing feedstock utilization*. Science Advances, 2017. 3(5).
  2. Huang, K., et al. *Improving Economics of Lignocellulosic Biofuels: An Integrated Strategy for Coproducing 1,5-Pentanediol and Ethanol*. Applied Energy, 2018. 213, 585-594.

Technical Approach – Economic Analysis

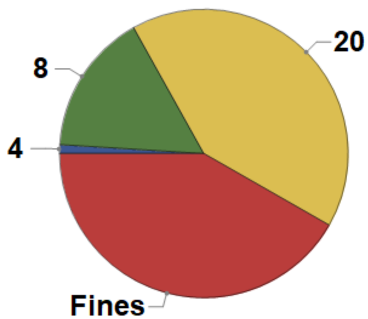


1. Gather data from process: Collect data for “Lignin upgrading” and “HMF production”; Update data for other process sections
2. Synthesis and analysis: model and simulation of integrated process; techno-economic analysis and sensitivity analysis (e.g., impact of functional carbon materials, HMF and furfural on MSP of ethanol)

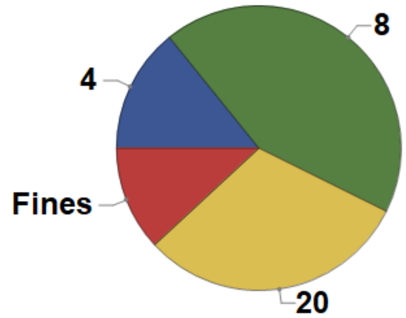
Technical Accomplishments/ Progress/Results

Sieve mesh size

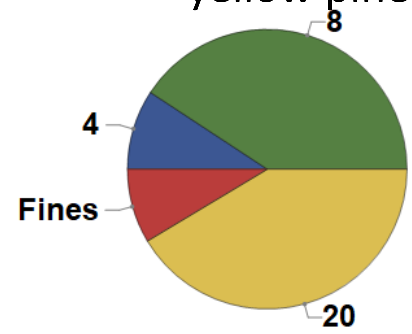
switchgrass



hybrid poplar

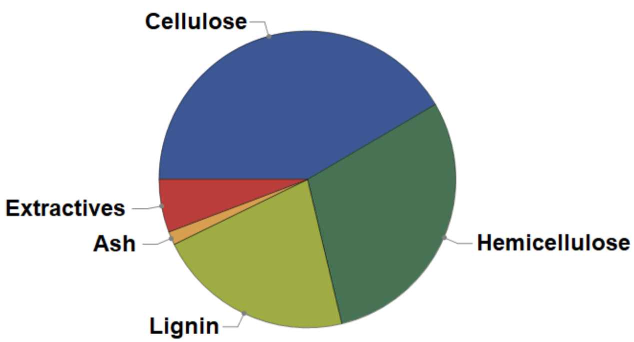


yellow pine

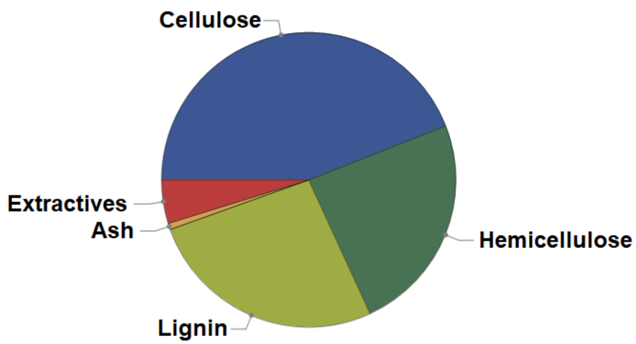


Composition

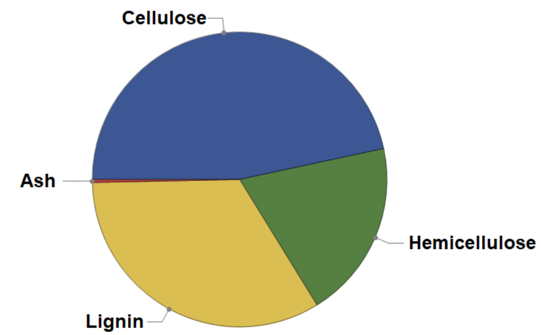
switchgrass



hybrid poplar

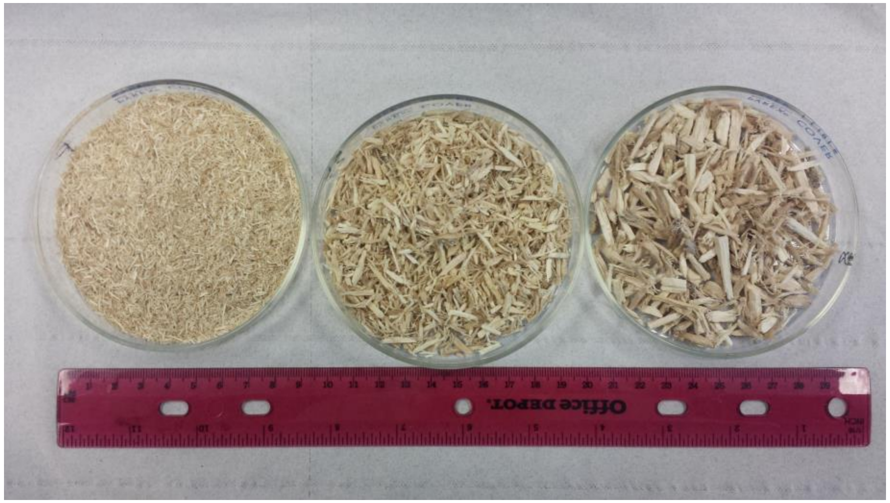


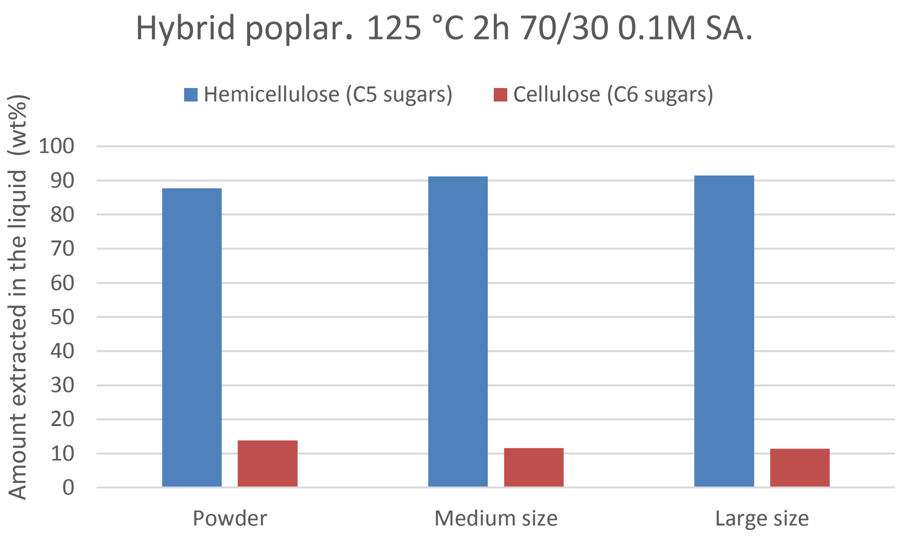
yellow pine



A variety of biomass types have been processed. This produced a range of biomass particle sizes and compositions to test fractionation process flexibility and economics.

Technical Accomplishments/ Progress/Results





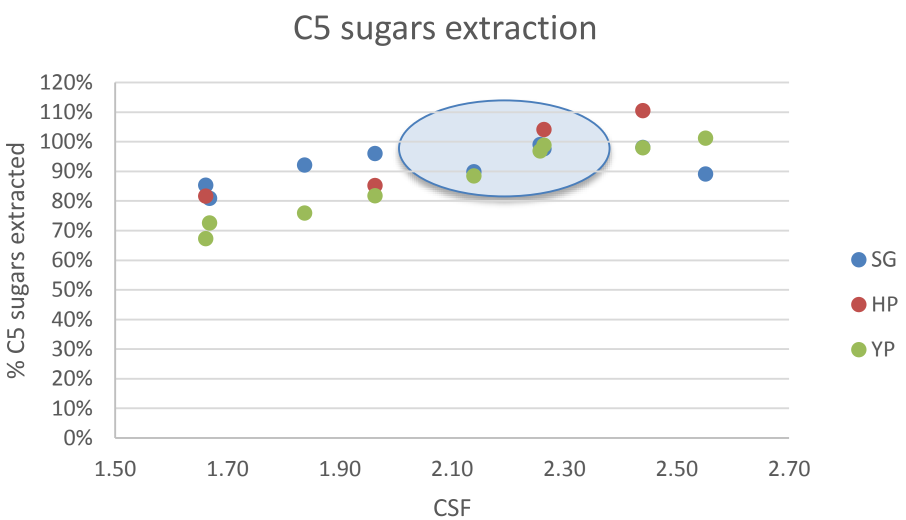
We can process different particle size feedstock with similar results.

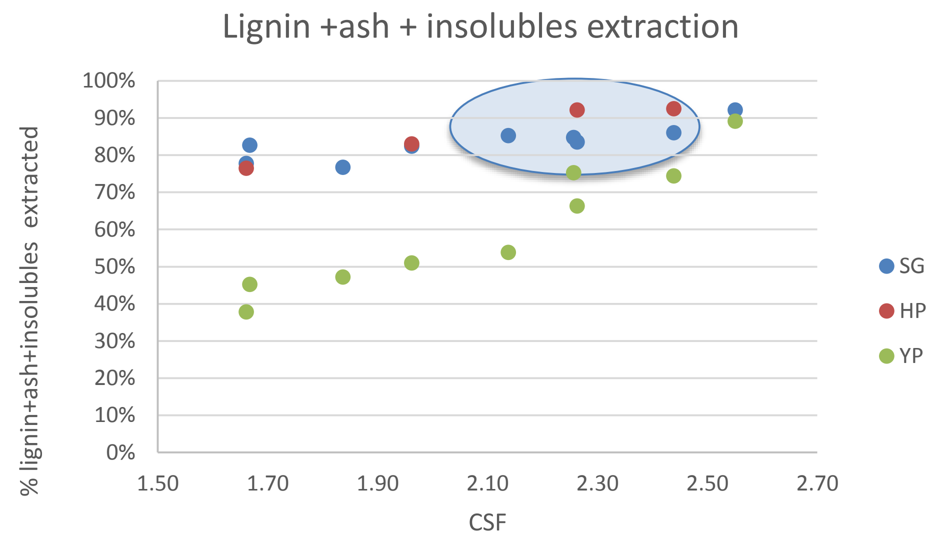
This facilitates the processing of mixed feedstock.

Penetration of the liquid inside the pores is the challenge to reduce mass transfer limitations.

Technical Accomplishments/ Progress/Results

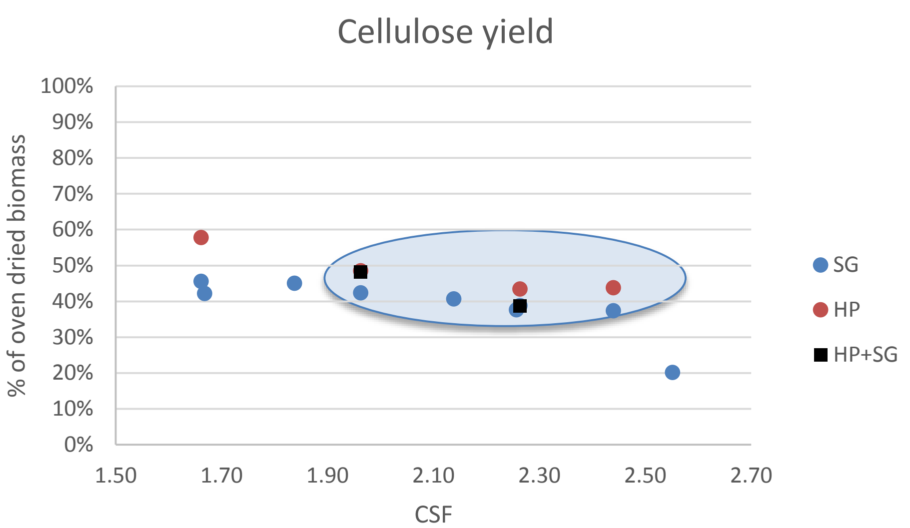
Combined Severity Factor (CSF) $= \log\left[t \cdot \exp\left(\frac{T-100}{14.75}\right)\right] - \mathrm{pH}$

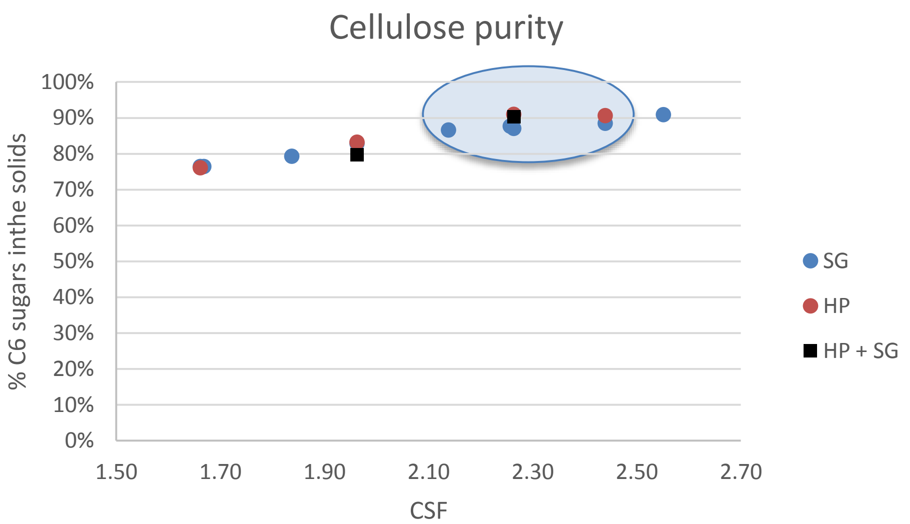


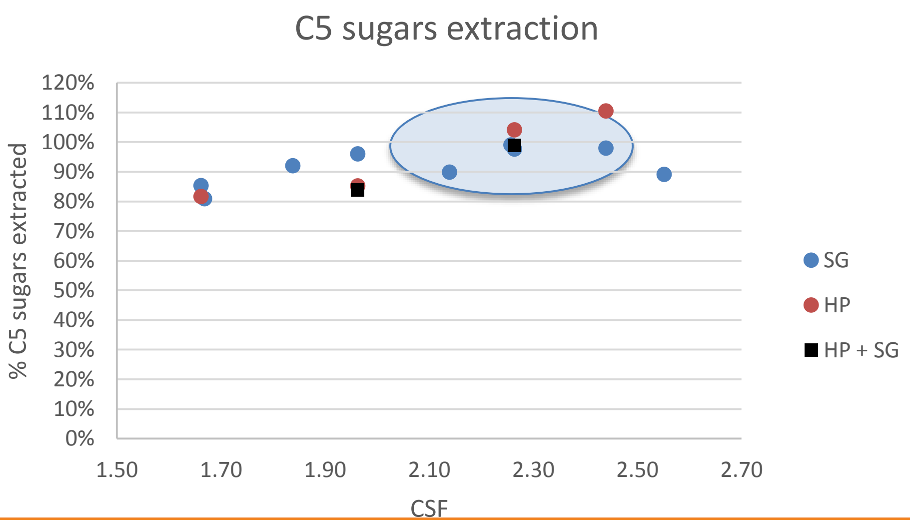


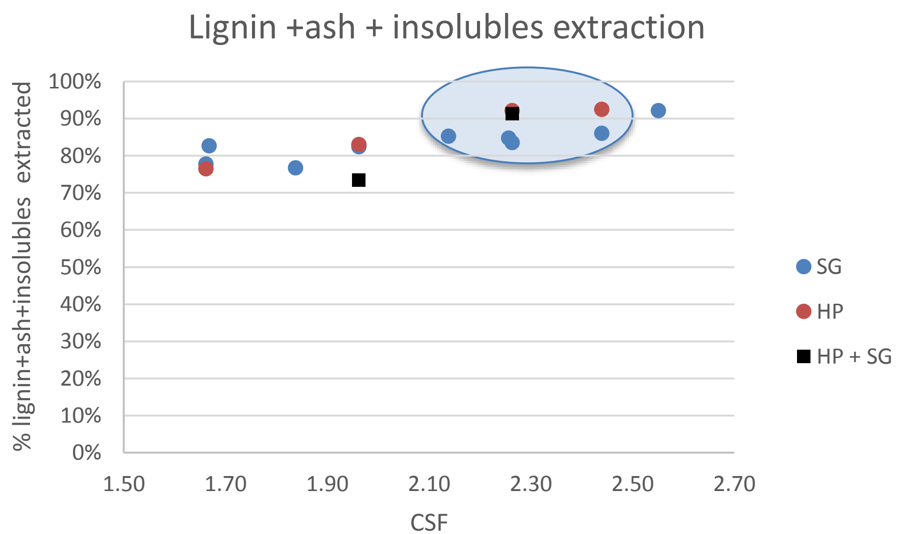
- Optimal process conditions to remove >90% of the lignin and >90% of the hemicellulose for the single feedstocks. There is an overlap between Hybrid poplar and switchgrass to process them together. Particle size is not a challenge.
- C5 and lignin yields at low CSF compares favorably to other organosolv methods (Bozell 10.1021/jf201850b; Brosse 10.1021/ie9006672; Goh 10.1016/j.biombioe.2011.06.034)

Technical Accomplishments/ Progress/Results









Relevance

Goal: *The goal is to separate biomass into high purity streams of its three main components, cellulose, hemicellulose and lignin in an integrated process to enable efficient and cost effective downstream conversion processes.*

Diverse

High Biomass Loading. Multiple feedstocks

High Yielding

>90% C_5
> 90% C_6
> 95% L

Simultaneous Deconstruction and Refinement

Pure

Product Purity
Furfural >98%
Cellulose >96%
Lignin >98%

Revenue Hat Trick

$

Three Product Co-Production
=
Cost Disruption

Produces clean streams of cellulose, furfural, and lignin that can be potentially picked by other biomass-derived industries (cellulosic ethanol, fermentation technologies, chemical industry)

Relevance

Relevance to BETO Goals and Barriers

- *High feedstock loadings (>30%)*
- *Operates under mild conditions (<140°C and <5 bar)*
- *Catalytic upgrading of sugars to aviation fuels*
- *Upgrades lignin to carbon for existing carbon markets*
- *Project metrics are driven by TEA/LCA*
- *<$3 GGE fuels productions*

Industrial Relevance

- *Technology accommodates herbaceous, hardwood, and softwood biomass allowing for geographic flexibility*
- *Technology performs equally well with varying sizes*
- *Maximize the value obtaining from biomass by valorizing cellulose, hemicellulose and lignin simultaneously.*
- *Produces low-cost platform chemicals increasing the flexibility of a future bio-refinery and enabling multiple downstream technologies (sugars, HMF, furfural, levulinic acid, GVL, butene) along with fuel (alkanes)*

Future Work

Fractionation

- *Deliver cellulose and lignin with >90% purity*
- *Go/No-go: Achieve greater than 90% purity lignin stream, >90% hemicellulose solubilized and greater than 90% purity cellulose at greater than 85% yield for one feedstock stream*

Lignin upgrading

- *Activated carbon foams from lignin via hydrothermal processing*

Chemical intermediates and fuels

- *Convert hemicelluloses to furfural with >75% yield*
- *Convert glucose the HMF > 75% yield*
- *HMF to LA >90% yield and furfural to LA at >70% yield*
- *Produce alkenes from GVL*

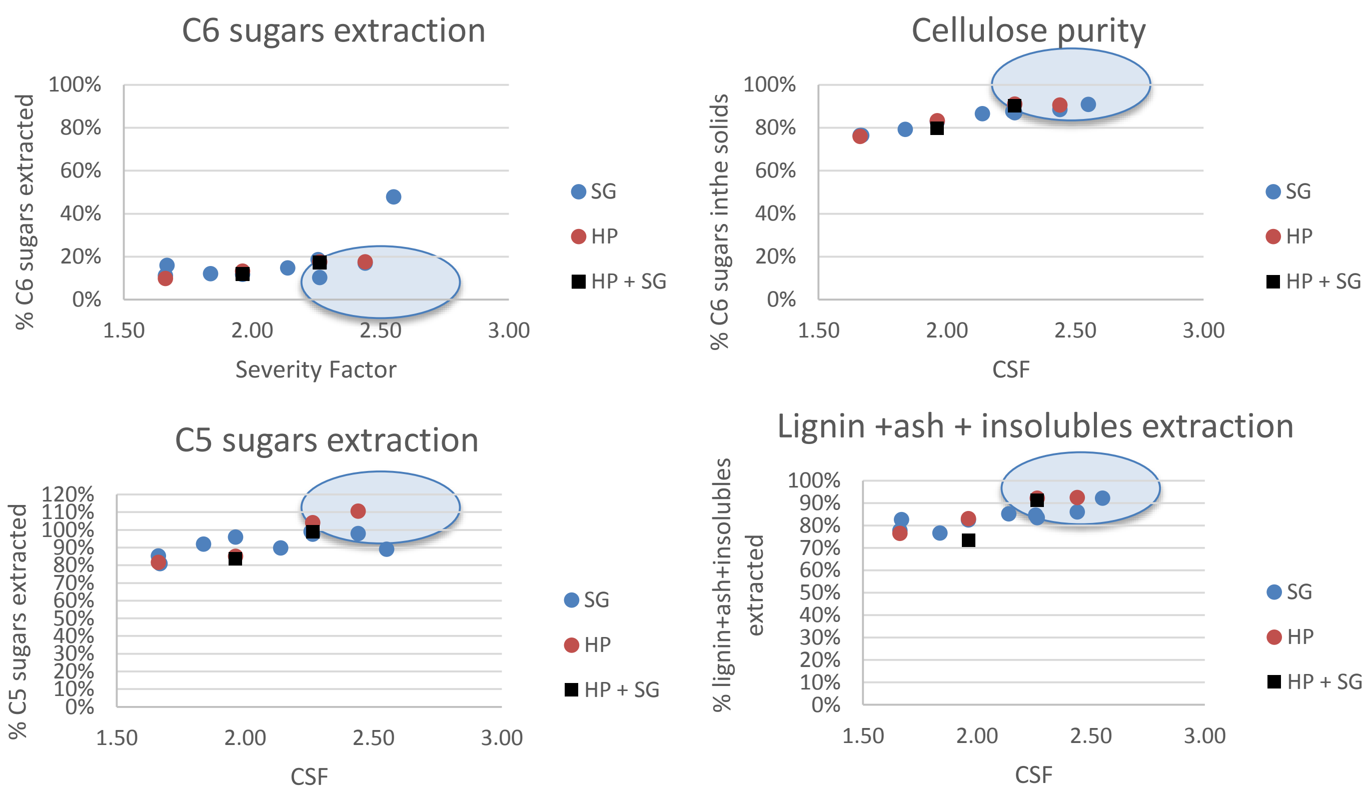
Economic analysis

- *Demonstrate <$3 GGE ethanol production in year 1 (based upon economic models)*
- *Demonstrate <$3 GGE alkane production in year 2*

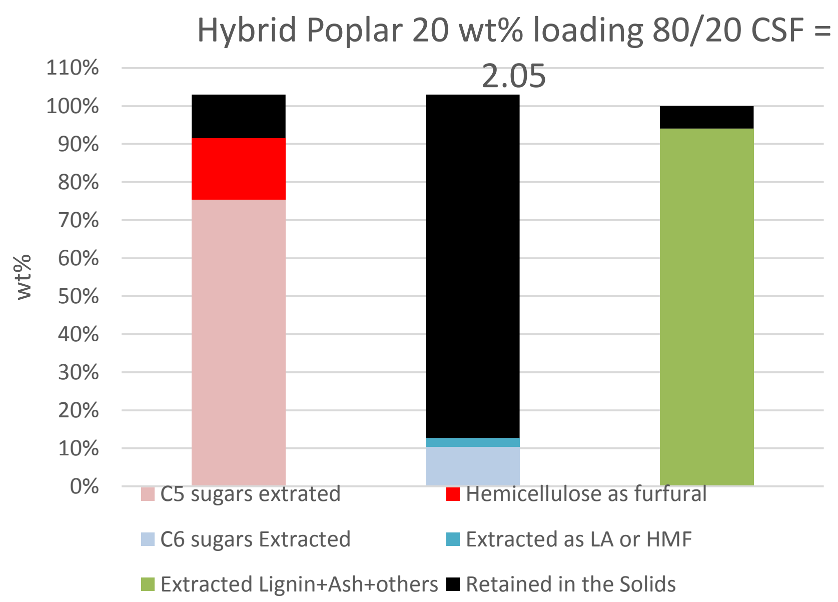
Summary

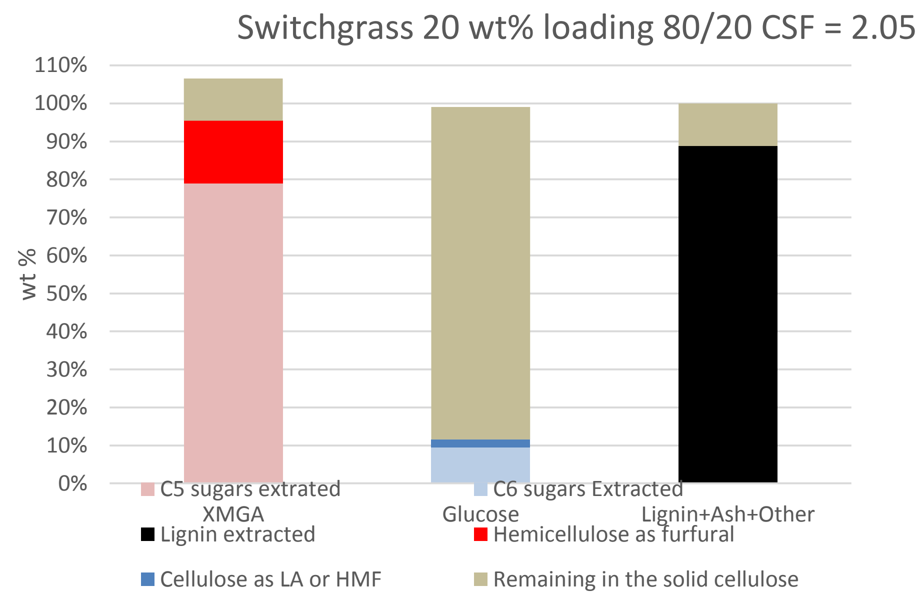
1. Approach
   – Fractionate a variety of feedstocks (softwood, hardwood, and herbaceous) with varying geometries into pure streams of hemicellulose, lignin, and cellulose
   – Upgrade pure streams into chemicals, materials, and fuels
   – Use TEA/LCA to select product distribution
2. Technical accomplishments
   – Optimized fractionation conditions for multiple feedstocks of with varying size distribution
   – Removed >90% lignin, solubilized >90% hemicellulose
3. Relevance
   – Lignin coproducts needed to meet cost targets through existing markets
   – Addresses multiple barriers: fractionates at high biomass loadings, removal of impurities, and operates under mild conditions
   – Produce next generation aviation biofuels
4. Future work
   – Optimize fractionation conditions for multiple feedstocks
   – Production of activated carbon foam FY 2019
   – Produce alkanes from GVL FY 2020
   – Demonstrate <$3 GGE ethanol FY 2019 and <$3 GGE jet fuel FY 2020

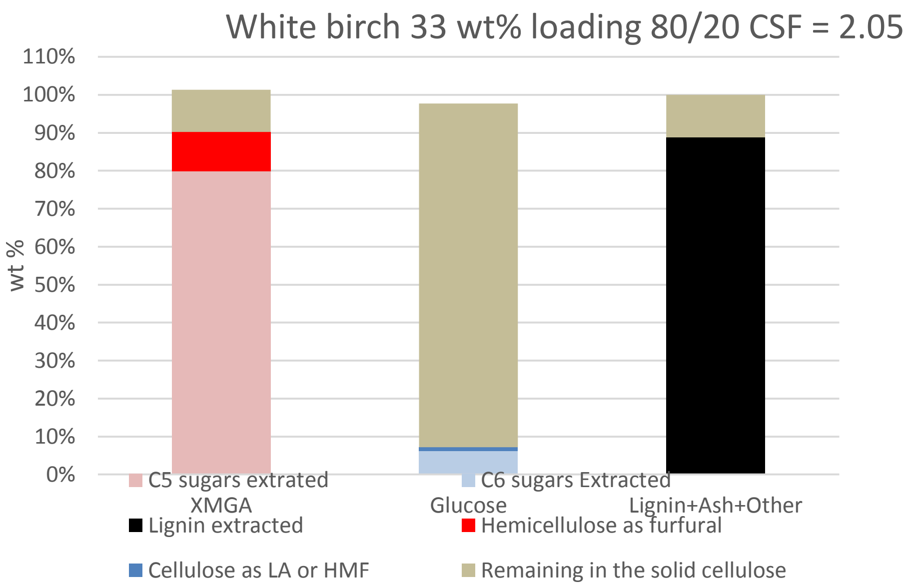
Additional Slides



C6 sugars extraction
% C6 sugars extracted
100%
80%
60%
40%
20%
0%
1.50
2.00
2.50
3.00
Severity Factor
SG
HP
HP + SG
Cellulose purity
% C6 sugars inthe solids
100%
80%
60%
40%
20%
0%
1.50
2.00
2.50
3.00
CSF
SG
HP
HP + SG
C5 sugars extraction
% C5 sugars extracted
120%
110%
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
1.50
2.00
2.50
3.00
CSF
SG
HP
HP + SG
Lignin +ash + insolubles extraction
% lignin+ash+insolubles extracted
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
1.50
2.00
2.50
3.00
CSF
SG
HP
HP + SG


Hybrid Poplar 20 wt% loading 80/20 CSF = 2.05
110%
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
wt%
C5 sugars extrated
Hemicellulose as furfural
C6 sugars Extracted
Extracted as LA or HMF
Extracted Lignin+Ash+others
Retained in the Solids


Switchgrass 20 wt% loading 80/20 CSF = 2.05
110%
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
wt %
XMGA
Glucose
Lignin+Ash+Other
C5 sugars extrated
C6 sugars Extracted
Lignin extracted
Hemicellulose as furfural
Cellulose as LA or HMF
Remaining in the solid cellulose

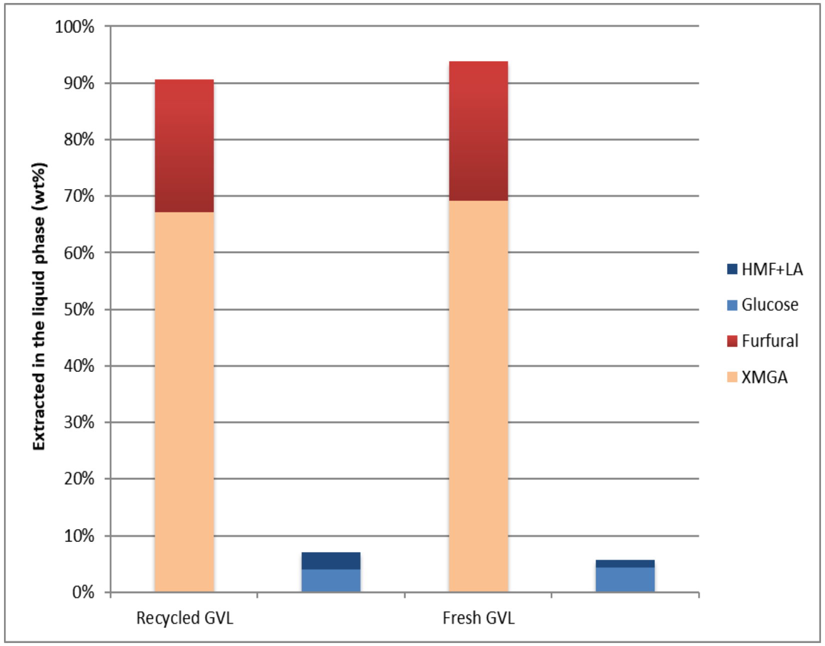


White birch 33 wt% loading 80/20 CSF = 2.05
110%
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
wt %
XMGA
Glucose
Lignin+Ash+Other
C5 sugars extrated
C6 sugars Extracted
Lignin extracted
Hemicellulose as furfural
Cellulose as LA or HMF
Remaining in the solid cellulose

Solvent cost. $ per MT of dry biomass

Biomass loading (wt%)	Solvent cost	Solvent loss (%)				
		95	98	99	99.5	99.9
10 %	$500/MT	175	70	35	18	4
	$1000/MT	350	140	70	35	7
	$2000/MT	700	280	140	70	14
20 %	$500/MT	88	35	18	9	2
	$1000/MT	175	70	35	18	4
	$2000/MT	350	140	70	35	7
30 %	$500/MT	58	23	12	6	1
	$1000/MT	117	47	23	12	2
	$2000/MT	233	93	47	23	5

Similar results using recycled GVL in the fractionation step



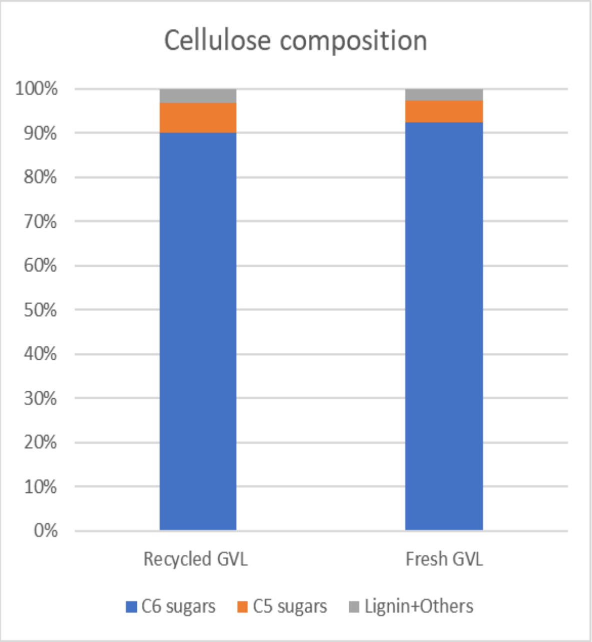
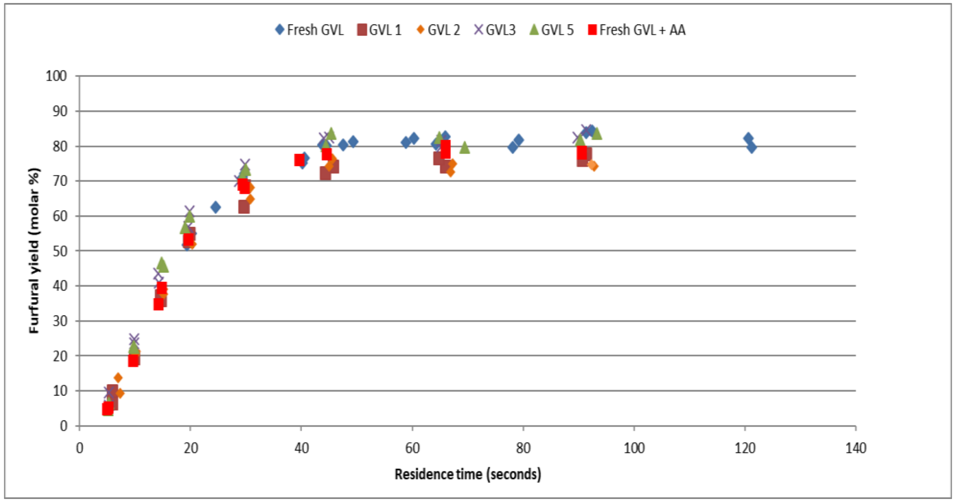
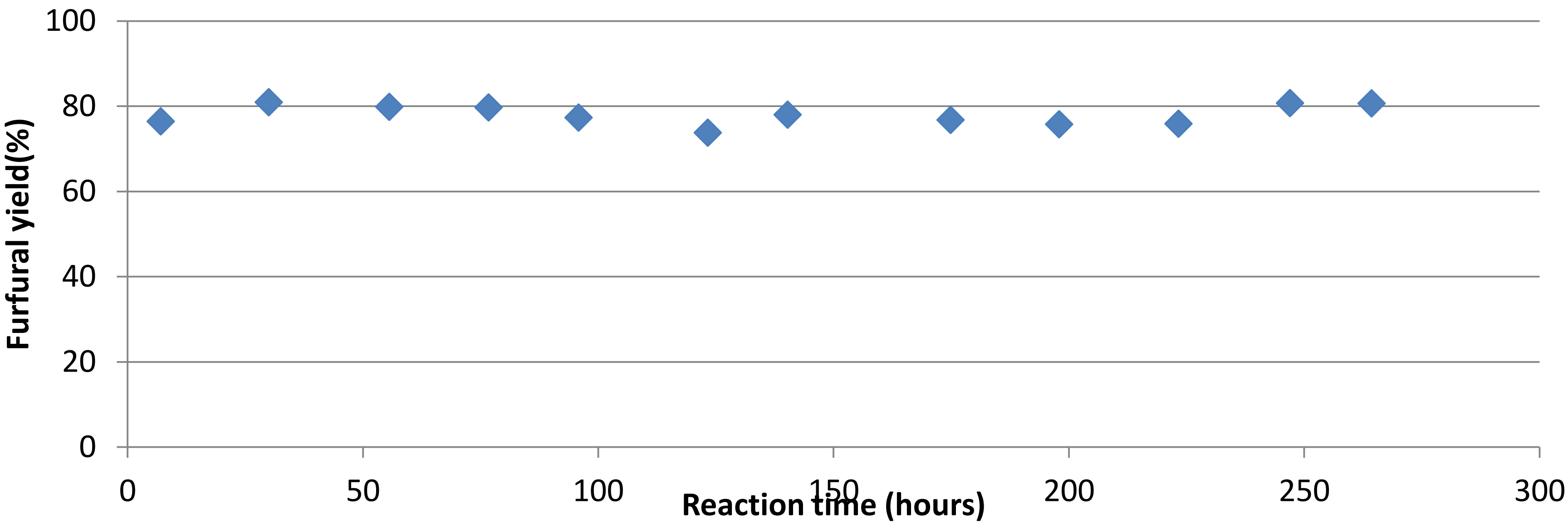


Figure 4. shows that there are no major differences between fresh GVL and the recycled GVLs samples. Furfural production rate was similar in all cases and furfural yields around 80%



ID	Recovery (wt%)	Purity (wt%)	Solids (wt%)	Furfural (wt%)	Others (wt%)	Notes
GVL 1	Not calculated	85	11.6	0.32	3	GVL was used to extract C5 from WB and to produce furfural. Obtained after distilling furfural and water. Used to produce the other GVL samples
GVL 2	100.7 identified	82	18	0.06	0	Obtained after concentrating GVL 1. This is the residue.
GVL 3	100.7% identified	>99	0	1.15	0.1	Obtained after concentrating GVL 1. This is the distillate
GVL 4	99.5-101	>99.9	0	0.1	0.04	Obtained from GVL 2 by simple evaporation. Brute Force
GVL 5	99.9-100	>99.9	0	0.1	0.05	Obtained from GVL 2 by evaporation using Therminol 66
GVL 6	99.5-102	>99.9	0	0	0	Obtained from GVL 1 by evaporation using Therminol 66

Simple reactor configuration. Plug flow.
Sulfuric acid does not deactivate
No solids accumulation in the reactor



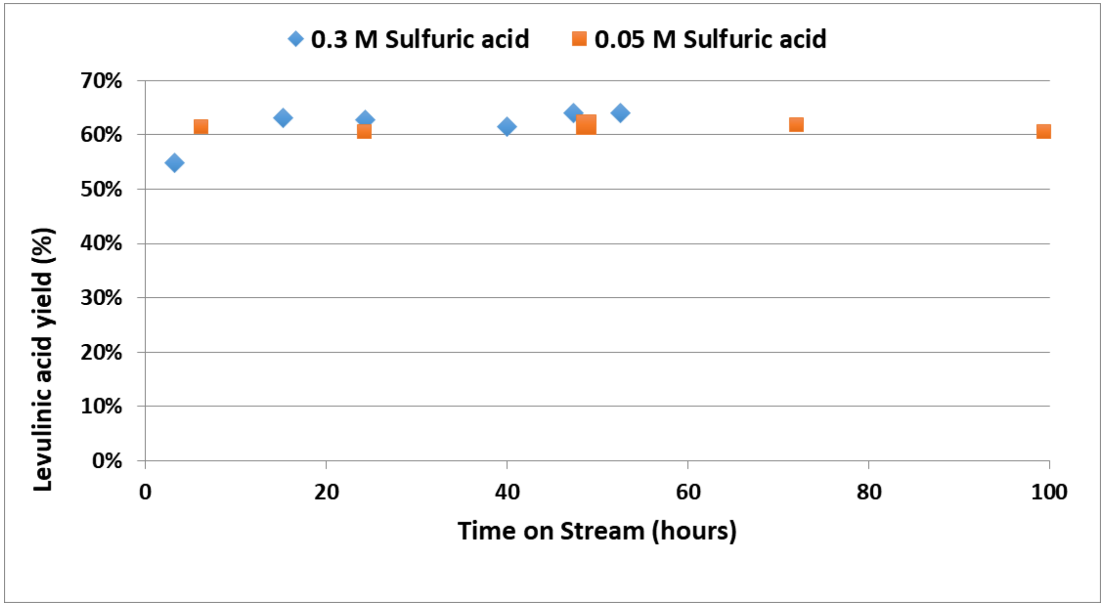


Figure 10. Production of levulinic acid from fructose in a continuous reactor. 3 wt% fructose, 50/50 GVL/water solvent, 220 °C, 15 min residence time for 0.3 M SA experiment and 45 min residence time for 0.05 M SA experiment.

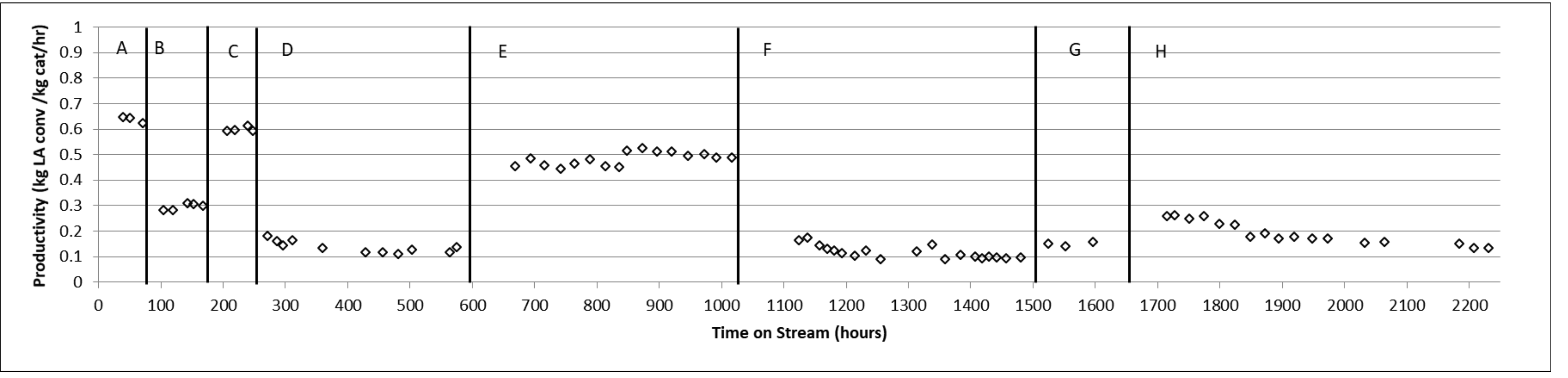


Figure 11. RuSn/C stability plot. Several reaction conditions and feedstocks.

Responses to Previous Reviewers' Comments

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

Publications, Patents, Presentations, Awards, and Commercialization

- None to report at this time