DOE Bioenergy Technologies Office (BETO) 2021 Project Peer Review

Condensed Phase Catalysis Technology for Fuels and Carbon Products

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Catalytic Upgrading

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Project Overview

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 γ-valerolactone (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.*

Relevance to BETO’s Goals

Our Goal: *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 > 20% feedstock agnostic

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

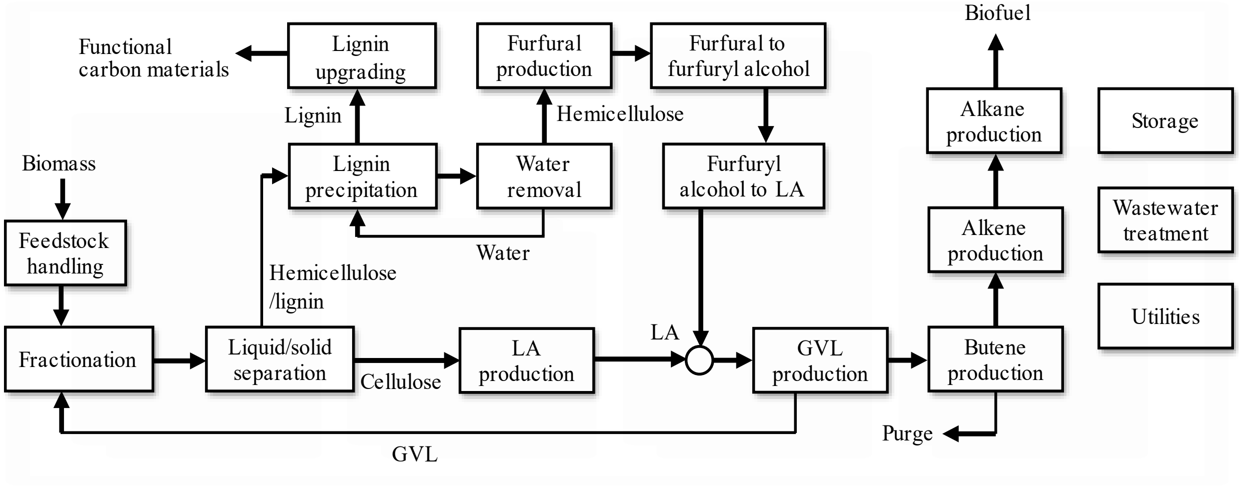
Produces clean streams of cellulose, furfural, and lignin that can be potentially picked by other biomass-derived industries (cellulosic ethanol, fermentation technologies, chemical industry)

1 - Project 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 – formerly Christos Maravelias now George Huber (UW)*
  - *Collect all process and economic data for LCA and TEA analysis*

2 - 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.
- **Go/No-go**: Achieve fractions of >90% lignin purity *and* >90% hemicellulose solubility *and* >90% purity cellulose *and* >85% yield for one feedstock
  - Purpose: demonstrate the ability to convert feedstocks to pure streams for upgrading



2 - Technical Approach - Fractionation

Use biomass derived solvent (GVL) to fractionate diverse feedstocks

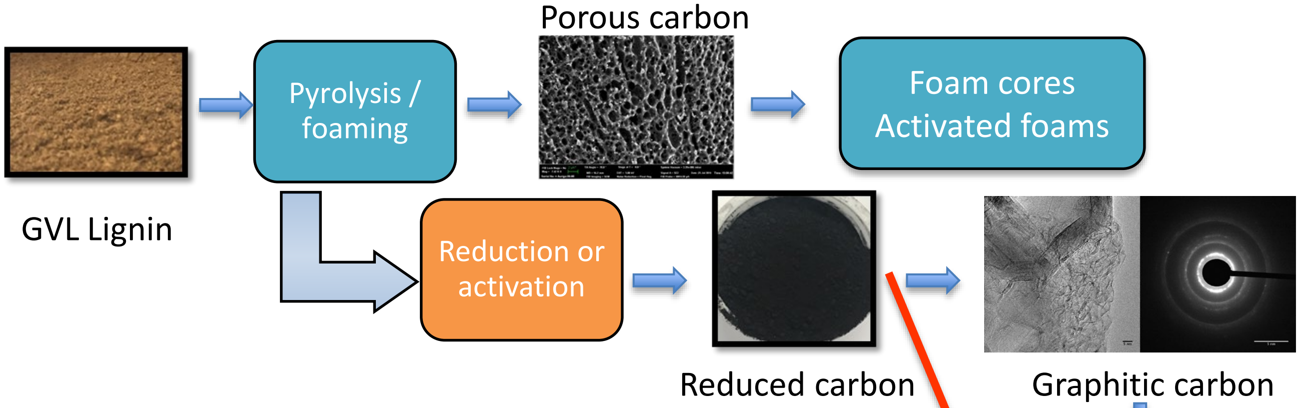
- Switchgrass (Panicum virgantum), hybrid poplar (Populus spp.), and Southern yellow pine (Pinus spp.)
- Processing several feedstocks together (at least 2 types) with minimal pre-processing (wet samples)
- Minimal degradation of any of the fractions (retain >85% cellulose, >90% hemicellulose, >70% lignin)
- Maximize biomass loading, >20 wt% loading (hemicellulose and lignin soluble)
- Minimize separation steps (GVL solvent is the intermediate to produce fuels)
- Reuse the solvent and recycle as many streams as possible

Potential challenges

(Solution)

- Different lignin structure and hemicellulose composition of hard/soft wood and grasses may complicate mixed feedstock upgrading – upgrading was successful, yields varied with feedstock
- Solvent must be recovered and recycled – successfully tested
- Accumulation of impurities in the recycle streams – was not an issue
- Lignin products, chemicals and fuels must meet market specifications – will have to evaluate this beyond the scope of this project
- Biomass species leads to variation in particle size distribution and chemical composition – varying particle sizes and biomass types fractionated successfully
- Switchgrass normally contains higher extractives and ash content than wood species – not an issue
- Removing bark from hybrid poplar may not be realistic in future large-scale operations – not tested

2 - Technical Approach – Lignin Products



Porous carbon

GVL Lignin

Pyrolysis / foaming

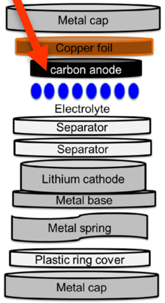
Foam cores Activated foams

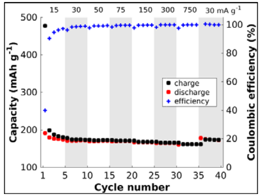
Reduction or activation

Reduced carbon

Graphitic carbon

- ***Use GVL fractionated lignin to produce carbon products***
  - *Evaluate lignin streams*
  - *Develop carbons for energy storage*
- ***Possible challenges - solutions***
  - *Not enough lignin generated from GVL process early in the project – used softwood kraft as a model*
  - *Pore distribution – used chemical activation agents*
  - *Cracking of carbon monoliths – used in powdered form*
  - *Extra processing steps guided by the TEA*

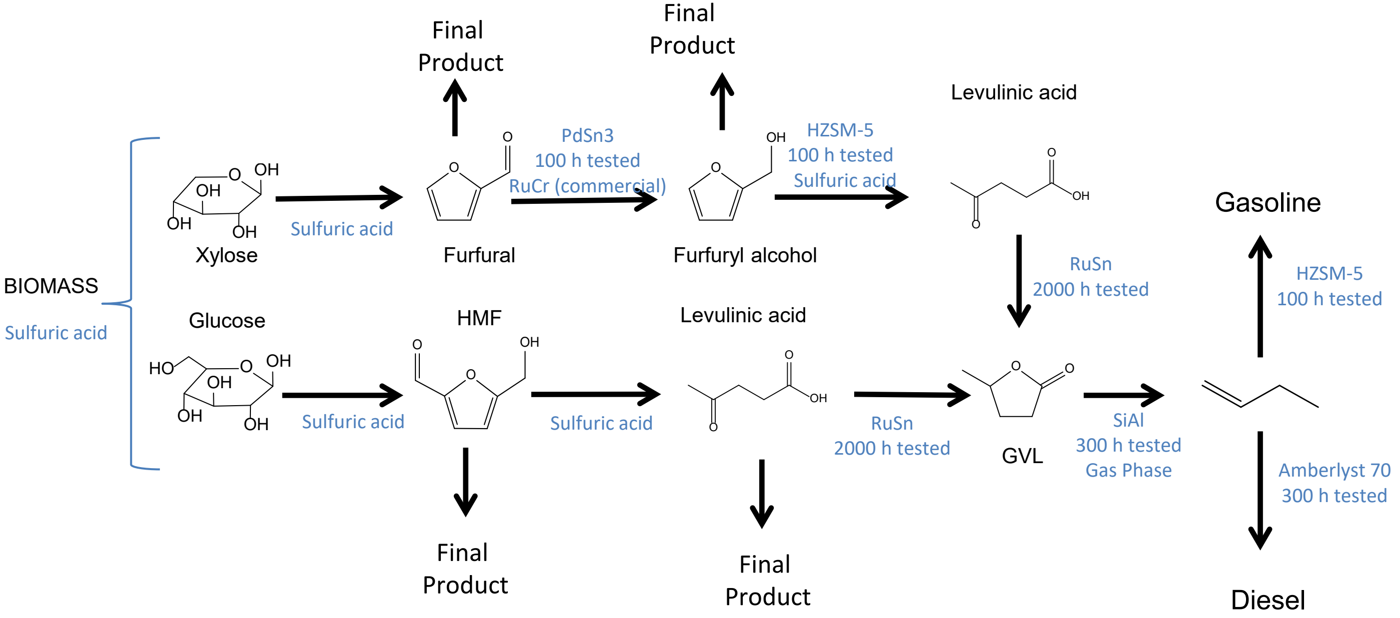




GVL lignin-carbon battery anode

2- Technical Approach: Chemicals, Intermediates, and Fuels

Mixed feedstocks: hybrid poplar and switch grass



BIOMASS

Sulfuric acid

Xylose

Sulfuric acid

Furfural

Final Product

PdSn3
100 h tested
RuCr (commercial)

Furfuryl alcohol

Final Product

HZSM-5
100 h tested
Sulfuric acid

Levulinic acid

RuSn
2000 h tested

Glucose

Sulfuric acid

HMF

Final Product

Sulfuric acid

Levulinic acid

Final Product

RuSn
2000 h tested

GVL

SiAl
300 h tested
Gas Phase

HZSM-5
100 h tested

Gasoline

Amberlyst 70
300 h tested

Diesel

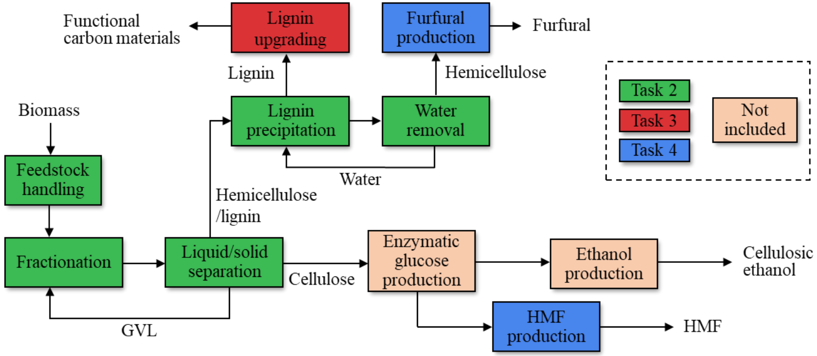
2 - Technical Approach – Chemicals, Intermediates, and Fuels

- *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)*

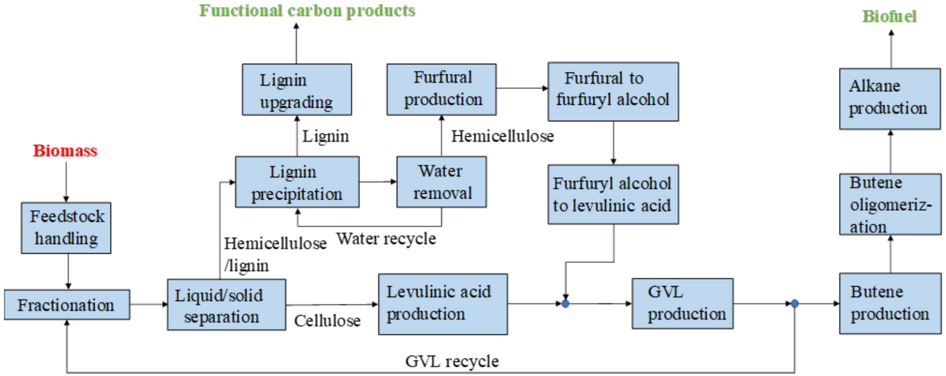
- *Potential challenges*
    - *Catalyst stability (Metal catalyst RuSn has been stable >2000 h) – Demonstrated catalysts used can be regenerated with no loss in efficacy*
    - *Low furfural production using feedstocks with low C5 sugars content – TEA demonstrates the cost target is still met*
    - *Valorization of C6 sugars in the hemicellulose fraction (can be used to make-up the solvent) - TEA demonstrates the cost target and yields are still met*

2 - Technical Approach – Economic Analysis

Year 1 Process Model for Ethanol



Year 2 Model for Next Gen. Biofuel (alkenes)



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)
3. Process and economic models available for coproduction of cellulosic ethanol, lignin and furfural (Alonso, D.M., et al., Science Advances, 2017. 3(5); Huang, K., et al. Applied Energy, 2018. 213, 585-594) in BP 1
4. Apply economic analysis from data gathered for the entire process for next generation of biofuels (alkenes)

3- Impact and Relevance to BETO and Industry

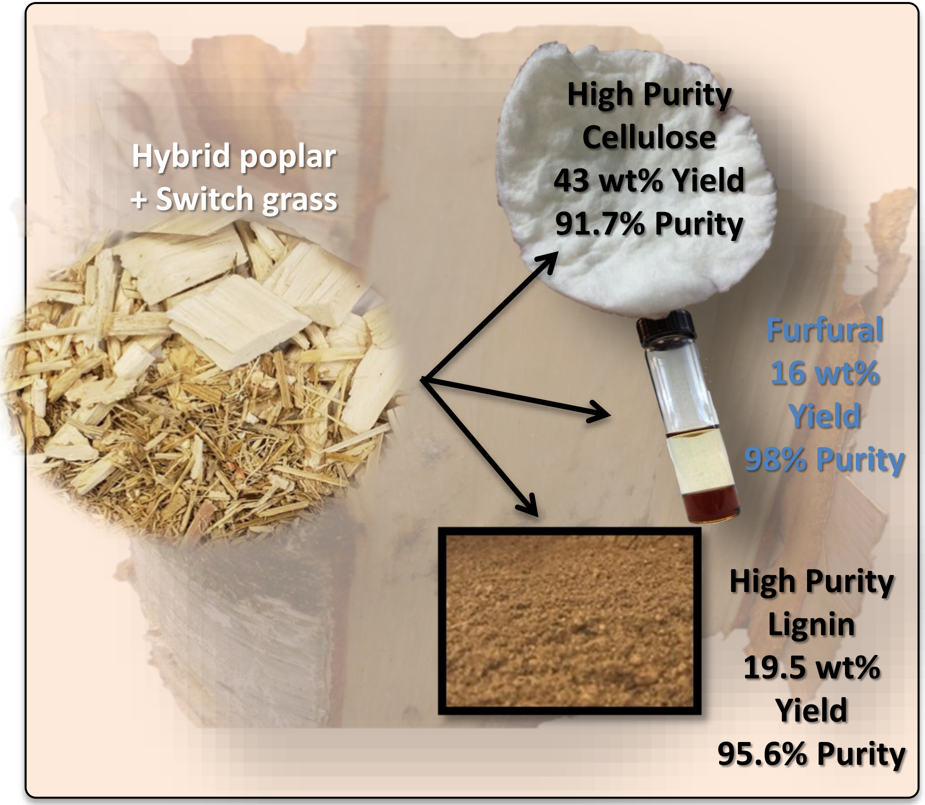
Relevance to BETO Goals and Barriers

- *High feedstock loadings (>30%)*
- *Operates under mild conditions (<140°C and <5 bar)*
- *Solvent is derived from biomass and has proven to be recyclable with no decline in yield*
  - GVL to butenes (>90%) -> liquid biofuels C_{+8} (~100%)
- *Chemical intermediates are produced at high yields >70%*
- *Demonstrated catalytic upgrading of sugars to alkanes (biofuels) with high yields*
- *Upgrades lignin to high value carbon for existing carbon markets*
- *Project metrics are driven by TEA/LCA*
- *<$3 GGE fuels productions demonstrated*

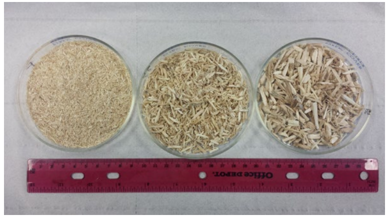
Industrial Relevance

- *Accommodates herbaceous, hardwood, and softwood biomass allowing for geographic flexibility*
- *Technology performs equally well with varying sizes of biomass*
- *Maximize the value obtaining from biomass by valorizing cellulose, hemicellulose and lignin simultaneously through materials, fuels, and chemical intermediates.*
- *Technology is scalable with no loss quality and yields*
- *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)*

4 - Outcomes - Fractionation



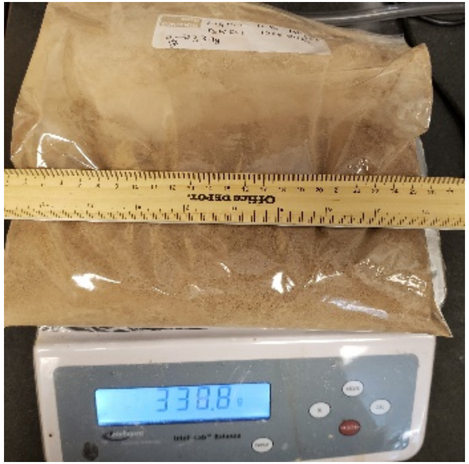
- Process combines biomass fractionation with chemical production
- >80% of the initial wood converted to high purity products
- Fractionation is feedstock flexible
  - All lignin purity >95%
  - All cellulose yields > 80% except yellow pine (this increased to > 80% when mixed)
  - Cellulose purity for all samples > 70%
  - Cellulose purity does not degrade GVL production
- Several mixtures of feedstocks treated
  - Hybrid poplar and Hybrid poplar + switchgrass met Go/No-go goal
- High biomass loading 20-30 wt%
- >99% solvent recovery
  - >98% purity
- Biomass size did not influence purity and yield



4 - Outcomes - Fractionation

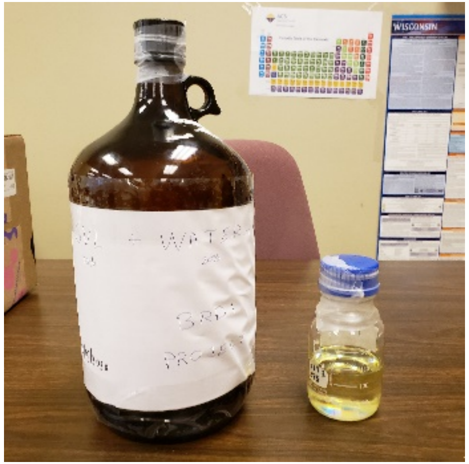
Cellulose

- 4 kg of high purity cellulose produced
- >85 % yield
- >90% purity
- Used to produce GVL and liquid fuel



Lignin

- 2 kg of lignin produced
- >90% Lignin extraction
- >70% Overall yield
- >95% purity
- Handed off to UT for upgrading

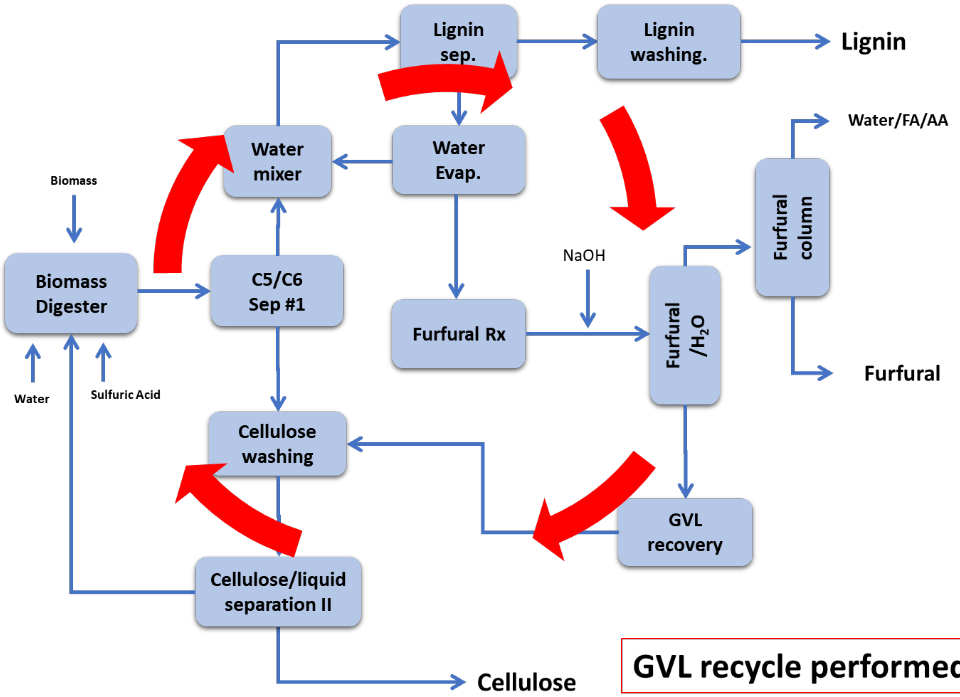


Furfural

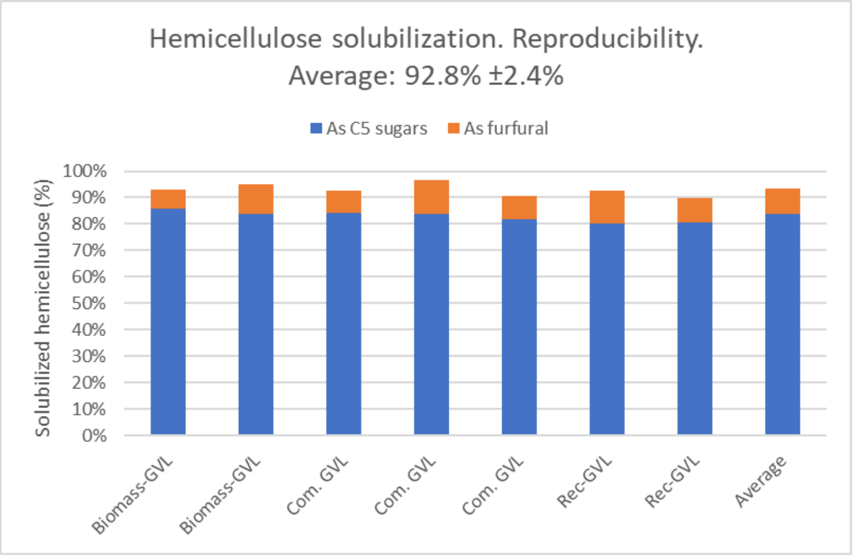
- 500 g of furfural produced
- >90% hemicellulose extraction
- >75% Furfural yield from C5
- >98% purity
- Used to produce liquid fuel

4 - Outcomes - Fractionation

Recovery and reutilization of GVL



GVL recycle performed 3x



4 - Outcomes – Fractionation

Milestone 2.1. Create a database with optimal process conditions to remove >90% of the lignin and >90% of the hemicellulose for the single feedstocks(M6). Completed

Milestone 2.2. Recover >70% of the solubilized lignin by addition of recycled water with >90% purity (M8). Completed.

Milestone 2.3. Create a database with optimal process conditions to produce cellulose >90% purity (M8). Completed.

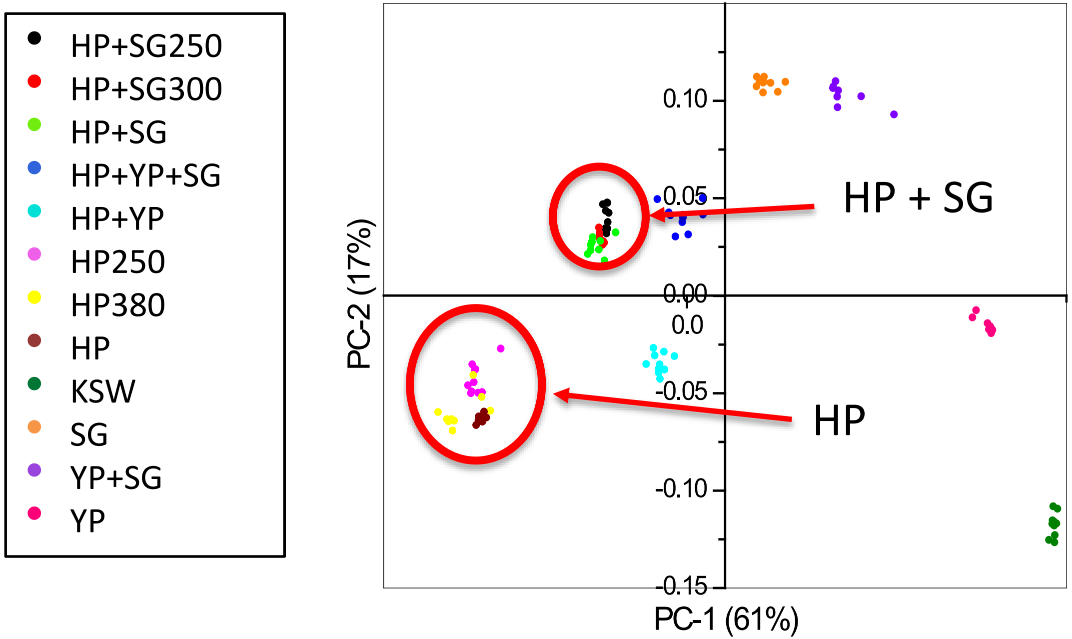
Milestone 2.4: Deliver lignin samples (100 g) from single, two and three mix feedstocks with >90% purity produced in a batch reactor (50 ml) (M9). Completed in 1 L reactor.

Milestone 2.5. Deliver cellulose samples (50 g) with 90% purity for the 2 and 3 mix feedstocks in a batch reactor (50 ml) (M12). Completed

Milestone 4.1. Demonstrate the conversion of solubilized hemicellulose produced in task 2 to furfural >75% yield in a continuous flow reactor (grams scale) (M9). Completed

4 – Outcomes: Lignin Scale Up

Principal component analysis (PCA) of Fourier Transform Infrared (FTIR) spectra yields Purity of 95% for 3 HP batches of 100, 250, 380 g and HP + SG batches of 100, 250, and 300 g



Scaling of the fractionation process produces no statistically discernable chemical difference.

4 – Activation Results

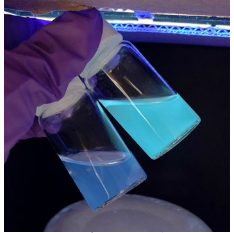
Samples	Method	Surface Area (m^2/g)	Surface Area from micropores	Surface Area from mesopores
GVL HP	Physical	266	64.46%	35.54
GVL SG	Physical	384	89.15%	10.85%
GVL YP	Physical	393	58.65%	41.35%
KSW	Physical	431	88.33%	11.67%
KSW lignin	2 step chemical	1,195.33	70.54%	29.46%
KSW lignin	2 step chemical	1,718.83	0.22%	99.78%
KSW lignin	1 step chemical	3,531.28	34.06%	65.94%
KSW lignin	1 step chemical	4,497.34	16.26%	83.74%

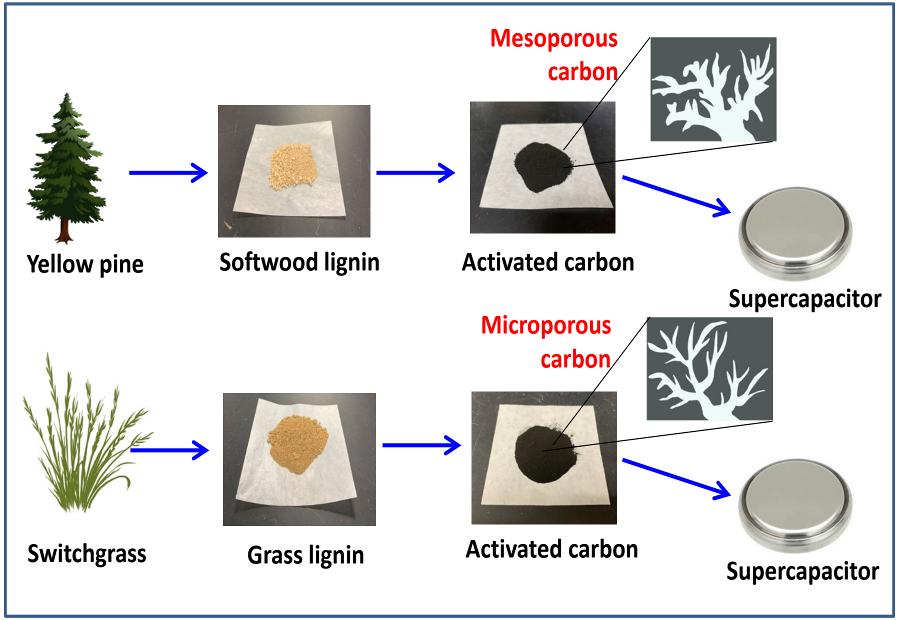
- 3 Activation processes were investigated
  - Physical activation with steam and CO_2
  - 2 Step chemical activation with pyrolysis + KOH
  - 1 Step chemical activation with KOH
- Higher surface area = higher capacitance (usually) as more sites are available for the electrolyte to bind to the carbon surface
- KSW (kraft softwood) – used as model because of limited GVL lignin
- Highest surface area ever observed from a biobased sample[1] produced with 1 step chemical activation process

[1] Lyu, L., et al. Recent development of biomass-derived carbons and composites as electrode materials for supercapacitors. Materials Chemistry Frontiers 2019, 3 (12), 2543-2570.

4 – Carbon Products

- Pine demonstrated the highest performance of 175 F/g and coulombic efficiency of 99.5% over 3,000 cycles
- Performance can be enhanced by including carbon quantum dots (CDs) where 302 F/g has been achieved with a physically activated lignin substrate
- Cost considerations:
  - Carbon black = $0.5 – 2 /kg
  - Activated carbon = $1/kg
  - Activated carbon (super capacitor grade) = $15/kg
  - Graphite (battery grade) = $22/kg
  - Carbon quantum dots = $83/mg

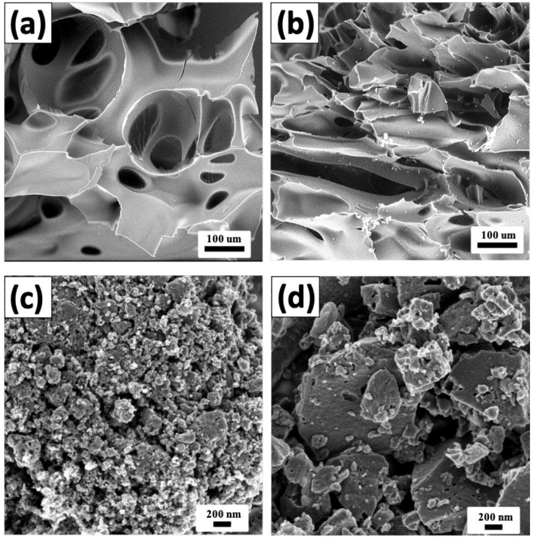

Lignin based CDs



4 – Carbon Products Status

ML 3.1 – complete - focus on carbons for supercapacitors

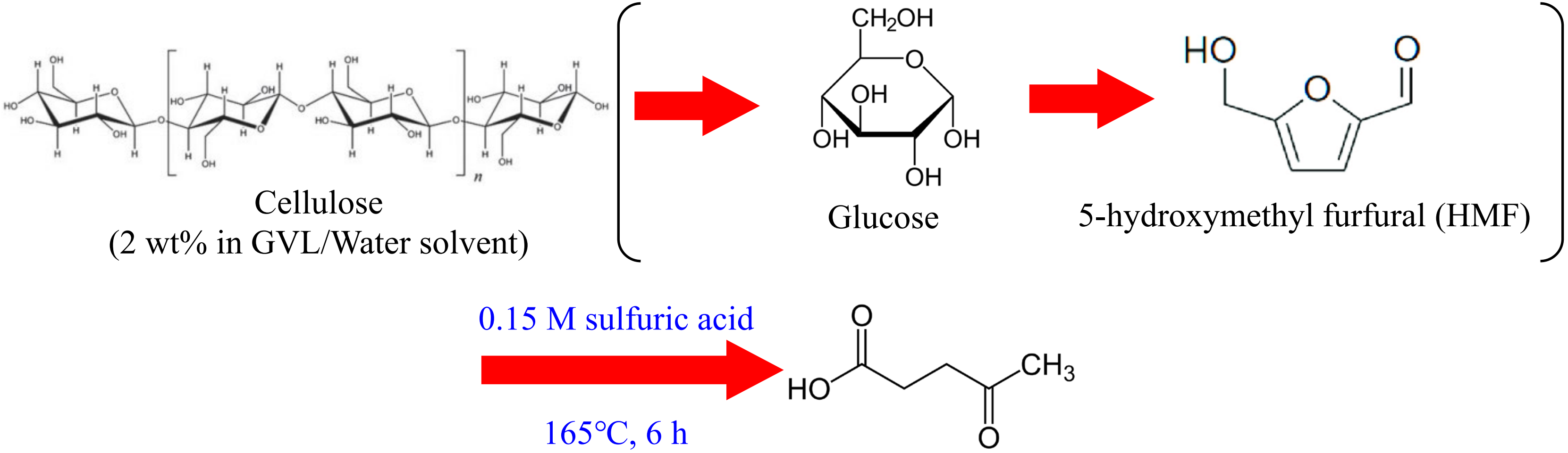
ML 3.2 – ongoing analysis of chemical activation of GVL lignins and performance results



SEM images of different lignin precursors: (a) YP-py and (b) SG-py and SEM images of different AC samples: (c) YP-AC and (d) SG-AC.

4 – Outcomes: Chemicals, Intermediates, and Liquid Fuels

- **Cellulose** upgrading to chemical intermediates in GVL/Water (1/1, wt/wt) solvent



Cellulose
(2 wt% in GVL/Water solvent)

Glucose

5-hydroxymethyl furfural (HMF)

0.15 M sulfuric acid

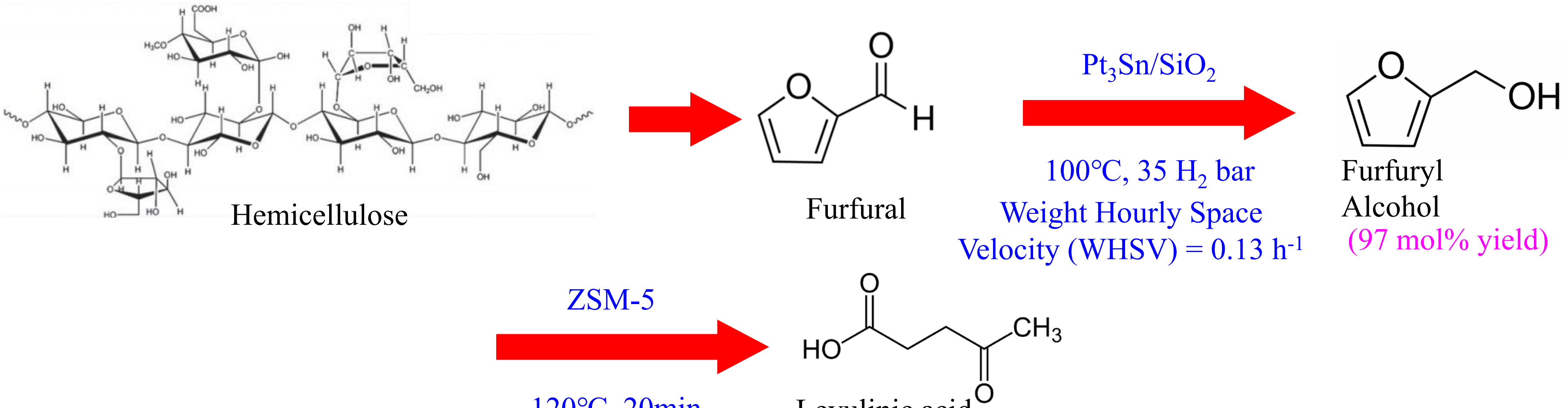
165°C, 6 h

Levulinic acid
(LA)
(72 mol% yield)

➔ Chemical intermediate (Levulinic acid) was synthesized from cellulose

4 – Outcomes: Chemicals, Intermediates, and Liquid Fuels

- **Hemicellulose** upgrading to chemical intermediates in GVL/Water (4/1, wt/wt) solvent



Hemicellulose

Furfural

Pt_3Sn/SiO_2

100°C, 35 H_2 bar

Weight Hourly Space Velocity (WHSV) = 0.13 h^{-1}

Furfuryl Alcohol

(97 mol% yield)

ZSM-5

120°C, 20min

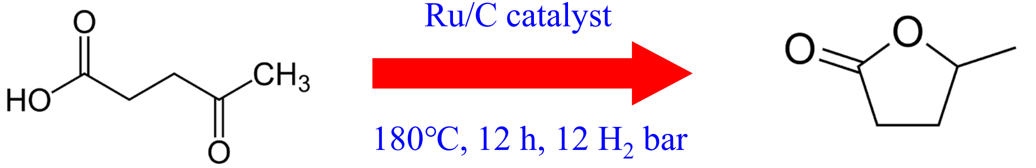
Levulinic acid (LA)

(70 mol% yield)

➔ Chemical intermediate (Levulinic acid) was synthesized from hemicellulose

4 – Outcomes: Chemicals, Intermediates, and Liquid Fuels

- Levulinc acid upgrading to γ-valerolactone (GVL) in GVL/Water (1/1, wt/wt) solvent



Ru/C catalyst

180°C, 12 h, 12 H_2 bar

Levulinic acid (LA)

γ-valerolactone (GVL)

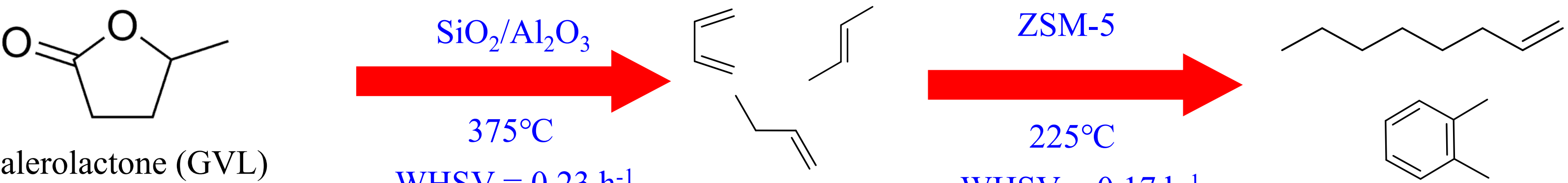
(74 mol% yield)

➔ Levulinic acid was converted to a fuel precursor (GVL)

- γ-valerolactone upgrading to **biofuels (alkenes)**

Butenes

Liquid fuels (C_{+8})



SiO_2/Al_2O_3

375°C

WHSV = 0.23 h^{-1}

ZSM-5

225°C

WHSV = 0.17 h^{-1}

γ-valerolactone (GVL)

(93 mol% yield)

(100 mol% yield)

➔ A range of liquid fuels were synthesized from GVL

4 – Outcomes: Chemicals, Intermediates, and Liquid Fuels Milestones

Task. 4.1. Convert hemicelluloses to furfural: 100% completion

Task. 4.2. Produce LA from cellulose: 100% completion

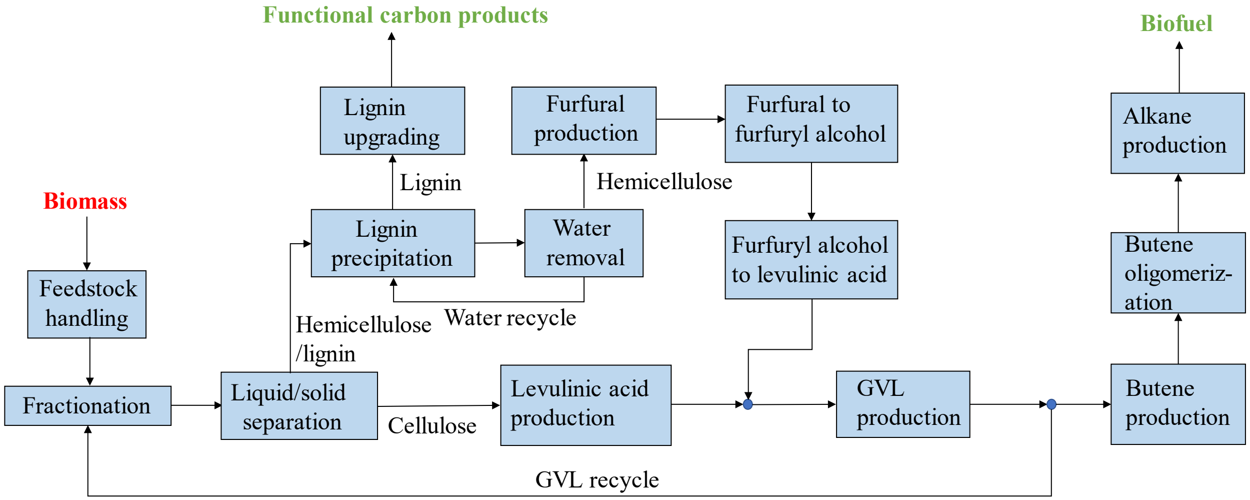
Task. 4.3. Produce LA from furfural: 100% completion

Task. 4.4. Produce GVL from LA: 100% completion

Task. 4.5. Produce alkenes from GVL: 10% completion

➔ Task. 4.5. requires the 1L production of alkenes, but currently we have synthesized 0.1L of alkenes. We are continuously producing alkenes as much as possible to reach the milestone

4- Outcomes: TEA - Block Flow Diagram



Motivation

- Previously, lignin was used to satisfy part of energy requirements of the process
- Goal: upgrade the lignin to high value carbon products
- Focus on lignin upgrading to produce “supercapacitor carbon”
    - Lignin also explored as anode for ion batteries and carbon quantum dots as alternative products
- E.g., price of supercapacitor carbon ~ $15/kg
- Allow to sell biofuels (alkenes) at low price

https://www.materialstoday.com/electronic-properties/articles/s1369702113003027/

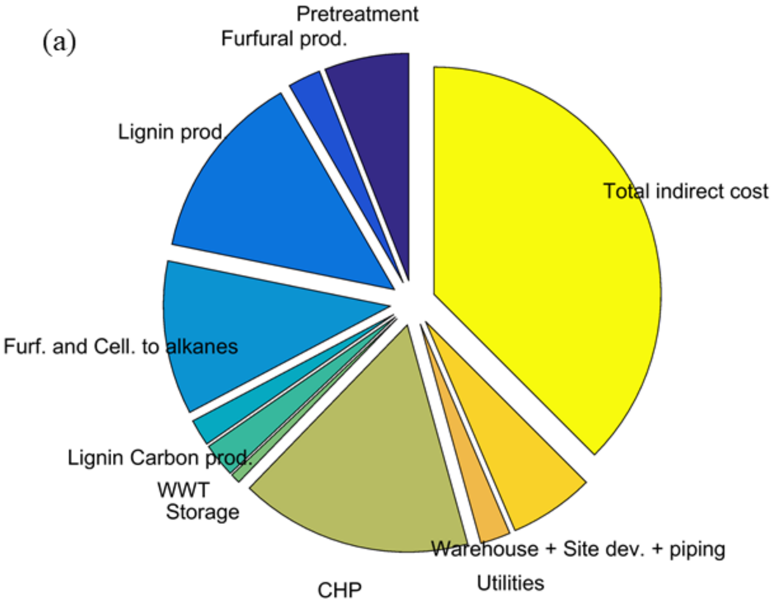
4 – Outcomes: Energetic and Economic Analyses

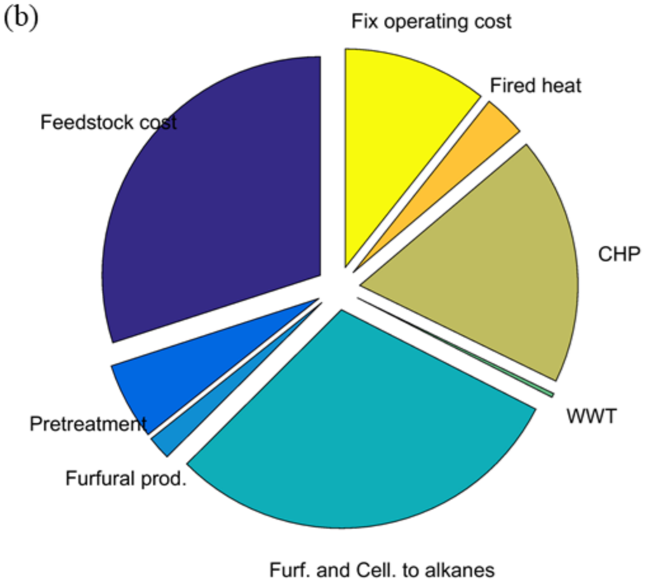
Energy analysis

- Basis: 2000 dry metric tons/day of biomass
- Heating – 268 MW
- Cooling – 373 MW
- Electricity – 21 MW

Economic analysis

- Total capital investment - $ 762 million
- Total operating costs - $ 178 million



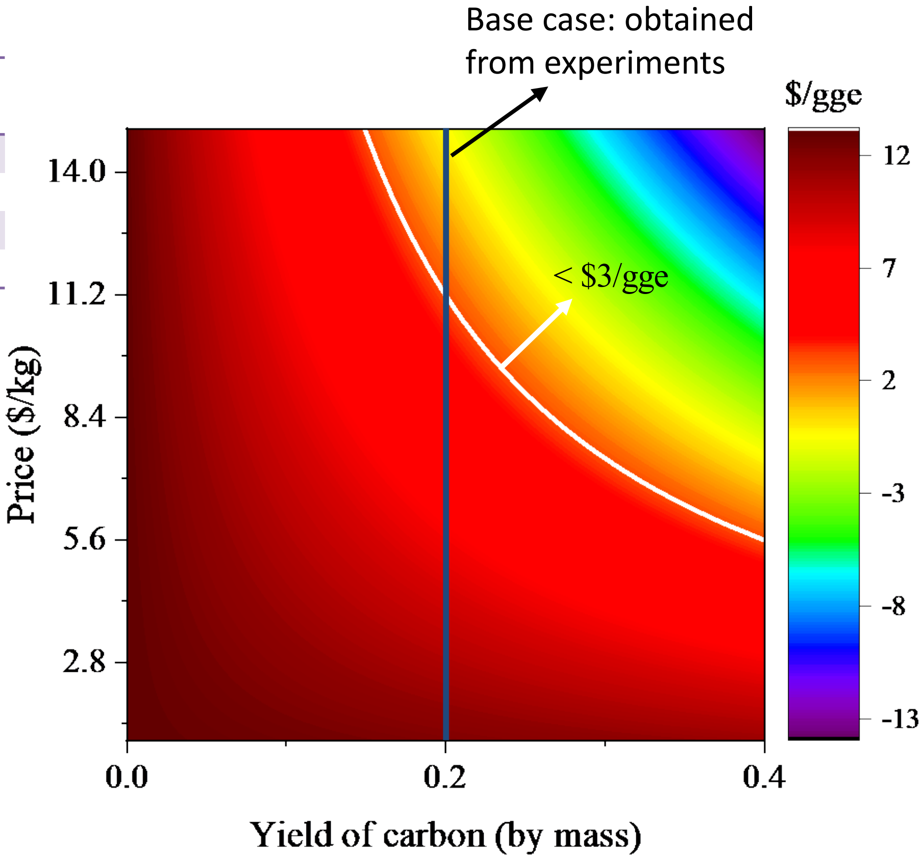


4 – Outcomes: Techno-economic Analysis

Parameter name	Parameter value	Source
Internal rate of return (%)	20	Twice of [1]
Tax rate (%)	21	[1]
Depreciation period (years)	7	[1]
Equity (%)	40	[1]

TEA

- y-axis: price of supercapacitor carbon
- x-axis: yield of carbon
- Heat map plotted to show MSP of aviation fuel as a function of price of supercapacitor carbon and its yield from lignin upgrading step
- Analyses suggest that integrated refinery concept producing supercapacitor carbon and alkanes is promising
- Price of supercapacitor carbon ~ $15/kg [2]
- Biofuel (alkenes) can be produced at < $3/gge


Base case: obtained from experiments

[1] Davis et. Al. (2018). *Technical Report*/NREL/TP-5100-71949
[2] https://www.materialstoday.com/electronic-properties/articles/s1369702113003027/

4 – Outcomes: TEA Milestone Summary

- Milestone 5.1: Produce ethanol at < $3/gge. **Completed**
- Milestone 5.2: Produce biofuel (alkenes) at < $3/gge. **Completed**

Project Summary

Approach

- ***Fractionate*** a variety of feedstocks (softwood, hardwood, and herbaceous) with varying geometries into pure streams of hemicellulose, lignin, and cellulose
- ***Upgrade*** into chemicals intermediates, materials, and alkenes (biofuels)
- ***Use TEA/LCA*** to select product distribution

Technical accomplishments

- Produced highly ***pure fractions of cellulose and lignin*** at high yields
- ***Recycled GVL solvent***, used solvent produced from cellulose
- Produced ***highest surface per gram material*** ever observed from published literature
- Produced ***biofuel (alkenes)*** from biomass
- ***Met our < $3/GGE goal***

Relevance

- Lignin coproducts needed to meet cost targets through existing markets
- Addresses multiple barriers: (1) fractionates at high biomass loadings, (2) removal of impurities, and (3) operates under mild conditions
- Produce next generation biofuels

Future/ongoing work

- Deliver 1L of alkenes (ongoing)
- Complete GVL lignin activation and performance evaluation (ongoing)
- Refine TEA for a range of lignin products (future)
- Commercialization of GVL process at larger scale (future)

Quad Chart Overview

Timeline

- Start date: 8/2018
- End date: 3/2021
- Percent complete: 95%
- Funded by 2017 BRDI FOA - DE-FOA-0001637
- Award Number: DE-EE0008353

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

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

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

Additional Slides

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Response to Previous Reviews (paraphrased)

- Why the need for biomass combinations?
  - There are many regional and seasonal differences that may result in changing feedstock supply. We wanted to demonstrate feedstock flexibility over a range of physicochemical characteristics.
- More in-depth investigation of GVL recycling and mass transport?
  - We proved that GVL recycling is possible using a commercial GVL and that we produced from our cellulose. 3 repetitions were used with no loss in yield.

Publications, Patents, Presentations, Awards, and Commercialization

- Publications
  - Synthesis of biomass-derived feedstocks for the polymers and fuels industries from 5-(hydroxymethyl) furfural (HMF) and acetone, *Green Chem.*, 2019, 21, 5532-5540
  - Catalytic strategy for conversion of fructose to organic dyes, polymers, and liquid fuels, *Green Chem.*, 2020, 22, 5285-5295
  - Chemical-Switching Strategy for Synthesis and Controlled Release of Norcantharimides from a Biomass-Derived Chemical, ChemSusChem 2020, 13, 5213 – 5219
  - L. Yu, C-T. Hsieh, D.J. Keffer, H. Chen, G. A. Goenaga, S. Dai, T.A. Zawodzinski, D. P. Harper, "Hierarchical Lignin-Based Carbon Matrix and Carbon Dot Composite Electrodes for High-Performance Supercapacitors", ACS Omega (2021) (submitted)
- Presentations
  - Lu Yu, Valerie García-Negrón, David J. Keffer and David P. Harper, "Process Control of Lignin-derived Carbon Composite Nano- and Meso-Structure for Energy Storage". International School for Materials for Energy and Sustainability VIII, California Institute of Technology, Jul. 2019, Pasadena, CA
  - Lu Yu, Kendhl Seabright, Valerie García-Negrón, David Alonso, Orlando Rios, David J. Keffer and David P. Harper, "Microporous Carbons from Different Lignins through Controlled Activation". 2019 MRS Fall conference, Dec. 2019, Boston, Massachusetts
  - Lu Yu, Kendhl Seabright, Valerie García-Negrón, David Alonso, Orlando Rios, David J. Keffer and David P. Harper, "Microporous Carbons from Different Lignin through Controlled Activation", 4th Annual UTIA Graduate Research Poster Symposium and Competition, Dec. 2019, Knoxville, TN
  - Keffer, D.J., García-Negrón, V., Kizzire, D., Lu, Y., Seabright, K., Richter, A.M., Harper, D. P., Rios, O., "Lignin Carbon Composites as Renewable Components in Electrochemical Devices: Synthesis, Characterization & Modeling", AIChE Annual Meeting, Nov. 2020, San Francisco, CA.