Lignin Utilization
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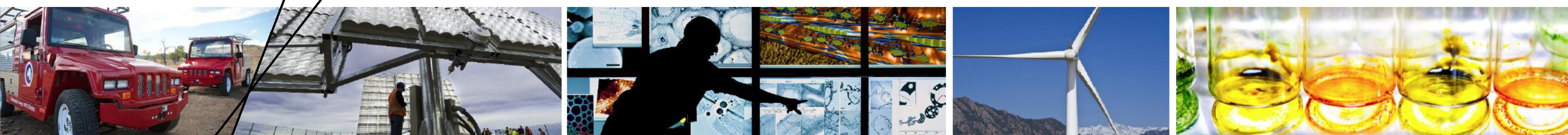


2013 DOE BioEnergy Technologies Office (BETO) Project Peer Review

Date: May 22nd, 2013

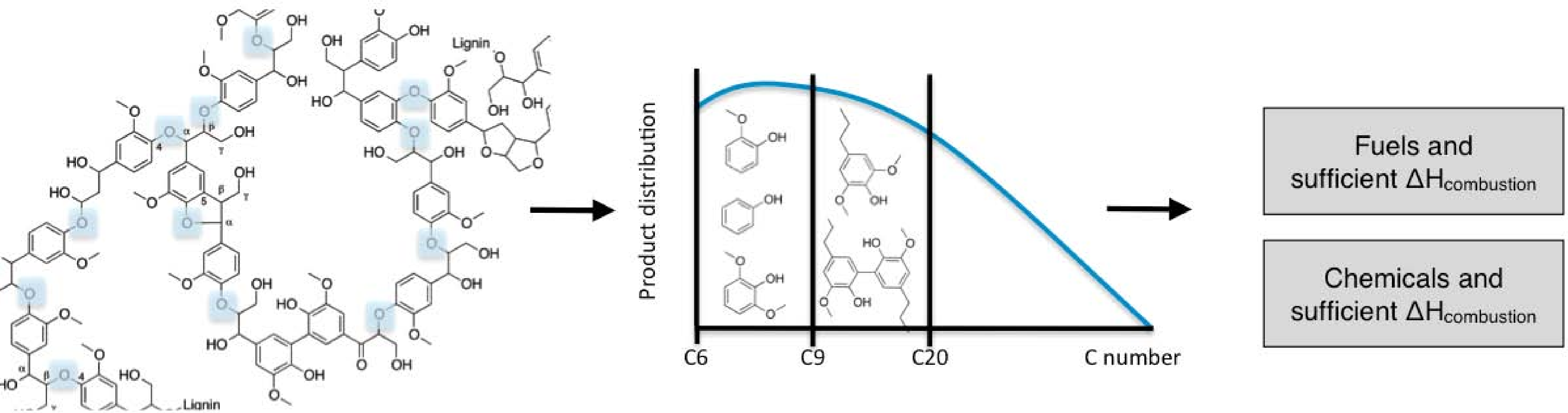
Technology Area Review: Biochemical Conversion

Principal Investigator: Gregg T. Beckham

Organization: National Renewable Energy Laboratory

Goal Statement

Goal: Develop processes to produce fuels and value-added chemicals from lignin to help meet 2017 and 2022 cost targets in support of Biological Conversion and Catalytic Upgrading of Sugars to Hydrocarbons



- Obtain sufficient lignin in a useful, liquid-phase form
- Quantify impact to carbohydrates

- Convert lignin to fuels and/or chemicals
- New upgrading processes represent novel foundation for lignin utilization
- Leverage known lignin deconstruction methods with a viable upgrading process

- Conduct TEA/LCA to identify cost-drivers and refine process options for lignin utilization
- Work with NREL and industry partners to adapt lignin utilization processes

Quad Chart

Timeline

- Start date: September 2012
- End date: September 2017
- Percent complete: 15%

Budget

- Funding for FY12: $150k
- Funding for FY13: $1 MM
- Duration the project has been funded: 9 months to date

Barriers

- Bt-A Biomass Fractionation/Bt-B Pretreatment Processing
- Bt-G Cellulase Enzyme Loading
- Bt-J Catalyst Development

Partners and Collaborators

- Shell Global Solutions (*Funds-in CRADA, $220k*)
- Virent
- Symbios Biotechnologies
- NREL tasks:
  - Biochemical Process Integration
  - Biorefinery Analysis
  - Pretreatment and Process Hydrolysis
  - Targeted Conversion Research
- BioEnergy Science Center, C3Bio (EFRC)
- National Advanced Biofuels Consortium industrial, national laboratory, and academic partners
- Colorado School of Mines (*subcontractor*)
- Swedish University of Agricultural Sciences
- Institute of Microbiology, Czech Republic
- University of Oxford
- Northwestern University
- University of Illinois Urbana-Champaign

Project Overview

Context:

- Lignin is up to ~20-30% of biomass … **significant carbon loss if not utilized**
  - Mixed feedstocks may include higher lignin content
- EtOH biorefineries typically burn lignin for excess heat and power
- TEA for Sugars-to-HCs Pathways suggests co-products from lignin are **essential** to meet cost targets: $3.00/gge by 2022

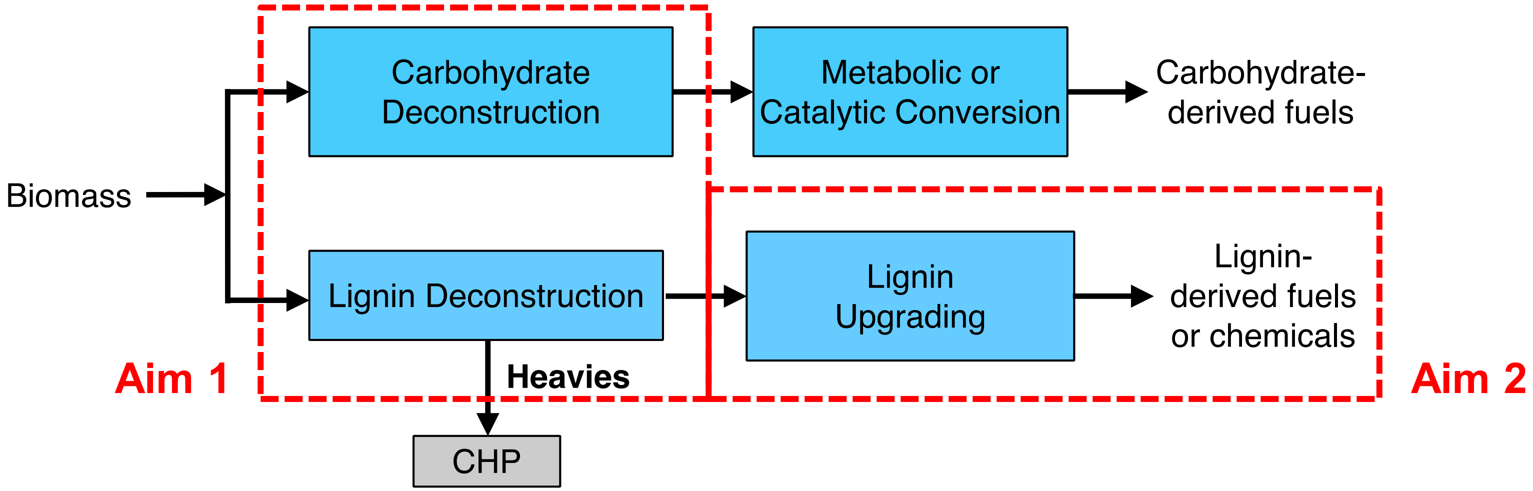
Project Objectives:

- *Define bench-scale, industrially-relevant pathway(s) for lignin **isolation** and **upgrading** to meet 2017 and 2022 cost targets*
- Requires integrated process development with carbohydrate utilization
- Employ TEA/LCA to develop process options based on bench-scale data

Project Structure: 3 sub-tasks with milestones centered around process evaluation in FY13

Lignin Isolation and Characterization	Biological Deconstruction and Upgrading	Catalytic Deconstruction and Upgrading

Approach



Aim 1: Obtain liquid intermediates

Approach:

- develop benchmarks for lignin isolation
- characterize lignin/carbohydrate streams

Initial Metrics:

- 40-60% yield of liquid-phase monomers and oligomers
- reduction in cellulase loadings

Aim 2: Upgrade liquid lignin intermediates

Approach:

- develop new routes for converting intermediates to fuels and chemicals
- examine markets for individual products
- develop new routes to additional markets

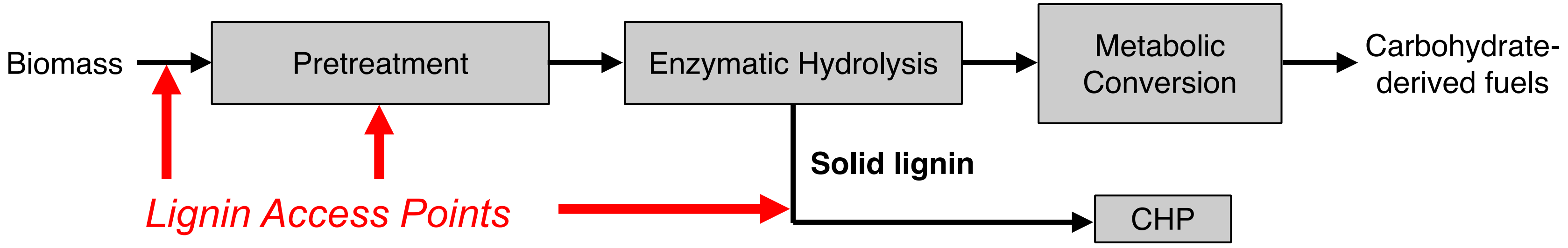
Initial Metric:

- bench-scale yield of fuel and chemical precursors

Employ TEA/LCA to identify cost drivers and technical challenges and to define quantifiable targets for process integration

Technical Results – Outline and Milestones

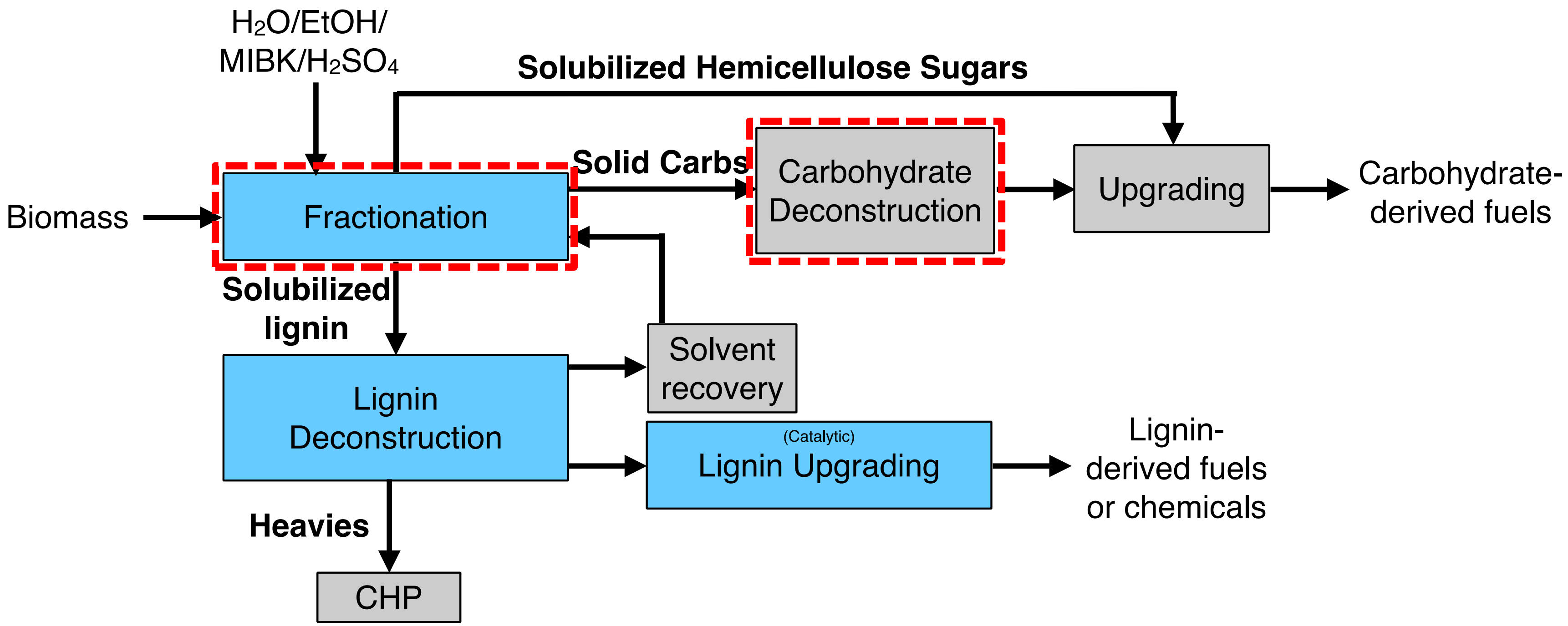
- **Lignin Isolation/Deconstruction**: Evaluating four established process technologies in FY13
  - Clean Fractionation (Organosolv)
  - NaOH pulping of biomass
  - ~~Enzymatic lignin deconstruction~~
  - Base catalysis of pretreated, enzymatically-hydrolyzed biomass



- **Impacts on Carbohydrate Deconstruction**: Evaluating ability to lower cellulase loadings with upstream lignin removal
- **Lignin Upgrading**:
  - Developing catalysts to maximize yield of liquid-phase products
  - Developing upgrading process to fuel and chemical precursors

Lignin Isolation via Clean Fractionation

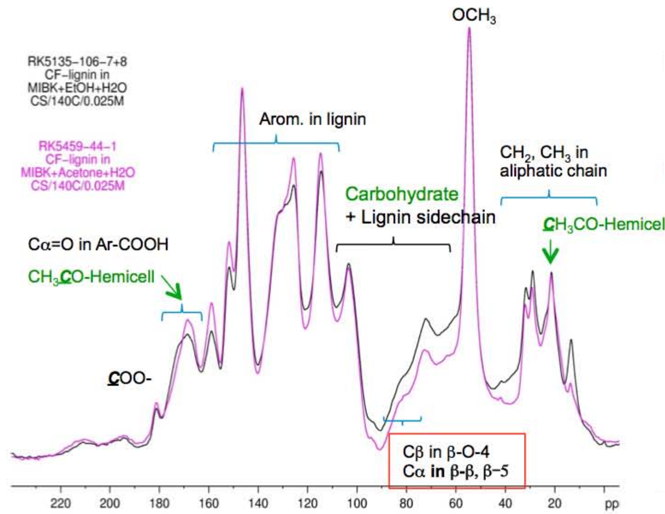
- Organic solvent and acid as a pretreatment catalyst
- Conducting mass balances on all components including solvent recovery
- Examining MW distribution and composition of resulting lignins
- Quantifying impact to cellulose digestibility with various enzyme cocktails
- Developing bench-scale data for TEA/LCA

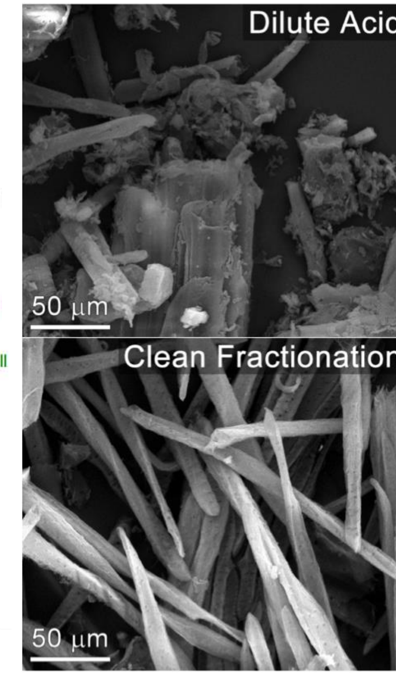


Lignin Isolation via Clean Fractionation

- Evaluating 2 CF technologies:
  - H_2O/Acetone/MIBK
  - H_2O/EtOH/MIBK
- 120°C, 140°C
- 0.025, 0.05, 0.1 M H_2SO_4
- Phase separation, recovery, and MW distribution improved with acetone
- Lignin requires further depolymerization

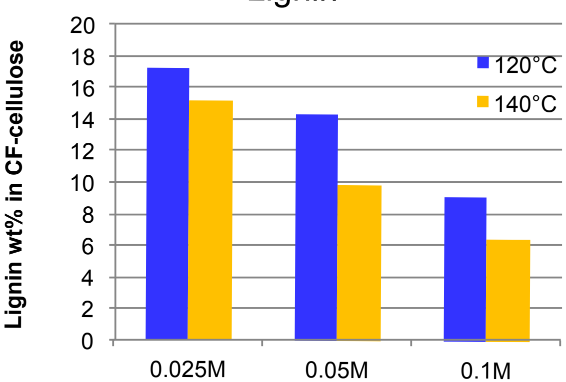
Acetone and EtOH CF lignins are chemically similar



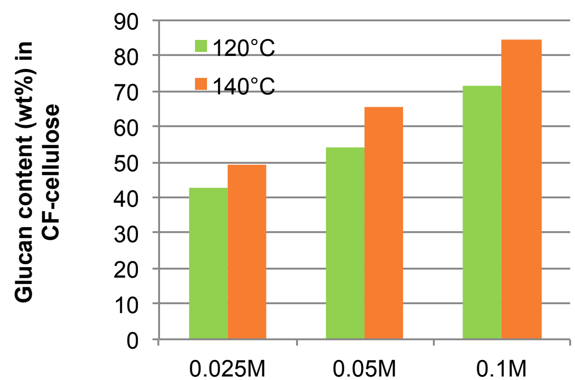


Acid loading greatly impacts lignin and hemicellulose removal

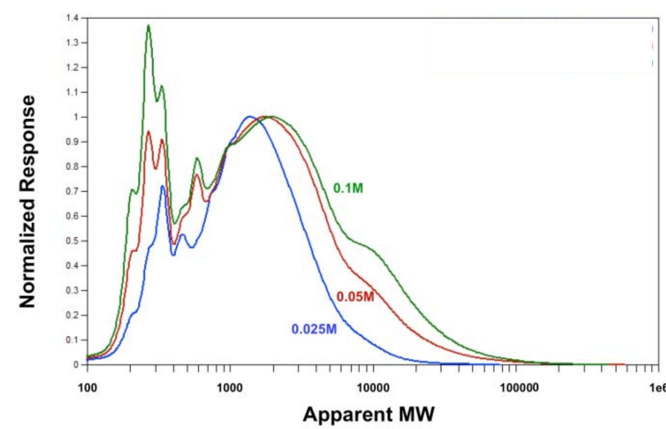
Lignin



Glucan



High delignification in CF

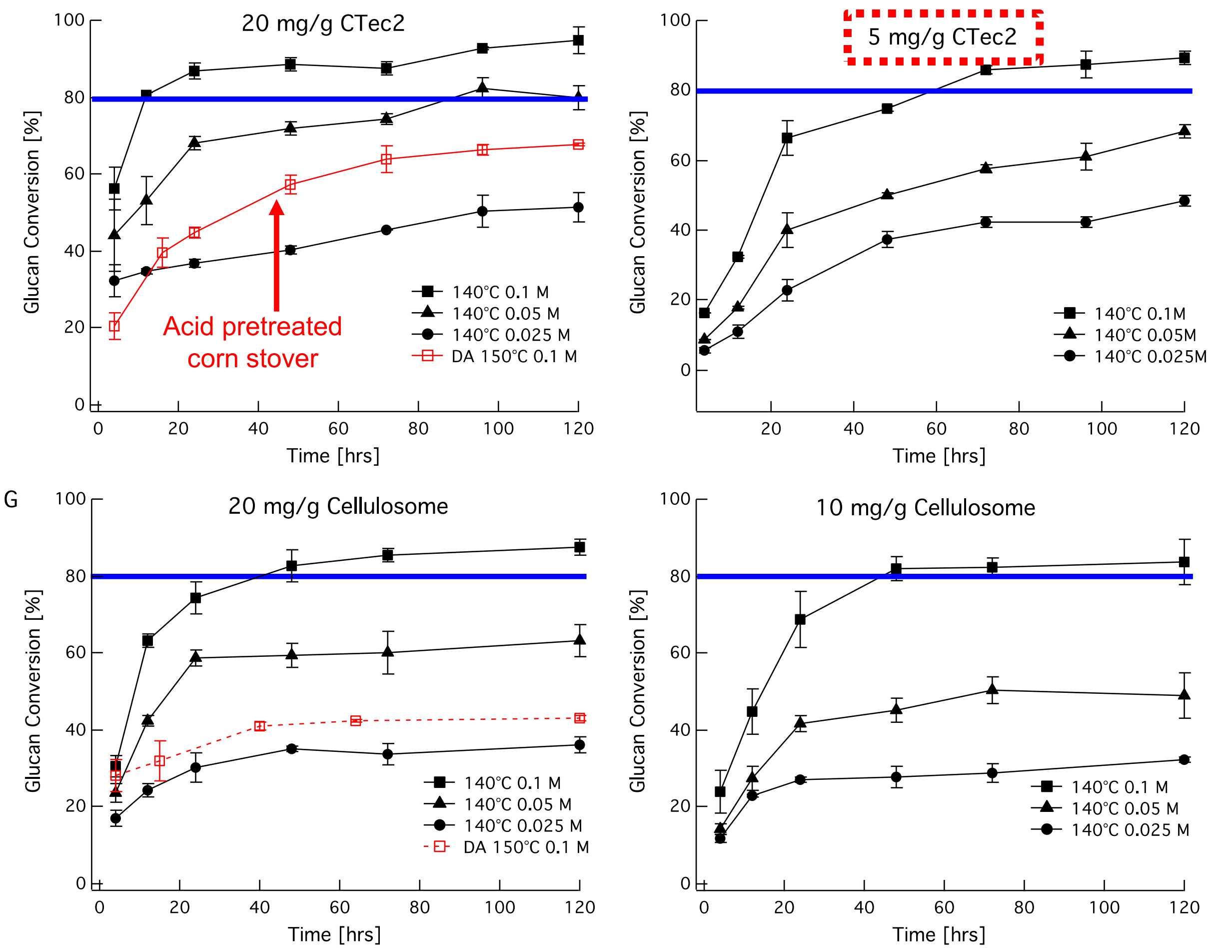


Broad lignin MW distribution

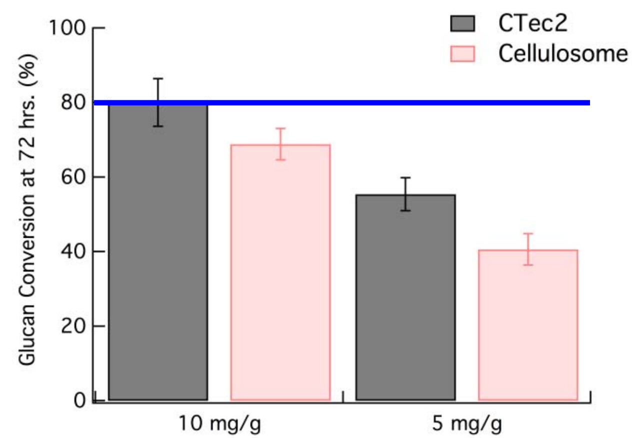
Lignin Isolation via Clean Fractionation

- Enzyme loading is a major cost driver in Biological Conversion and Catalytic Upgrading
- Screening enzyme cocktails including **CTec2** (Novozymes) and **Cellulosomes**

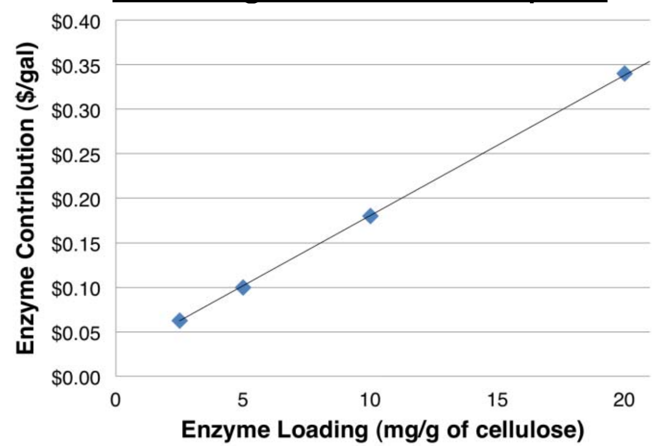
Low solids loadings, 50°C



High solids, 50°C, 3 days



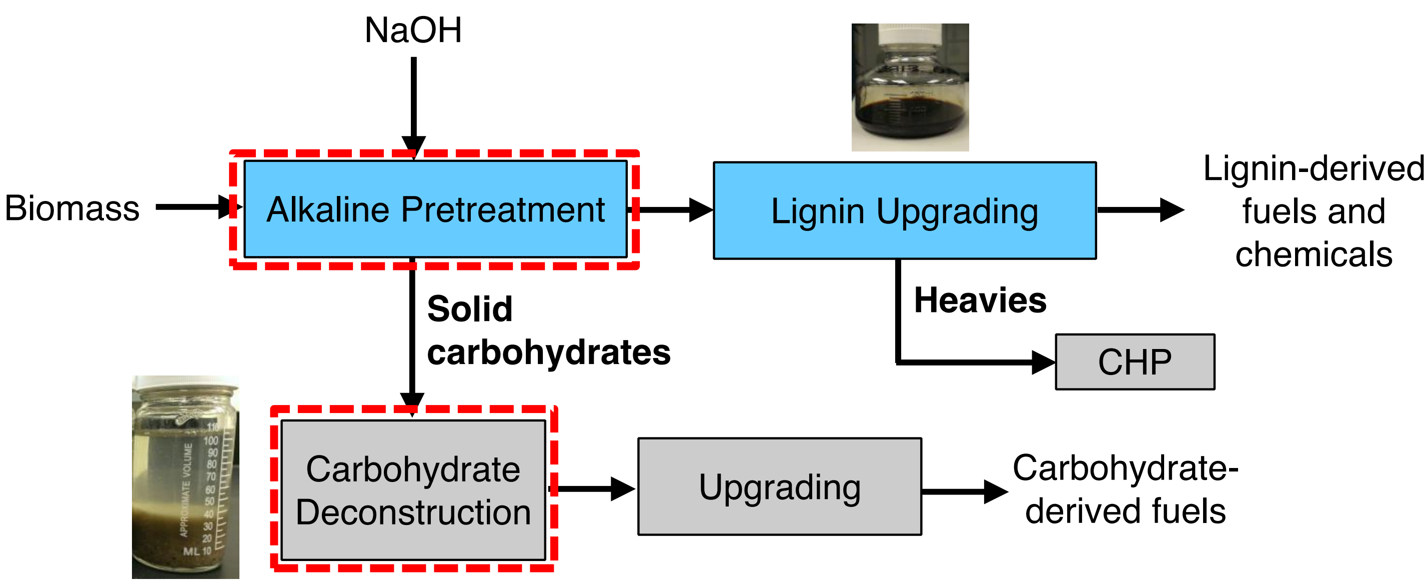
Loading Reduction Impact



Ethanol Design Case enzyme costs, Humbird *et al*. 2011

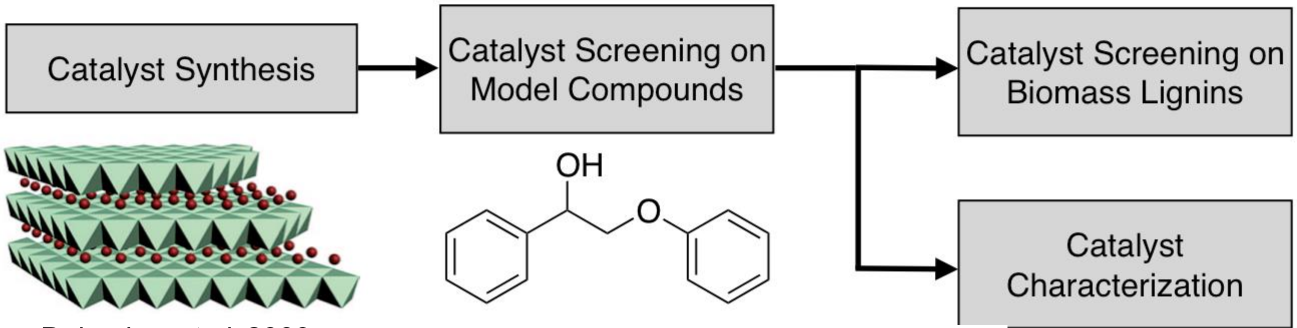
Lignin Isolation via Alkaline Pretreatment

- Using NaOH to deconstruct lignin and produce clean carbohydrates
  - Work began in April 2013
  - Based on success with deacetylation in EtOH demonstrations
- Applying the same approach as CF:
  - Full mass balances
  - MW distribution and composition of lignins
  - Cellulose digestibility with several enzyme cocktails
  - Bench-scale data for TEA/LCA including Materials of Construction and reactor costs
  - Examining hold step for additional depolymerization

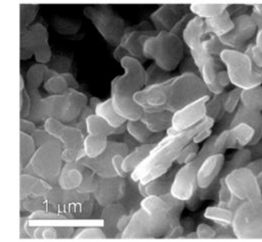


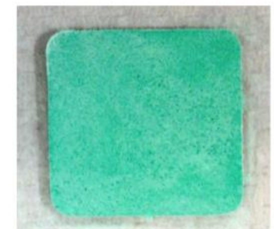
Catalysts for lignin depolymerization of pretreatment streams

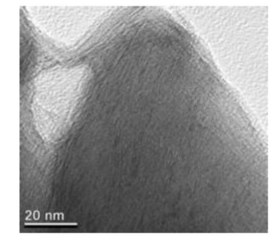
- Streams from CF and alkaline pretreatment may require depolymerization to increase liquid yield
- Developing solid-base heterogeneous catalysts

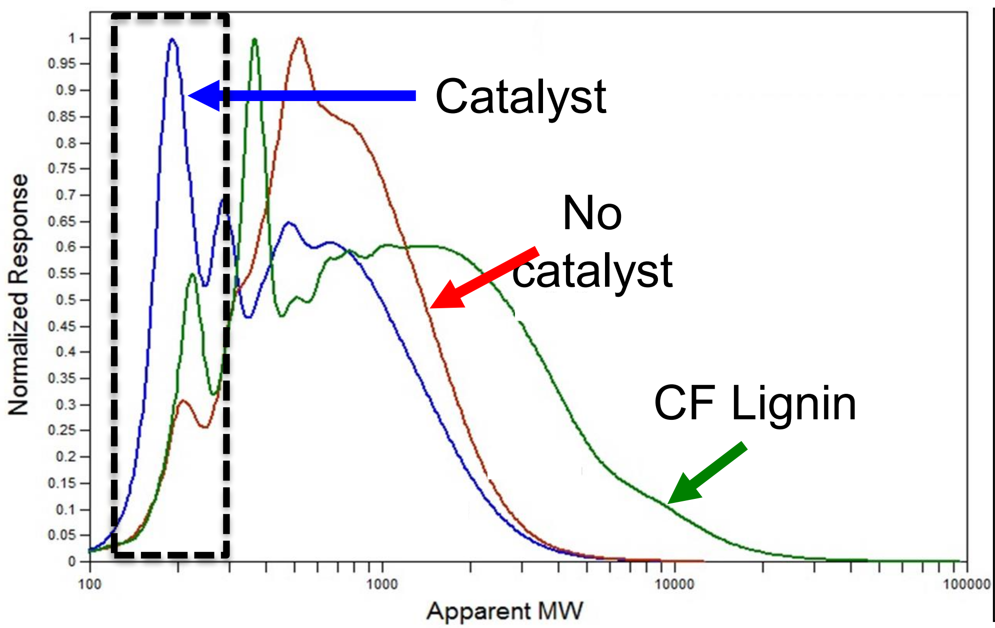


Debecker *et al.* 2009



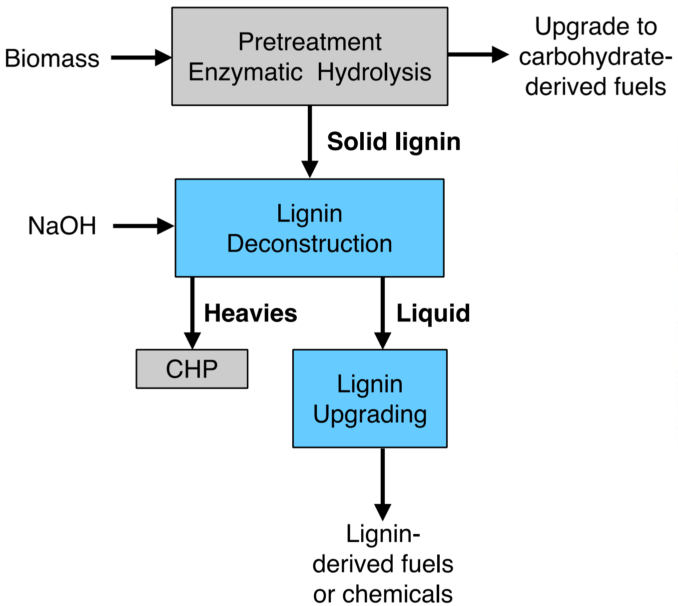




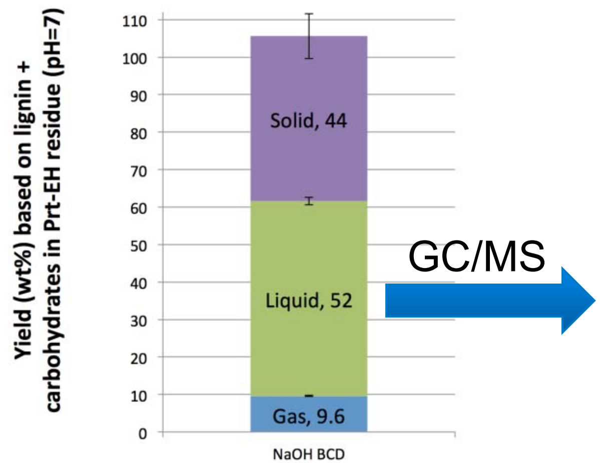


- Ni-catalyst is effective at lignin depolymerization at 285°C
- Catalyst regeneration: rehydration
- No H_2 present
- Optimizing conditions and catalyst for upstream isolation technologies
- Continuing catalyst development for combined depolymerization/deoxygenation

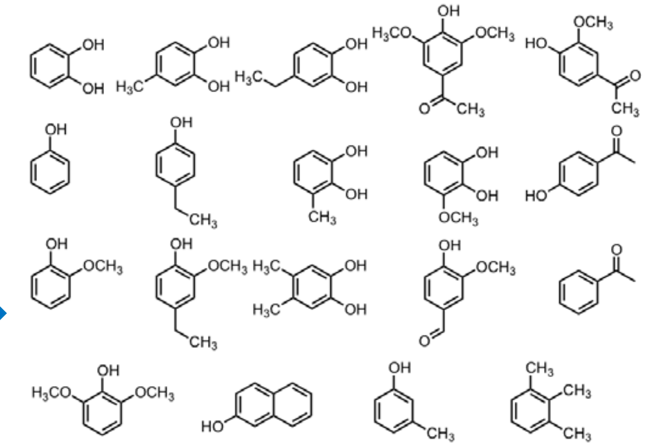
Lignin Deconstruction after Pretreatment/Enzymatic Hydrolysis

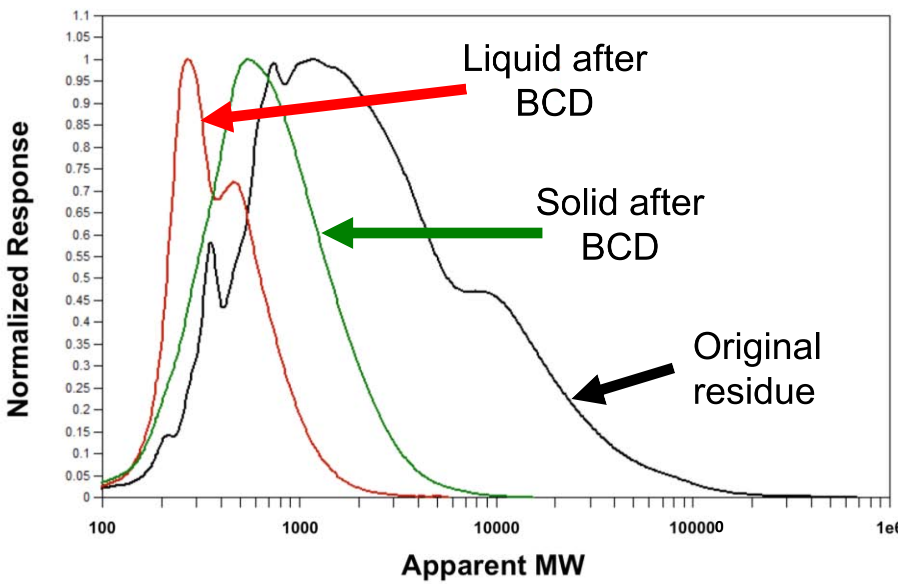


Liquid yield ~50%



Major products

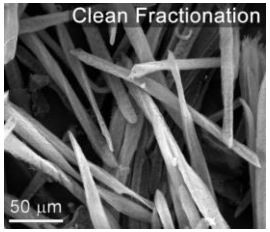




- Liquid yield is high, MW distribution is small
  - Potential stream for direct upgrading
- Quantifying composition of liquid fraction
- Optimizing conditions (NaOH and solids loadings, T, time) for maximum liquid yields
- Measuring $\Delta H_{combustion}$ of residual solid
- Examining product distribution as a function of pretreatment chemistry/severity
- Working with PPH task to examine new feedstocks (deacetylated, disk refined)

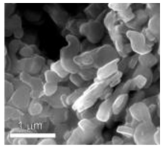
Summary of Lignin Deconstruction and Isolation

- Nearly completed **Clean Fractionation** evaluation
  - Demonstrated significant lignin removal from corn stover
  - Demonstrated substantial reduction in cellulase loading
  - Working on TEA/LCA to examine solvent recovery

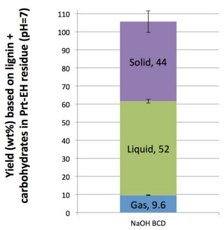


- Initiated **alkaline pretreatment** efforts

- Developed new catalysts for lignin depolymerization

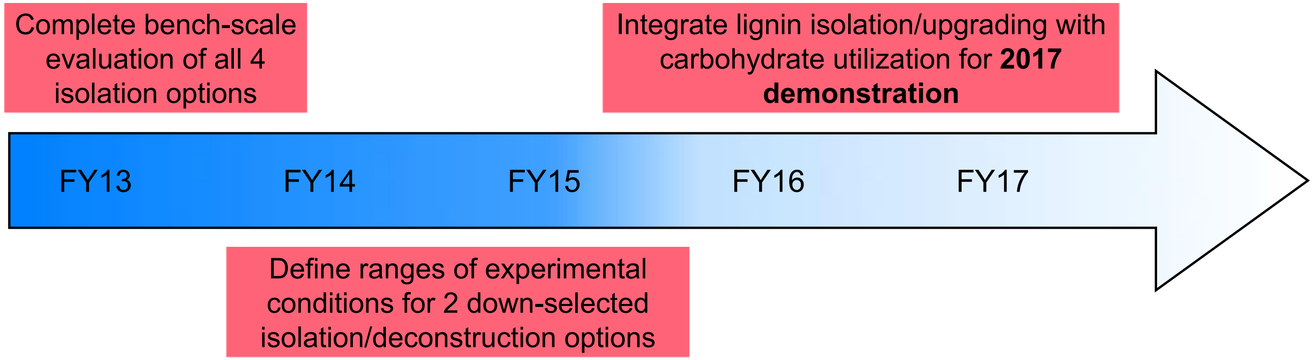


- Ruled out **enzymatic lignin deconstruction** as a viable process because of sugar losses

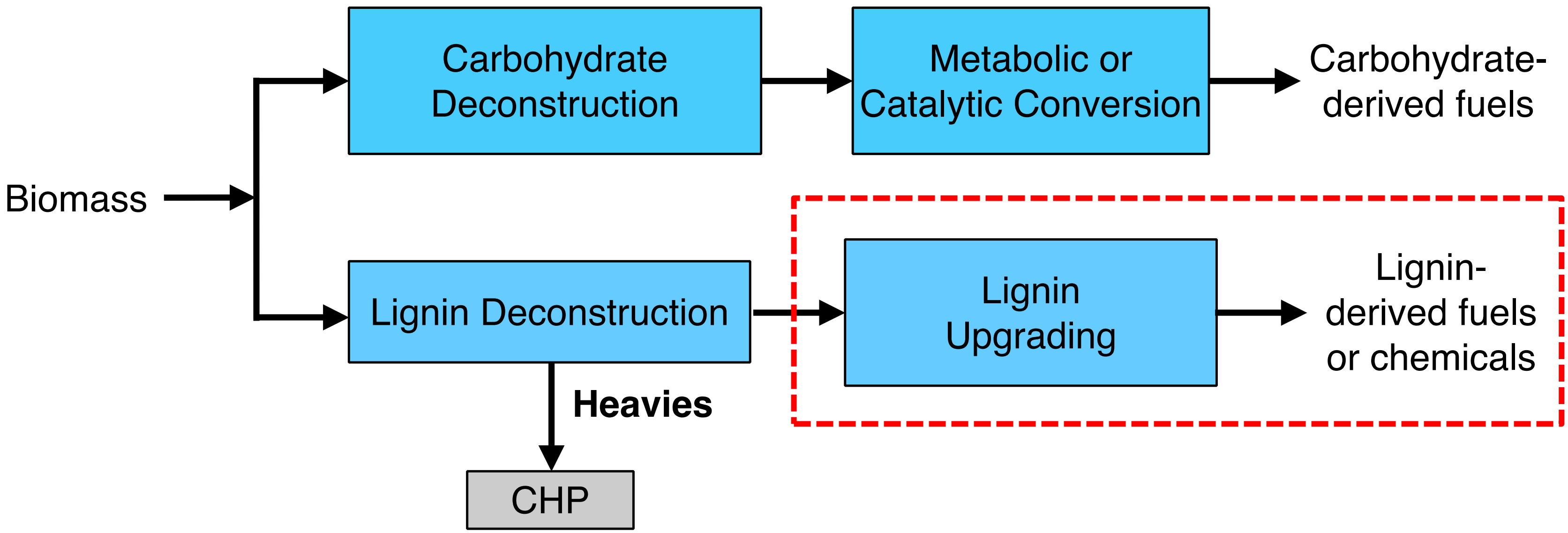


- **BCD provides good liquid yield of monomers and oligomers**

Isolation and Deconstruction work is on schedule

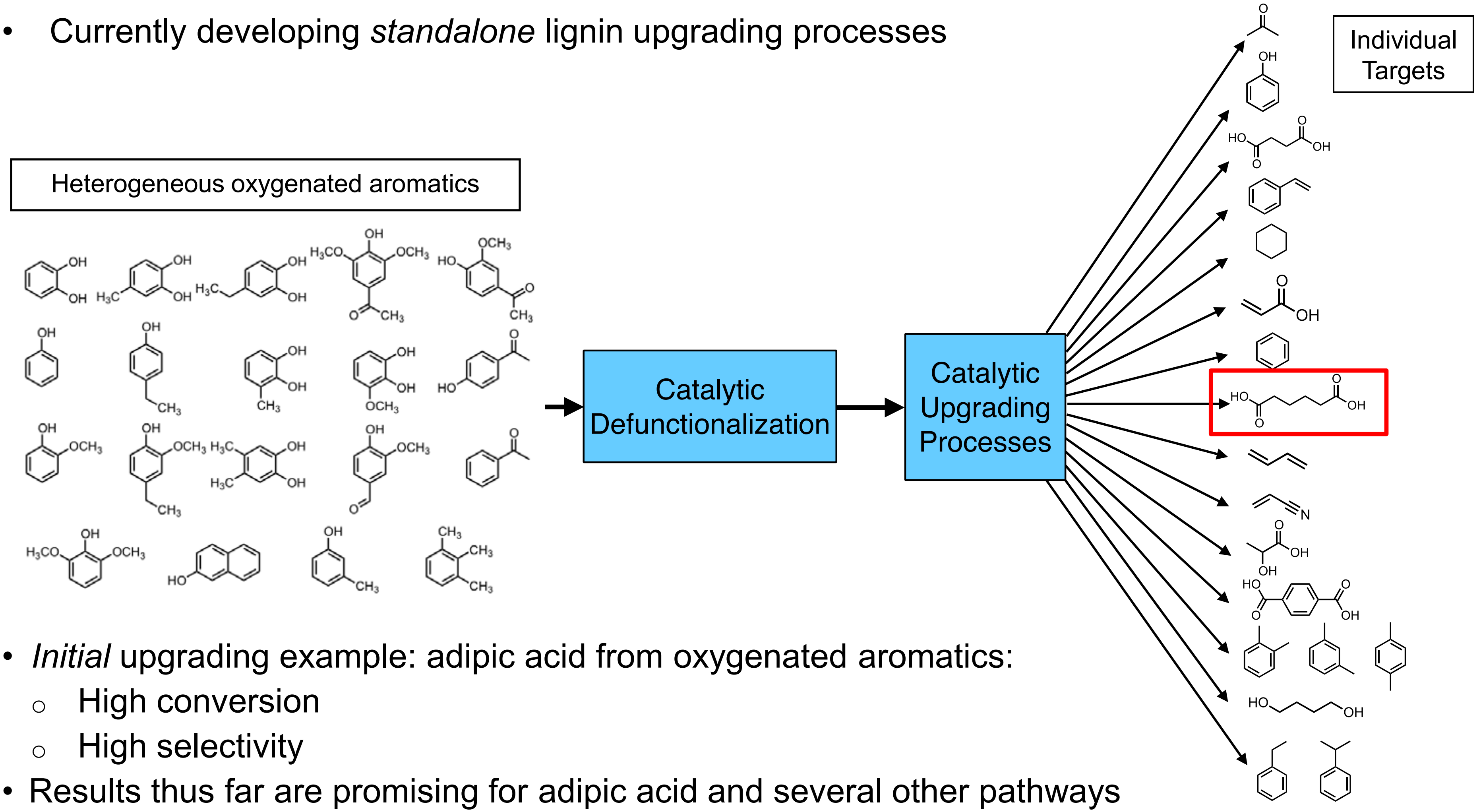


Lignin Upgrading



Standalone lignin upgrading process

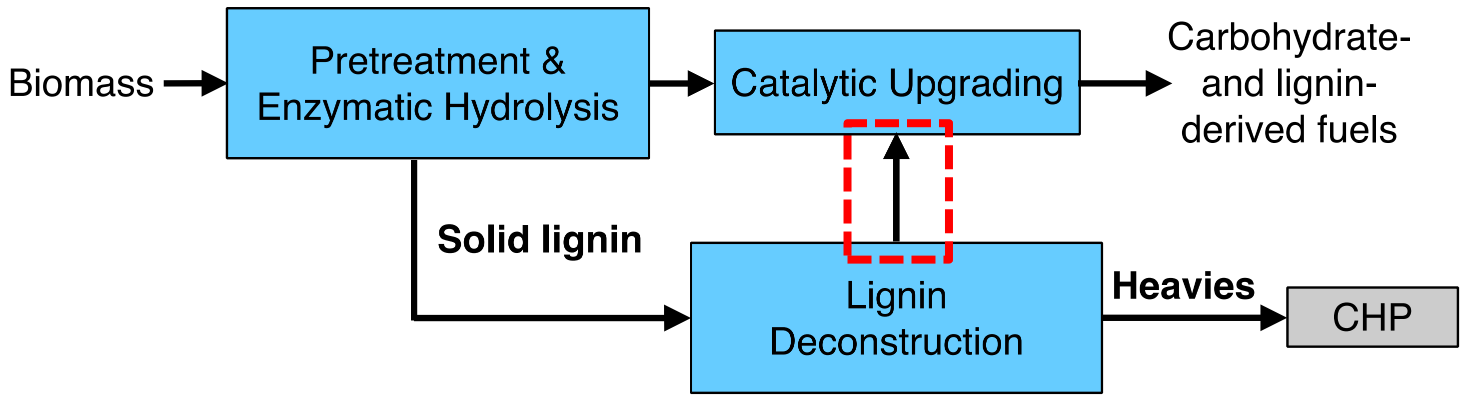
- Biological Conversion and Catalytic Upgrading likely warrant different upgrading strategies
- Currently developing *standalone* lignin upgrading processes

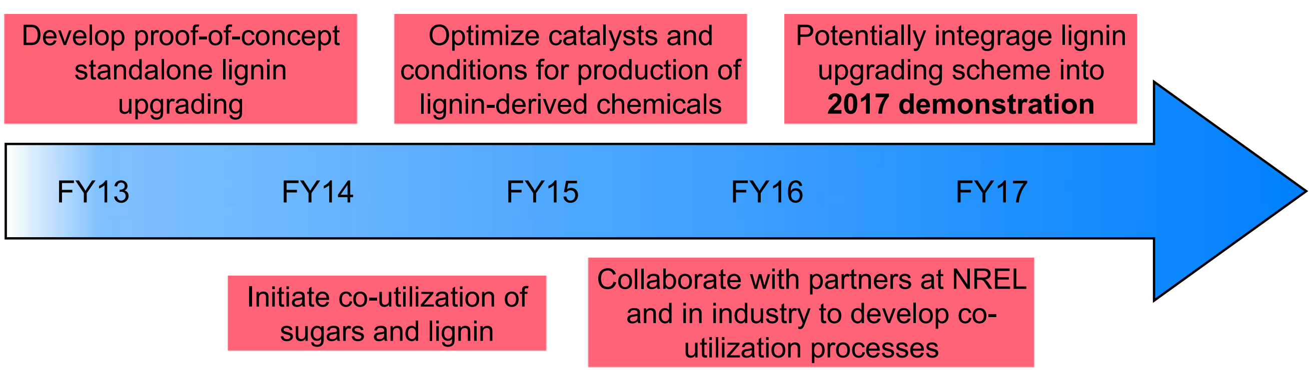


- *Initial* upgrading example: adipic acid from oxygenated aromatics:
  - High conversion
  - High selectivity
- Results thus far are promising for adipic acid and several other pathways
- Developing new routes from platform chemicals for **direct replacement** and **functional replacement**

Integrated carbohydrate-lignin upgrading processes

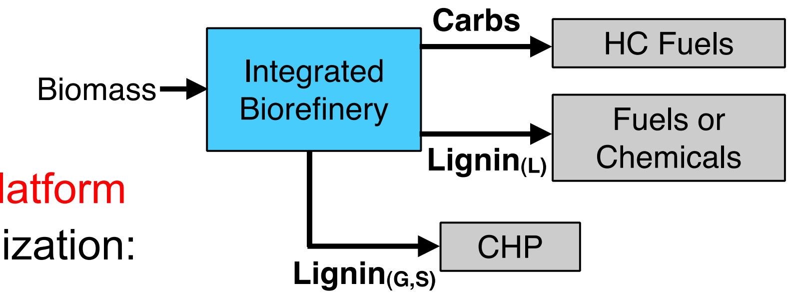
- In FY14, we will examine feeding lignin intermediates to sugar-upgrading catalysts
- Conduct this work in collaboration with industrial collaborators and NREL Pretreatment and Process Hydrolysis task





Relevance

Lignin utilization will be essential to achieve 2017 and 2022 HC fuel production cost targets



Highlighted in 2011 Review/CTAB as a key gap in BC Platform

Key MYPP areas for process improvement via lignin utilization:

<u>Biomass Fractionation/Pretreatment</u>
- Enables more selective, cheaper deconstruction and upgrading
- Reduces inhibition to enzymes, organisms, catalysts

<u>Cellulase Enzyme Loading</u>
- Upstream lignin removal greatly reduces enzyme loadings
- Leverage work in NREL and industry to adapt enzymes to lignin-lean substrates

<u>Catalyst Development</u>
- Developing chemical and biological catalysts for improved biomass utilization

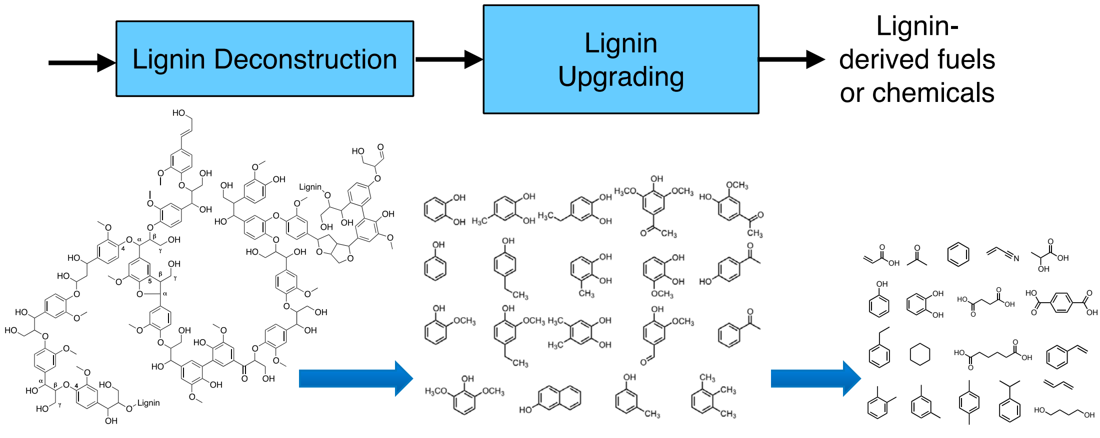
Key Stakeholders and Impacts:

- **Industrial and academic research focused on carbohydrate utilization can leverage lignin utilization processes**
- Work will enable adoption of lignin utilization in modern biorefinery designs
- Lignin impacts the "**Whole Barrel of Oil**" initiative
- **Portfolio of chemicals from lignin will diversify and accelerate development of the biomass value chain**
- Significant amounts of peer-reviewed science and IP will be generated from this work
- Methods to upgrade heterogeneous intermediates can be adapted by the Bio-Oil Platform

Critical Success Factors

Key Risks

- **Heterogeneity** of lignin and lignin-derived intermediates
- **Economic and sustainable processes** for deconstruction and upgrading
- **High product yields of fuels and portfolio of chemicals**



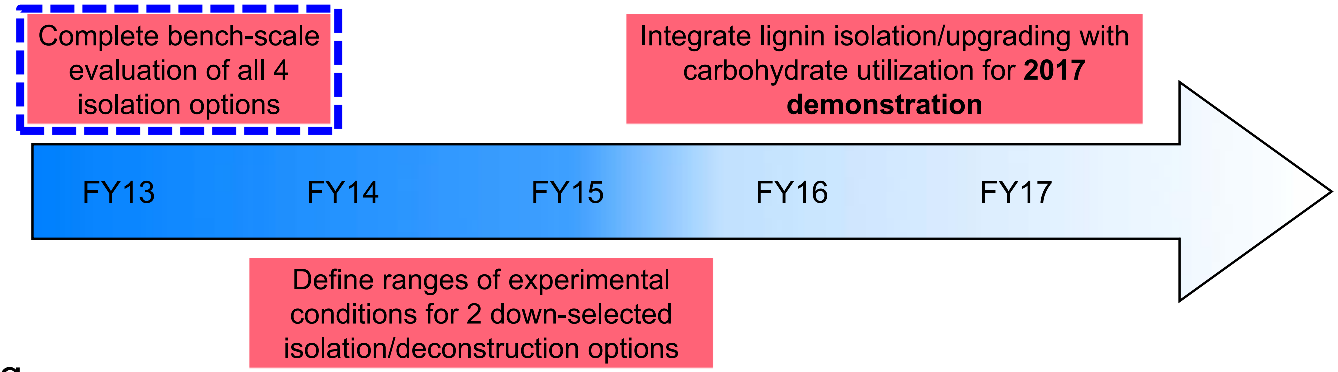
Critical Success Factors

- Fundamentals-driven science/engineering approach
- Employ a diverse, interdisciplinary portfolio of methods
- Employ TEA and LCA to identify cost-drivers early and refine integrated carbohydrate/lignin utilization models
  - Working with engineering design and construction firm to establish model inputs
  - Work closely with other NREL tasks for integrated carbohydrate/lignin utilization processes
- Developing novel upgrading strategies
- Collaborate widely with NREL, academic, and industrial partners to fill in gaps
- Engaging industrial stakeholders via established and new relationships

Future Work

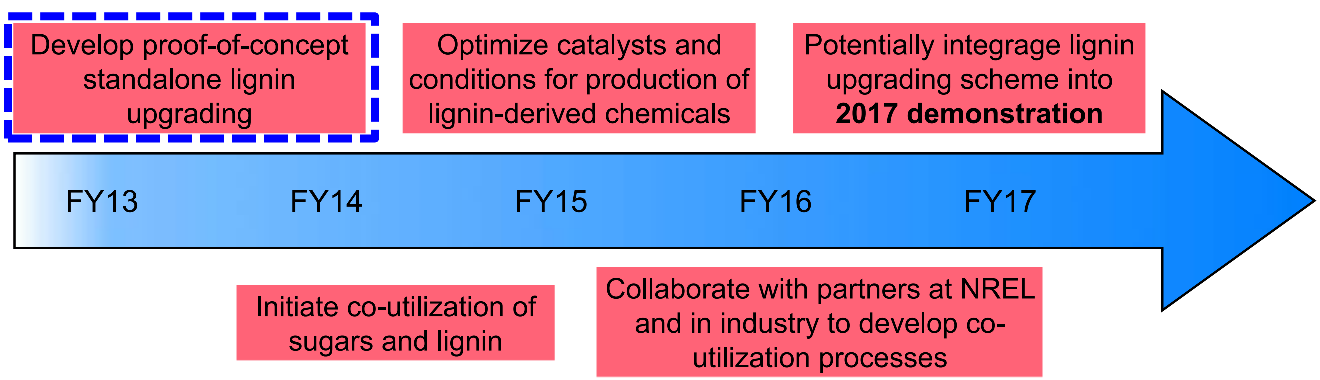
Lignin Isolation/Deconstruction

- Define comprehensive set of conditions by FY15 for viable isolation efforts on uniform-format feedstock
- Slowly ramp down emphasis on isolation/deconstruction efforts



Lignin Upgrading

- Initiate both standalone and integrated (co-utilization) efforts in FY13-FY14 timeframe
- Ramp up upgrading efforts going forward



Summary

1) Approach:
   - **obtain** and **upgrade** lignin to chemicals and/or fuels with fundamentals-driven, interdisciplinary approach underpinned by TEA and LCA
   - collaborate widely with academic, national lab, and industrial partners including BC Platform tasks

2) Technical accomplishments – made significant progress in 9 months
   - demonstrated **desired yields** of liquid products from BCD
   - demonstrated significant **reduction in enzyme loadings** upon upstream removal of lignin
   - evaluating other pretreatment technologies and novel catalysts
   - developed novel upgrading approaches to overcome lignin heterogeneity – key to lignin utilization

3) Relevance
   - co-products essential to meet DOE hydrocarbon cost targets
   - addresses Whole Barrel of Oil Initiative and bolsters the biomass value chain

4) Critical success factors and challenges
   - Heterogeneity, **economic** *and* **sustainable** production of fuels/chemicals, high yields of products needed

5) Future work:
   - define range of conditions for isolation/deconstruction work by FY15
   - ramp up efforts on lignin upgrading as standalone process and co-utilization with carbohydrates

6) Technology transfer:
   - working with industry partners to build commercialization path to lignin utilization
   - **direct** and **functional replacement** chemicals from biomass

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- Ling Tao
- Min Zhang

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NABC National Advanced Biofuels Consortium

Additional slides

- Previous Reviewer Comments from 2011 Peer Review related to lignin
- Publications, Patents, and Presentations
- Acronyms
- Tools used in our group
- Simplified process flow diagrams for 4 isolation technologies
- Clean Fractionation Methodology
- Clean Fractionation Enzymatic Digestions
- Alkaline Pretreatment Initial Mass Balances
- Base-Catalyzed Depolymerization Methodology
- Base-Catalyzed Depolymerization liquid stream characterization
- Simplified process flow diagrams for 2 carbohydrate/lignin co-utilization processes

Previous reviewer comments regarding lignin

Lignin Utilization is a new task, but herein are included comments from the 2011 reviews on the Biochemical Conversion platform related to lignin.

- *"Expansion of the approach to lignin might be worth some analysis as it is a quite significant fraction of the total cellulosic biomass available."*

- *"Lignin is a major component of biomass, yet it is given relatively little attention in the Platform work (other than its negative impact on saccharification). This is undoubtedly due to the difficulty in making liquid fuels from lignin, especially via a biochemical process. Our perception is that it is reasonable to begin to expand the work directed at finding value-added uses for lignin (there is one such international project). If successful in this effort, then it seems this would have a major impact on the cost of converting the carbohydrate component to ethanol."*

Publications and Patents

Publications in print regarding lignin:

1. S.C. Chmely, S. Kim, P.N. Ciesielski, G. Jiminez-Oses, R.S. Paton, G.T. Beckham, "Mechanistic study of a Ru-xantphos catalyst for tandem alcohol dehydrogenation and reductive aryl-ether cleavage", *ACS Catalysis* 2013.
2. S. Kim, S.C. Chmely, M.R. Nimlos, Y.J. Bomble, T.D. Foust, R.S. Paton, G.T. Beckham, "Computational study of bond dissociation enthalpies for a large range of native and modified lignins", *J. Phys. Chem. Letters* 2011.

We have multiple publications in preparation describing recent lignin isolation/deconstruction/upgrading work and TEA modeling for lignin utilization including:

1. "Bench-scale evaluation of Clean Fractionation as a process option for biofuels production from corn stover: (I) Bench-scale fractionation and component characterization"
2. "Bench-scale evaluation of Clean Fractionation as a process option for biofuels production from corn stover: (II) Characterization and enzymatic digestibility of the solid carbohydrates"
3. "Bench-scale evaluation of Clean Fractionation as a process option for biofuels production from corn stover: (III) Techno-economic analysis identifies the primary cost-drivers in organosolv-based pretreatment options"
4. "Evaluation of NaOH pretreatment for biofuels production: (I) Bench-scale pretreatment and component characterization"
5. "Evaluation of NaOH pretreatment for biofuels production: (II) Characterization and enzymatic digestibility of the solid carbohydrates"
6. "Evaluation of NaOH pretreatment for biofuels production: (III) Techno-economic and life-cycle analyses"
7. "Lignin depolymerization by solid-base nickel catalysts", invited manuscript to *Green Chemistry* special issue for submission in June 2013
8. "A mechanistic investigation of acid-catalyzed cleavage of aryl-ether linkages: Implications for lignin depolymerization"
9. Several manuscripts in preparation on the **lignin upgrading** work for submission in late Summer 2013

Patents:

- G.T. Beckham, M.J. Biddy, M.R. Sturgeon, Base-catalyzed depolymerization of lignin with heterogeneous catalysts, provisional application 61/710,240 filed on 10/5/2012
- **We have multiple applications in preparation, especially describing recent lignin upgrading work including 6 new Records of Invention**

Recent Presentations

Presentations (primary presenter only listed):

1. G.T. Beckham, "Bench-scale process development for carbohydrate and lignin co-utilization", C2B2 Semi-Annual Meeting
2. G.T. Beckham, "Computational Modeling of biomass conversion systems", Frontiers in Biorefining
3. S.C. Chmely, "Deconstruction of lignin model compounds using layered double hydroxide catalysts", 245th ACS National Meeting
4. R. Katahira, "Characterization of clean fractionated cell wall components in corn stover", 35th Symposium on Biotechnology for Fuels and Chemicals
5. S. Kim, "Computational design of lignin depolymerization catalysts", 243rd ACS National Meeting
6. S. Kim, "Computational mechanistic studies of acid-catalyzed lignin model dimers for lignin depolymerization", 245th ACS National Meeting
7. S. Kim, "Computational and experimental studies of catalyzed lignin model dimers for lignin depolymerization" Seoul National University (upcoming)
8. M.G. Resch, "Fungal cellulases and complexed cellulosomal enzymes exhibit synergistic mechanisms in cellulose deconstruction", 35th Symposium on Biotechnology for Fuels and Chemicals
9. M.R. Sturgeon, "Experimental study of mechanistic acid deconstruction of lignin", 243rd ACS National Meeting
10. M.R. Sturgeon, "Mechanistic study of the acid degradation of lignin model compounds", 244th ACS National Meeting
11. M.R. Sturgeon, "A mechanistic investigation of acid-catalyzed cleavage of aryl-ether linkages: Implications for lignin depolymerization", 245th ACS National Meeting
12. M.R. Sturgeon, "Lignin depolymerization by solid-base nickel catalysts", MRS Fall Meeting 2013 (upcoming)

Acronyms

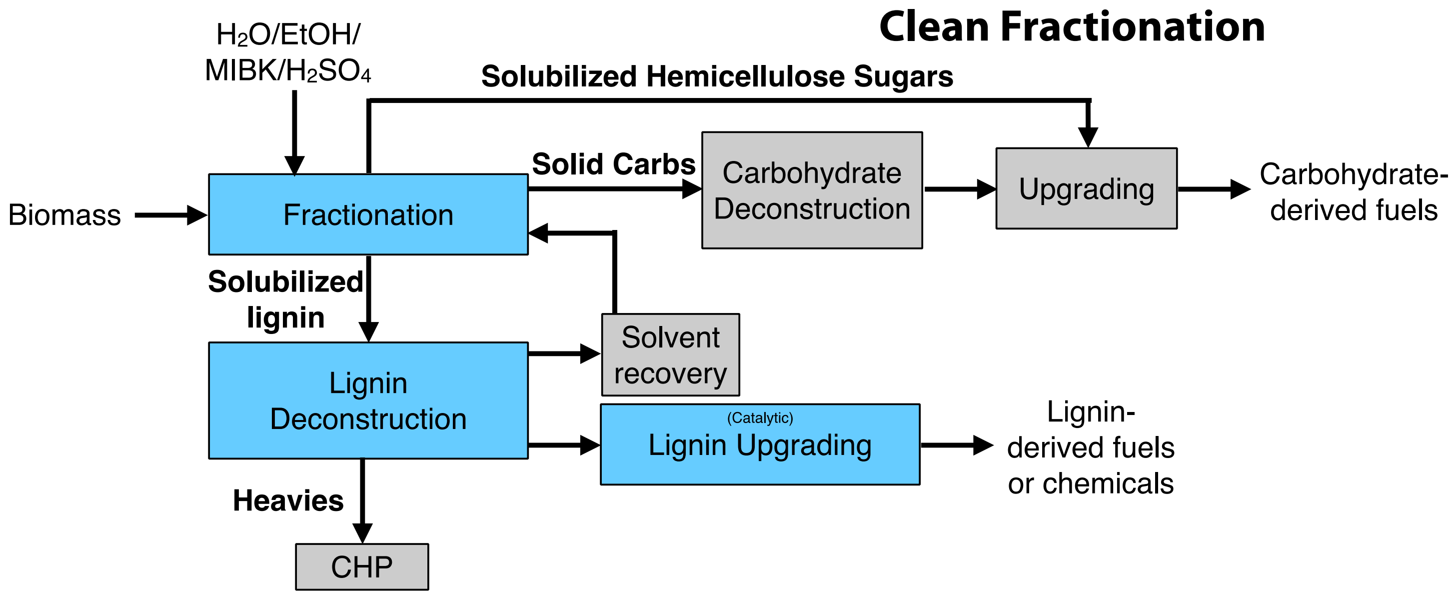
- BCD: Base-Catalyzed Depolymerization
- CF: Clean Fractionation
- CHP: Combined Heat and Power
- LCA: Life-Cycle Analysis
- MW: Molecular Weight
- NABC: National Advance Biofuels Consortium
- TEA: Techno-Economic Analysis

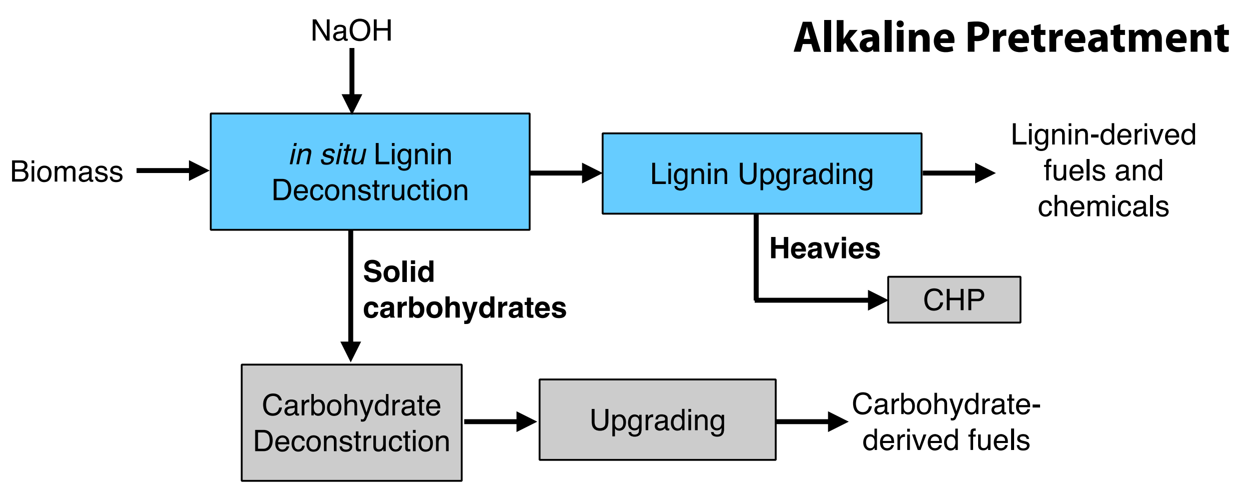
Tools used in our group

- Specialized spectroscopic and chemical methods for lignin
- Bench-scale process development and engineering
- Pretreatment and pulping chemistry
- Biomass compositional analysis
- Analytical tool development for characterizing lignin deconstruction
- Heterogeneous catalyst synthesis, characterization, and screening
- Advanced catalyst and biomass characterization
- Biocatalyst development
- Modeling and theory

Lignin Deconstruction via Fractionation and Alkaline Pulping

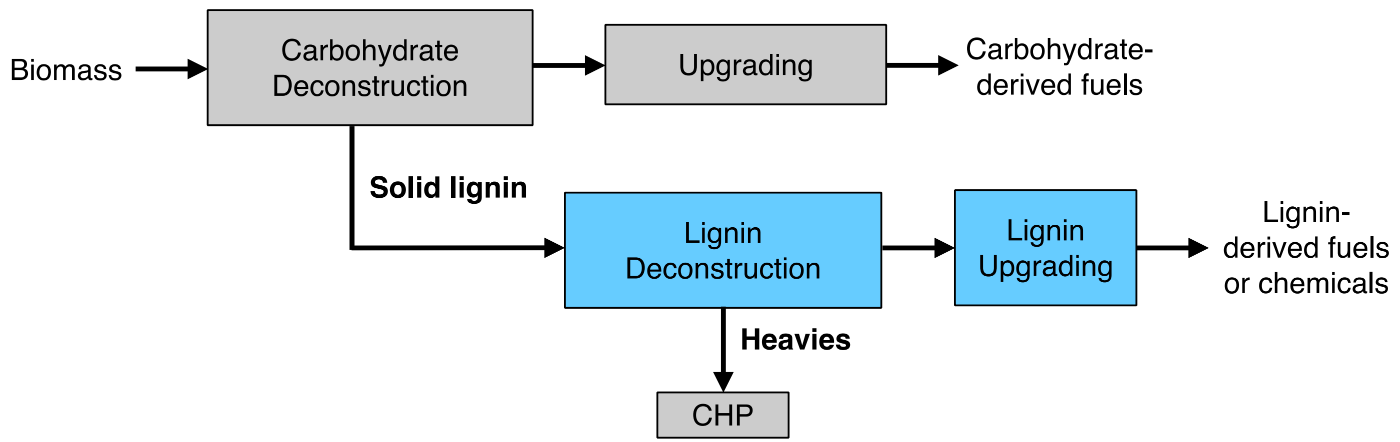
Evaluating four options at the bench-scale:



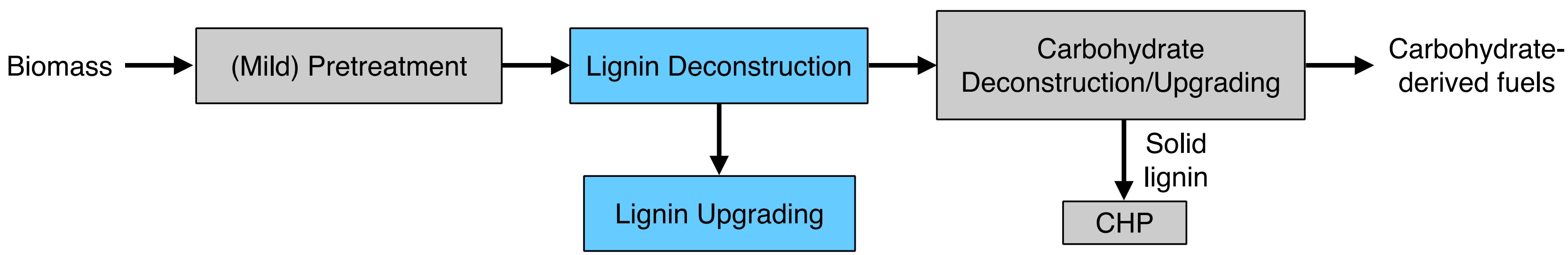


Lignin Deconstruction via Base Catalysis or Enzymatic Means

Base-Catalyzed Depolymerization



Enzymatic Lignin Deconstruction



FY13 Objectives:

- Conduct baseline research for each option
- build preliminary TEA models
- down-select options and focus research beyond

Bench-scale evaluation of Clean Fractionation

Corn stover (10 g)

- MIBK/EtOH/H_2O (16:34:50,w/w/w) (100ml) | MIBK/Acetone/H_2O (16:34:50,w/w/w) (100ml)
- 120/140°C, 0.025/0.05/0.1 M H_2SO_4, 56 min
- filtrate

Filtrate (Hemicellulose, Lignin)

- Phase separation
- Add H_2O (20 mL)

Solid residue (Cellulose)

MIBK layer (Lignin)

Lignin stream for further depolymerization and upgrading

Aqueous layer (H_2O+EtOH) (Hemicellulose)

- Acetone and EtOH yield similar cellulose and hemicellulose fractions
- Phase separation is somewhat improved for corn stover with acetone-based CF
- Cellulose fraction clearly looks delignified

Clean fractionation procedure (MIBK/Acetone/H_2O)

Corn stover (10g)

- MIBK/Acetone/H_2O (1:4:4,w/w/w) (100ml), 120/140°C, 0.025/0.05/0.1 M H_2SO_4, 56min

Filtrate (Hemicellulose, Lignin)

- Phase separation
- Remove original MIBK layer, then extracted with MIBK (20mL)

No Add MIBK & H_2O →

MIBK Border

→ H_2O layer — Extracted with more MIBK →

→ Original MIBK layer

- Combined MIBK layer was washed with H_2O

Solid residue (Cellulose)

↓ Enzymatic Hydrolysis

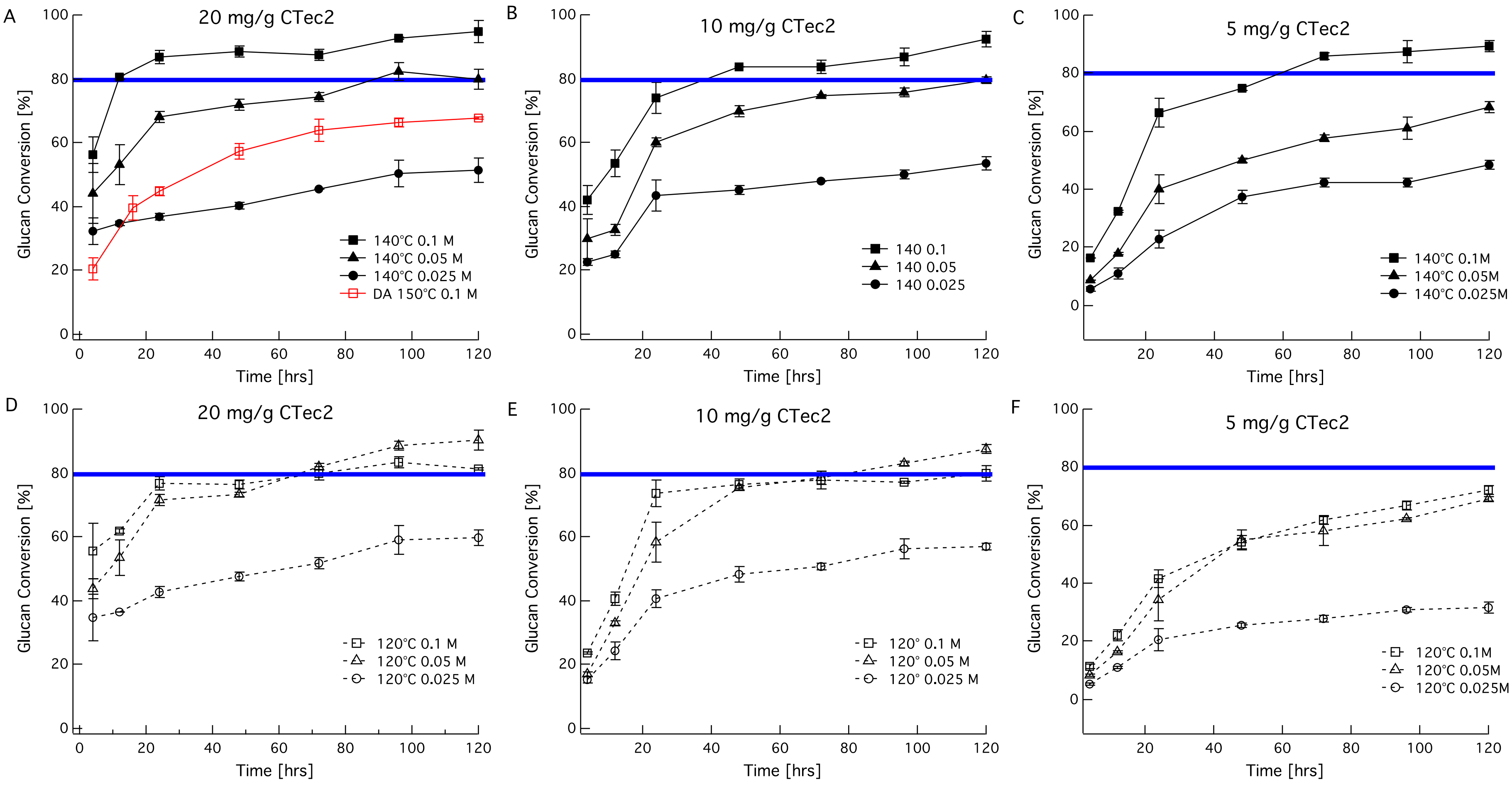
MIBK layer (Lignin) → Catalytic degradation

Aqueous layer (H_2O+Acetone) (Hemicellulose) → Enzymatic Hydrolysis

Sugar analysis

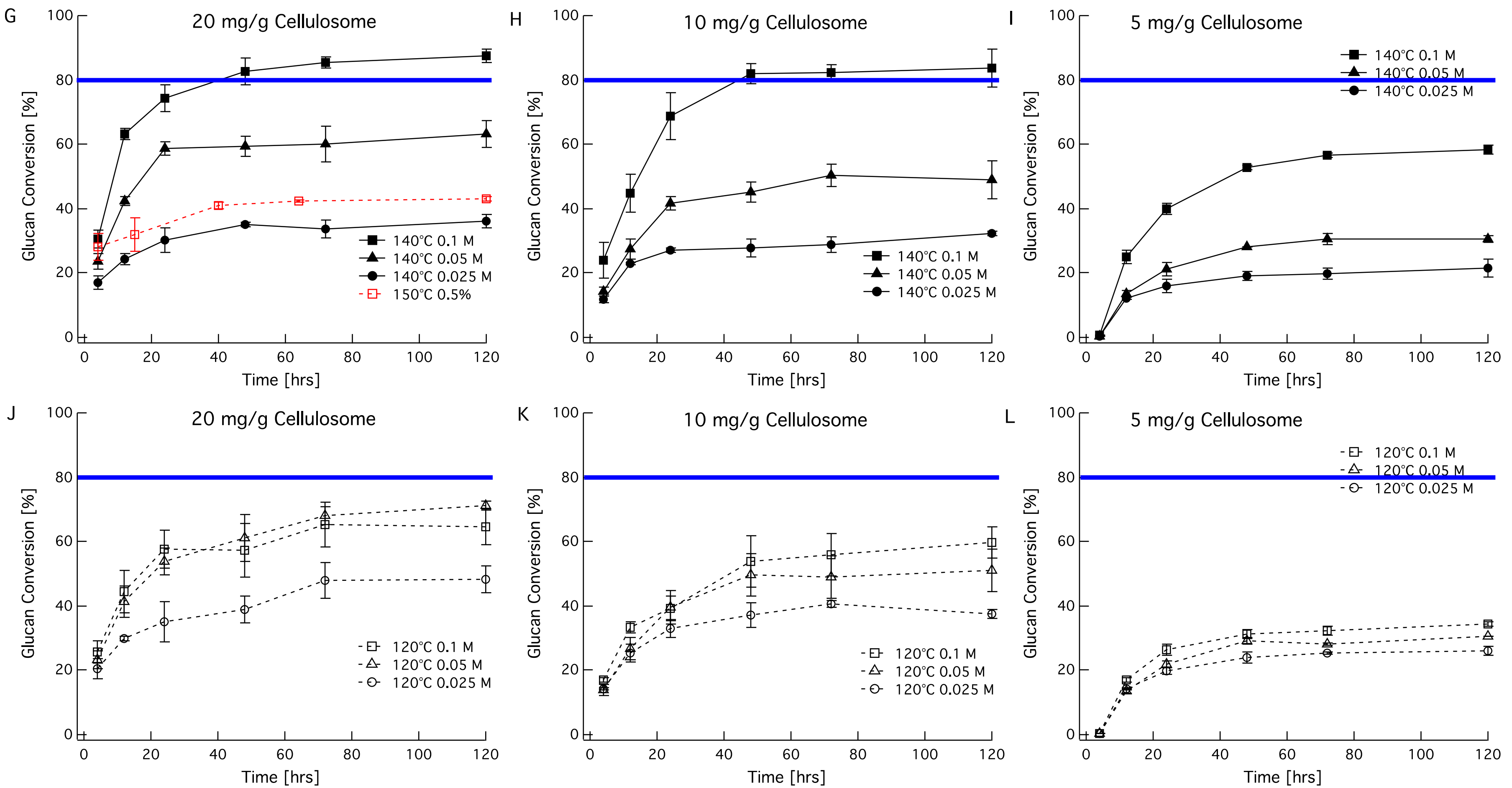
Clean Fractionation Enzymatic Digestions: CTec2

- CTec2 digestions of Acetone-Clean Fractionation Cellulose-enriched fraction
- 50°C, 1% solids loadings
- Red curve is dilute acid-pretreated corn stover at the same assay conditions
- Metric: 80% conversion in 2-3 days … denoted by blue line

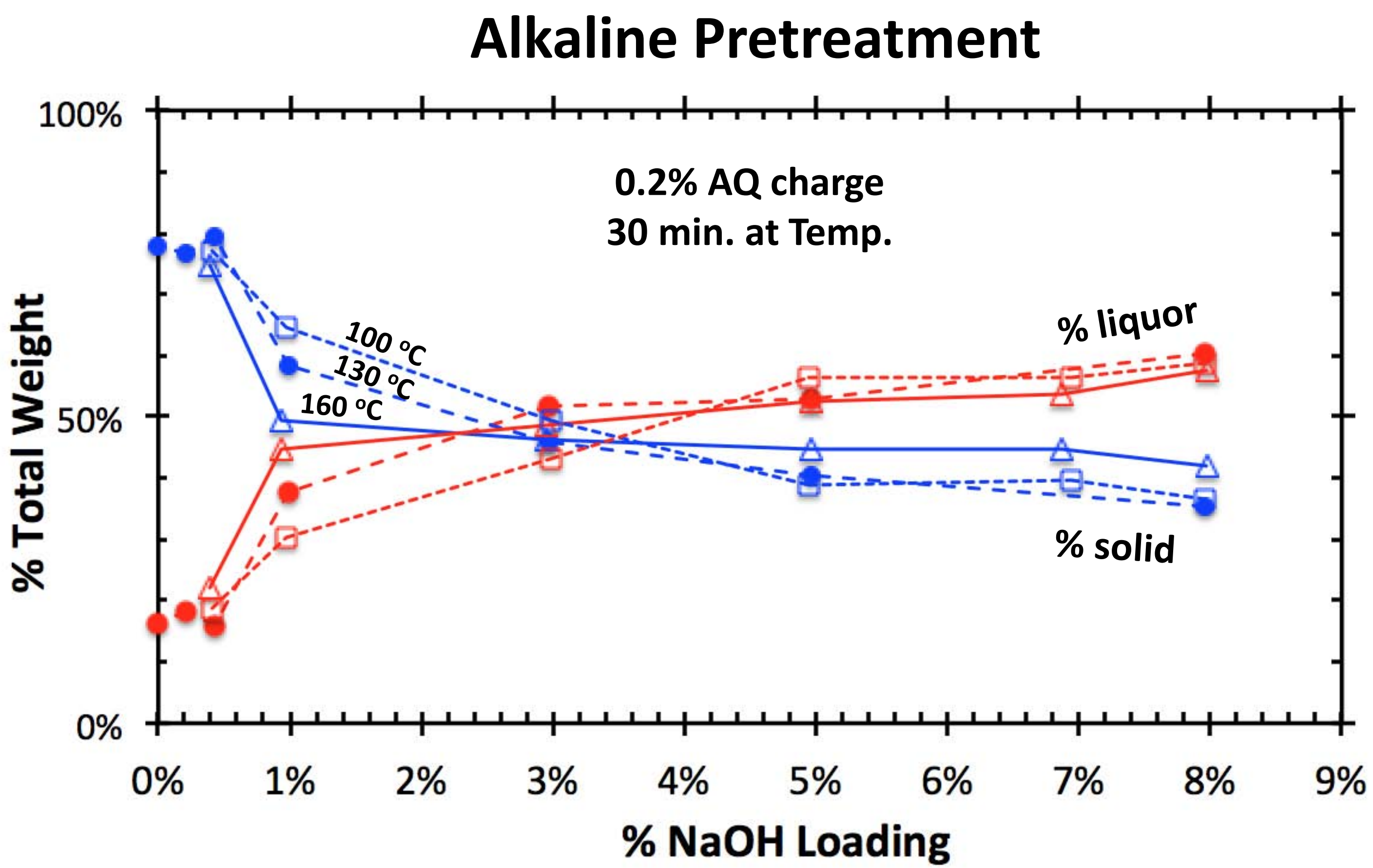


Clean Fractionation Enzymatic Digestions: Cellulosomes

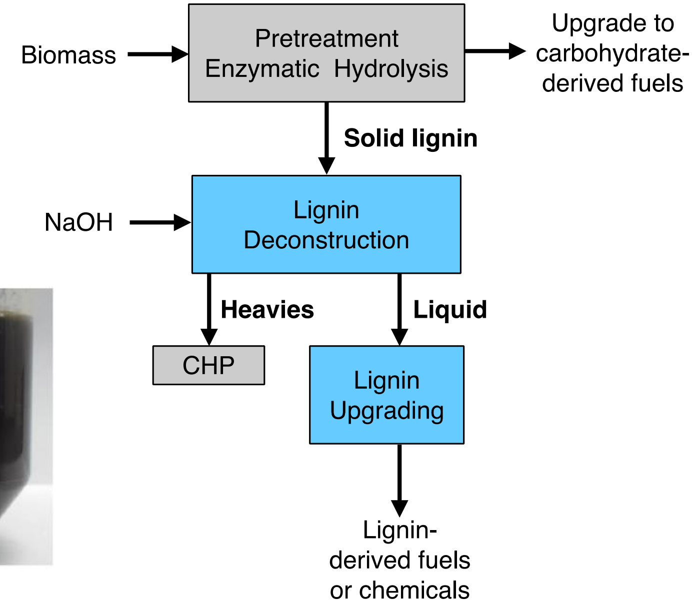
- CTec2 digestions of Acetone-Clean Fractionation Cellulose-enriched fraction
- 50°C, 1% solids loadings
- Red curve is dilute acid-pretreated corn stover at the same assay conditions
- Metric: 80% conversion in 2-3 days … denoted by blue line



Alkaline Pretreatment Initial Mass Balances



Base-catalyzed lignin Deconstruction after pretreatment/enzymatic hydrolysis



Substrate)

Conditions
- Batch reactor, 300°C, 40 min.
- 10 wt% Lignin
- 4 wt% NaOH

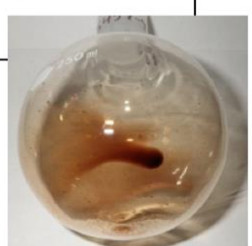
Aqueous reaction mixture (products & unconverted lignin)

- Acidify with to **pH=7**
- Centrifuge

Supernatant
Lignin degradation products (DP≤3), Salt

Solid residue
Unconverted lignin (DP≥4), High MW products

Organic phase
Lignin degradation products (DP≤3)



- Yield
- GCMS analysis

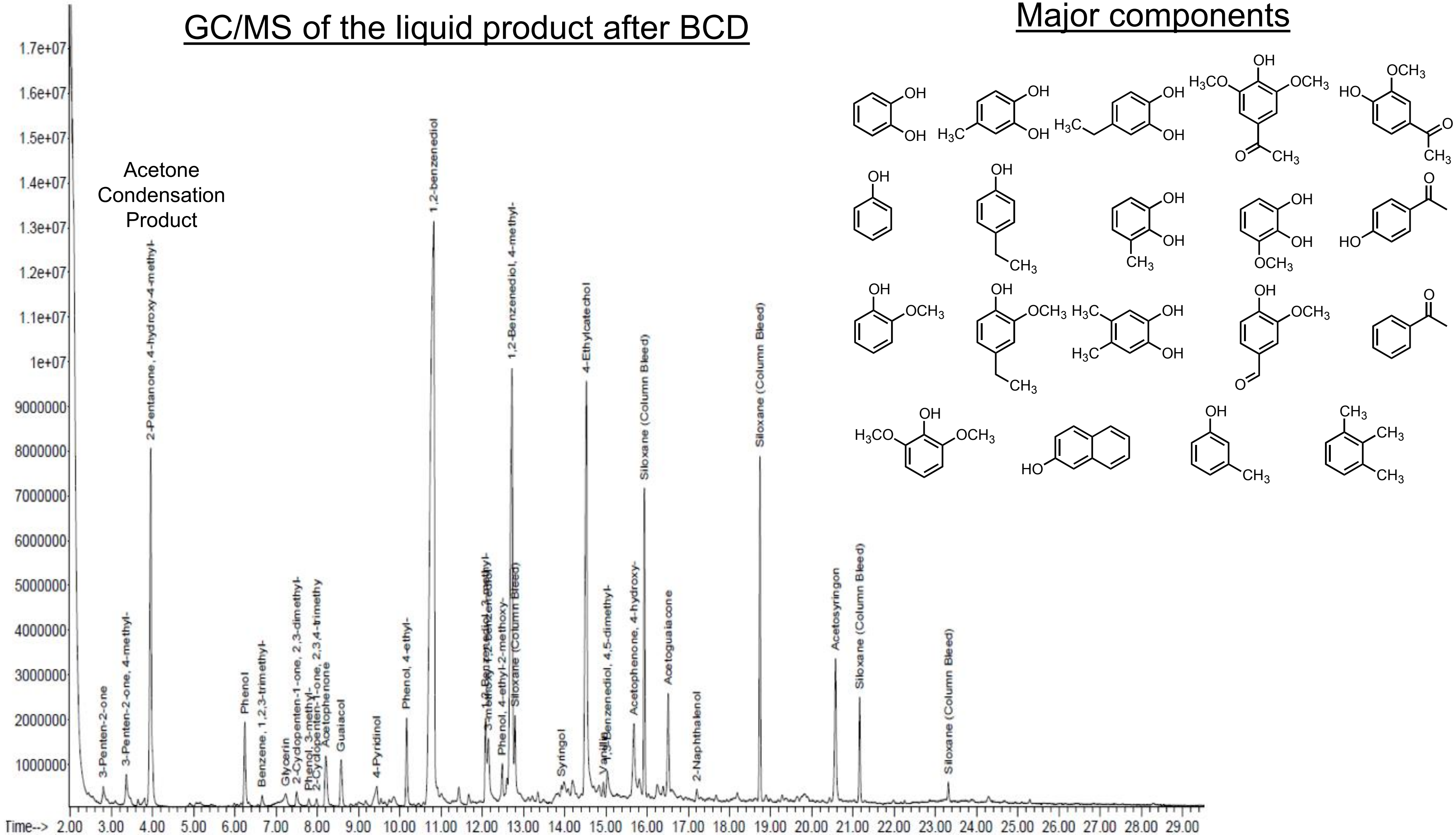
Aqueous phase
- Yield
- GCMS analysis

THF soluble
Unconverted lignin
High MW products
- Yield
- GPC analysis

THF insoluble char

Lignin Deconstruction after Pretreatment/Enzymatic Hydrolysis

GC/MS of the liquid product after BCD



Major components

Integrated carbohydrate-lignin upgrading processes

In FY14, we will examine feeding lignin streams to sugar-upgrading and/or HDO catalysts
Conduct this work in collaboration with NREL and industrial collaborators