# Techno-Economic Analysis and Life-Cycle Assessment for Gas Phase Catalytic Oxidation of Lignin to Produce Phenolic Compounds

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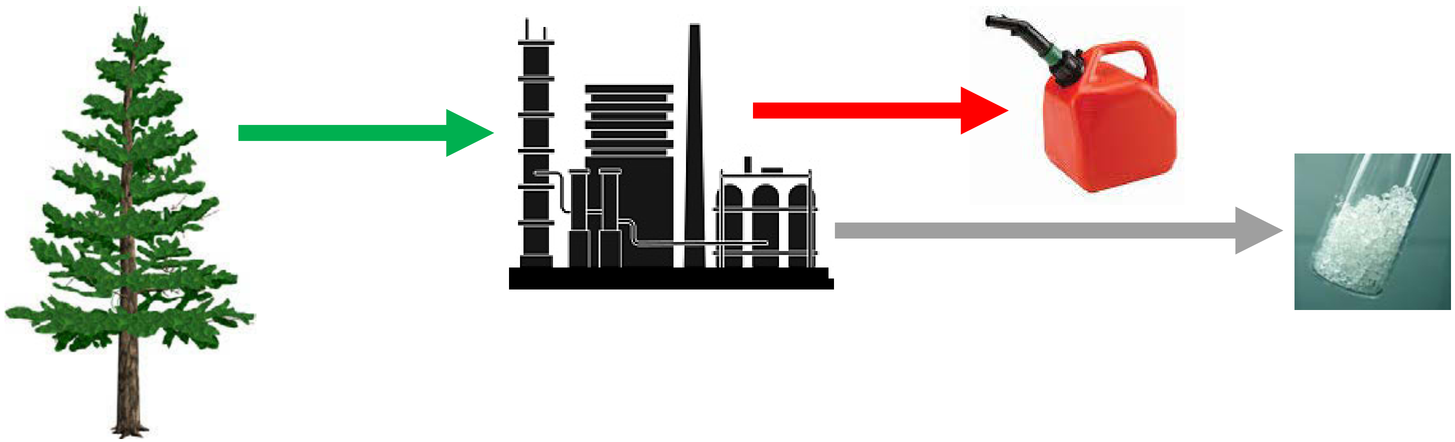
# Fuel co-products are integral to biorefinery economics

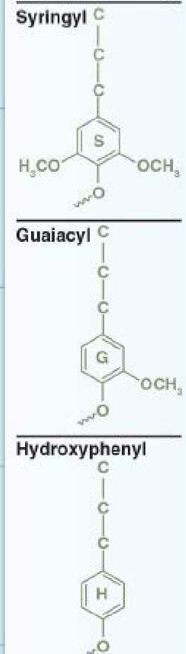


| Products | Amount of Biomass Carbon to Product | Conversion Cost | Product Value |
|---|---|---|---|
| Liquid fuels (e.g., gasoline, diesel, aviation)  | High | $$$ | $ |
| Chemicals  | Lower | $$$ | $$$ |

# Biomass Constituents for Selected Plant Resources

| Plant resource | % Hemicellulose | % Cellulose | % Lignin* |
|---|---|---|---|
| MISCANTHUS | 24-33 | 45-52 | 9-13 |
| SWITCHGRASS | 26-33 | 37-32 | 17-18 |
| CORN STOVER | 31 | 37 | 18 |
| POPLAR | 16-22 | 42-48 | 21-27 |
| EUCALYPTUS | 24-28 | 39-46 | 29-32 |
| PINE | 23 | 46 | 28 |

*Typical aromatic polymer containing:




Depending on the bioresource and isolation methodology, molecular weights for native lignin have been reported from 78,400 [in spruce (*118*)] to 8300 [in Miscanthus (*119*)] g mol[1], which are derived from C9 monolignols as described in Fig. 2.

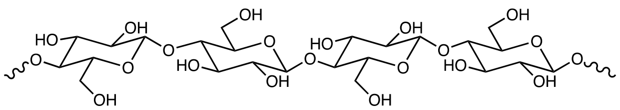
- Lignin constitutes a large fraction of biomass
  - ~15-30% of biomass mass
  - ~40% of biomass carbon

Source: Ragauskas, et al., Science, 344 (2014) http://science.sciencemag.org/content/344/6185/1246843.full

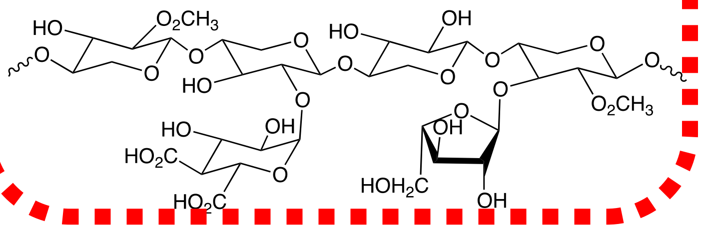
# Biomass Grand Challenge: Complex Functionality

## Biomass - $CH_{1.4}O_{0.6}$

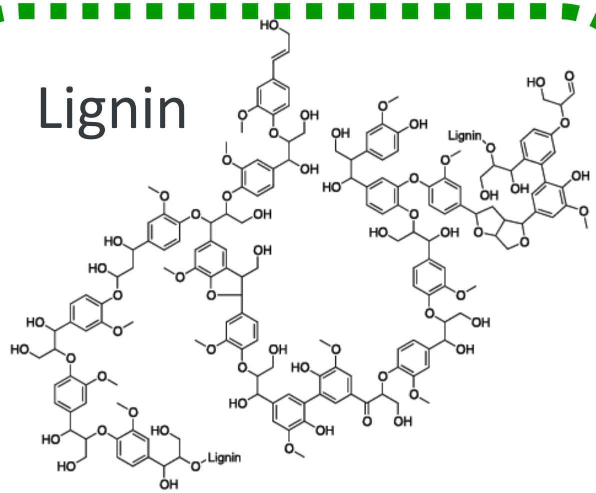
Cellulose



Hemicellulose



Lignin



***Biochemical Pathways***

**Reactions**

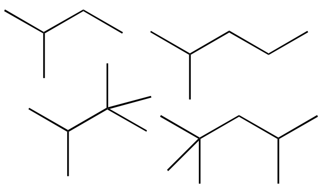
Enzymatic hydrolysis

Fermentation

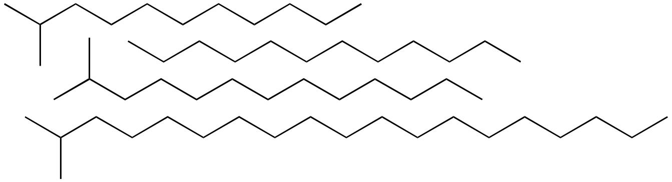
Biological or catalytic upgrading

## Fuels - $C_nH_{2n+2}$

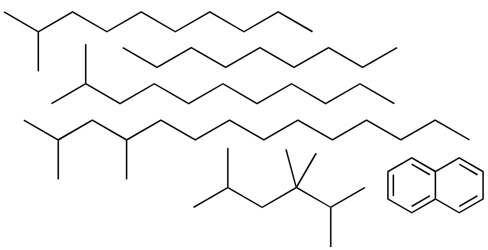
Gasoline



Diesel

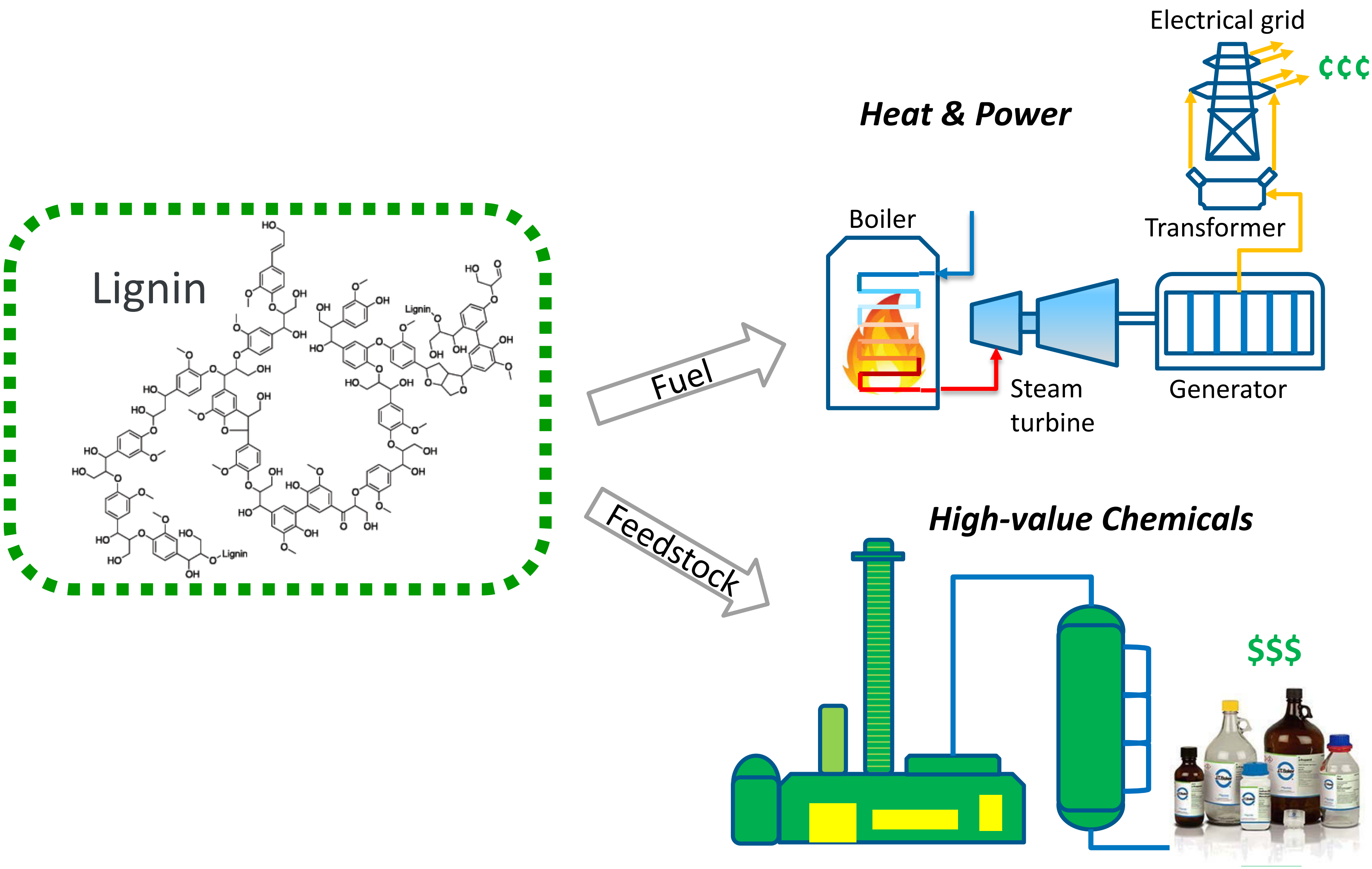


Jet Fuel

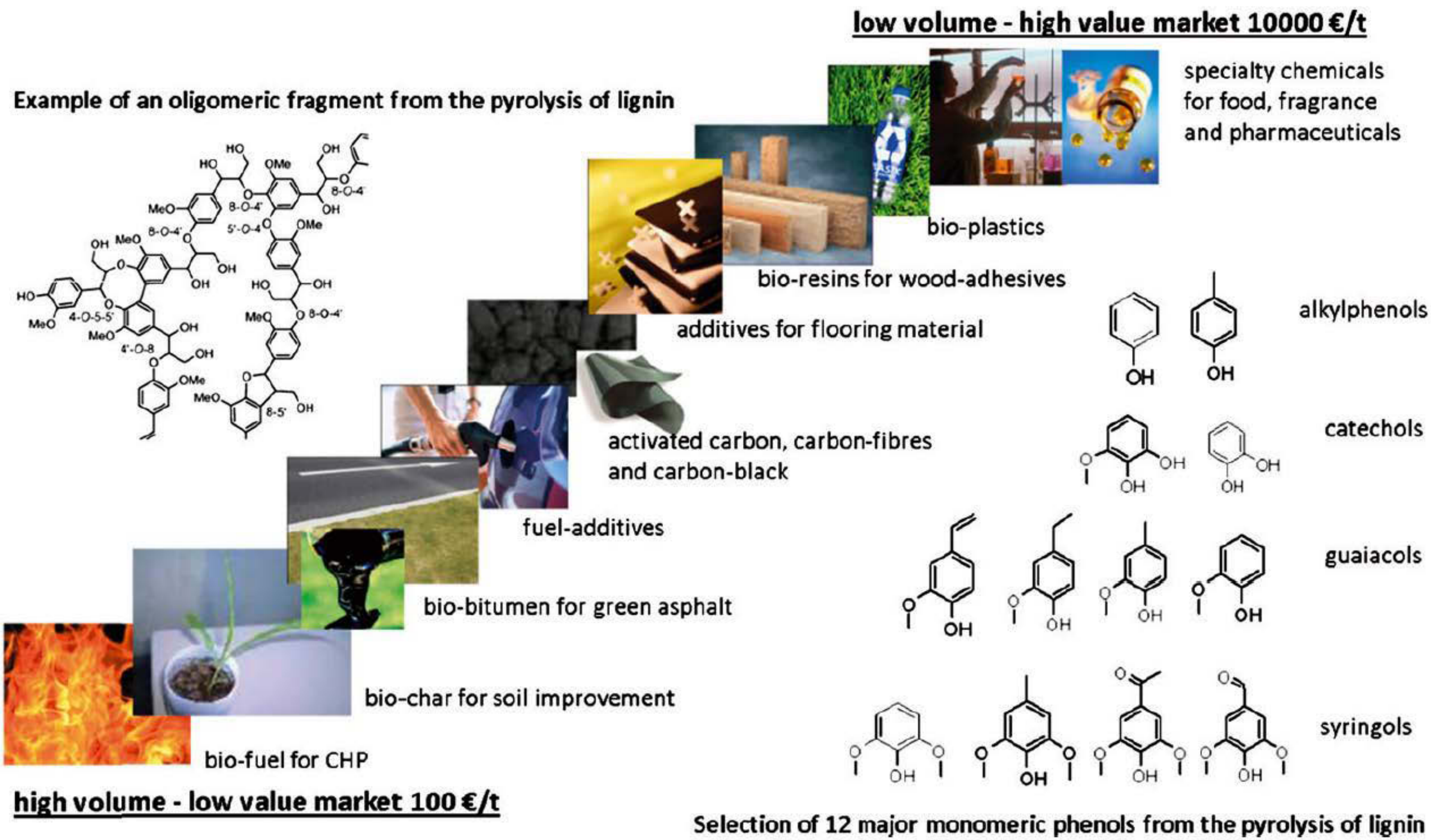


***Multi-functional catalysts are required to convert biomass into fuels***

# Lignin: Fuel vs. Feedstock



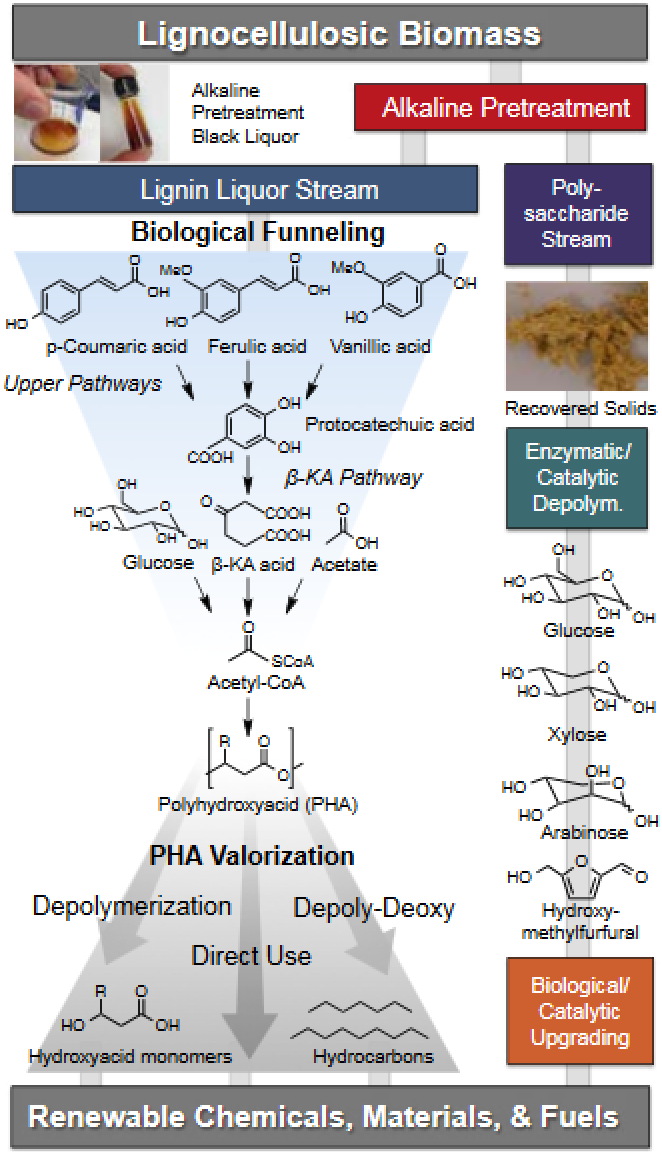
# Potential Market Applications for Lignin and Lignin-Derived Products



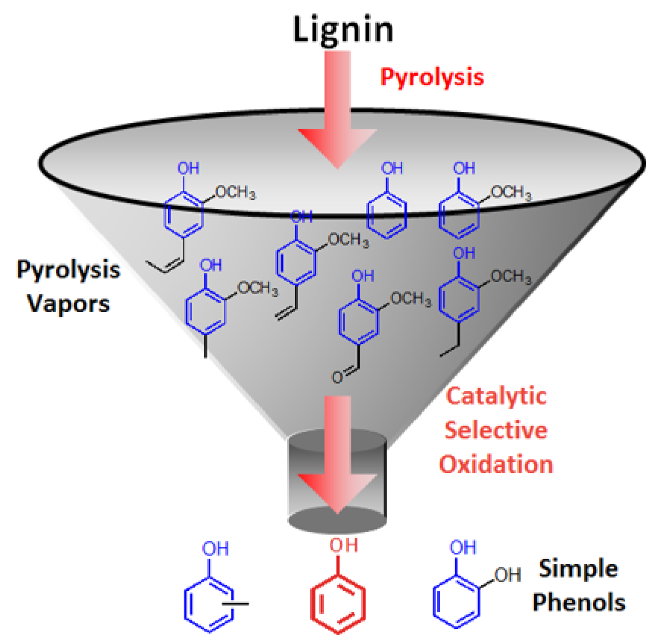

Source: De Wild, et al., Biofuels, Bioprod. Bioref. 8, 645-657 (2014).

# Lignin Valorization Pathways

Biological Route




Thermochemical Route




Using a “funneling” pathway inherent in nature, NREL researchers show that lignin can be converted into renewable fuels, chemical, and materials.

Source: Linger, et al. Proc. Natl. Acad. Sci., 2014.

# Selective oxidation of lignin showing some potential co-products and their markets. The focus of this study is phenol, shown in red.

**Goal:** Convert lignin to valuable phenolic compounds

Lignin pyrolysis → partial oxidation of lignin to remove methoxy side chains → create "simple phenols" (phenols with no methoxy groups)

**Scope:** Preliminary TEA and LCA evaluation

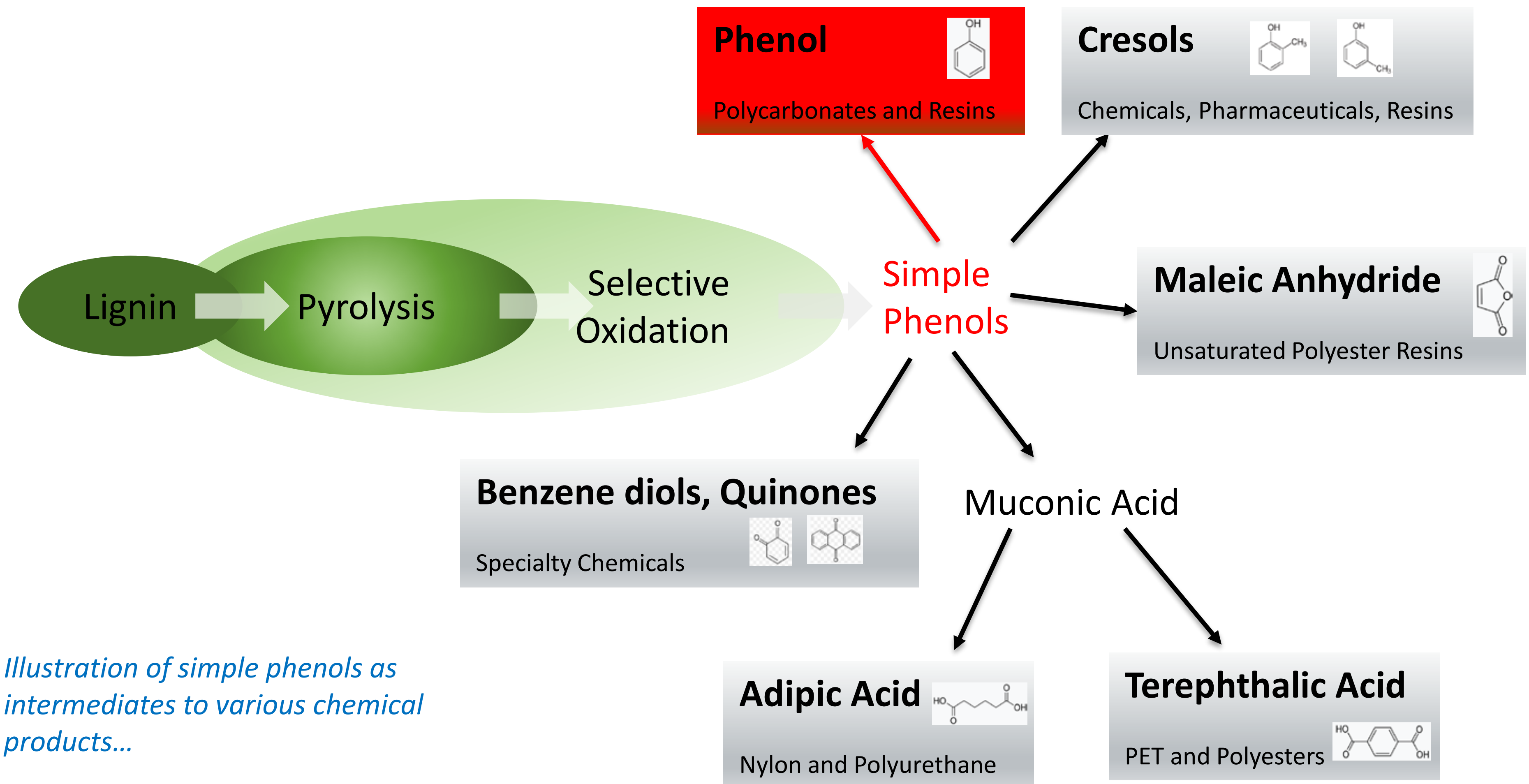
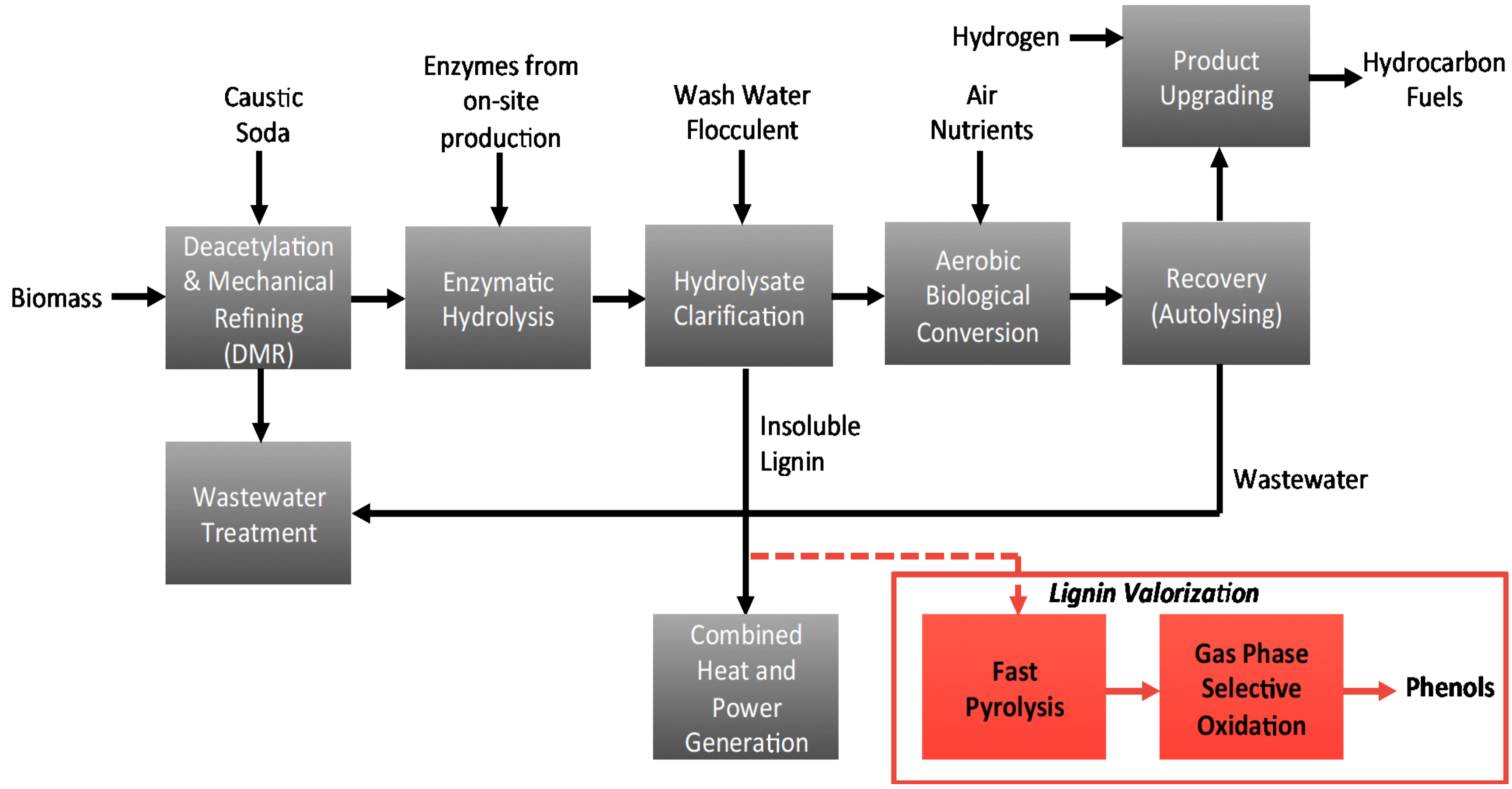


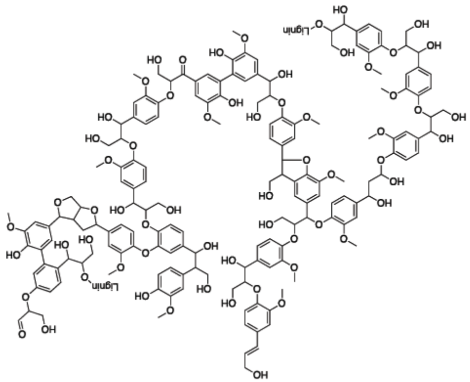

*Illustration of simple phenols as intermediates to various chemical products…*

# Hydrocarbon production via lipid pathway, with valorization of lignin through the fast pyrolysis and subsequent gas phase selective oxidation to phenols.

For TEA and LCA, we have developed and modeled this hybrid process:
1) biochemically converting C5/C6 sugars from biomass to a hydrocarbon blendstock, and
2) thermochemically converting lignin from biomass, via selective partial oxidation of lignin pyrolysis vapor, to phenols.



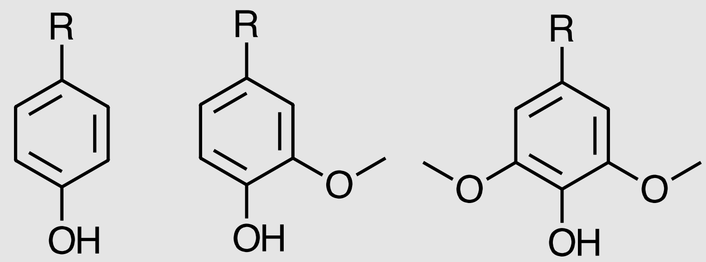
# Oxidative removal of lignin-chains for co-products



LIGNIN FROM BIOCHEM. PROCESS

***Pyrolysis***

***LIGNIN PYROLYSIS PRODUCTS***




Char

(recalcitrant C-C linkages in lignin)

***Catalytic partial oxidation***

*Vanadia-based catalysts*

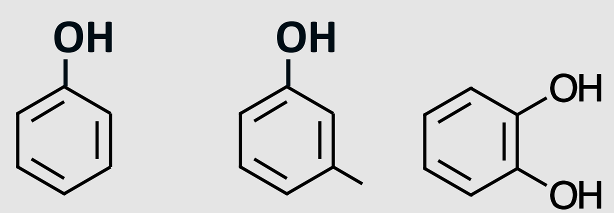
$CO$ and $CO_2$

(undesired oxidation products)

**Paper 695a**
**Thursday, 11/1/2018**
**at 3:30 PM**

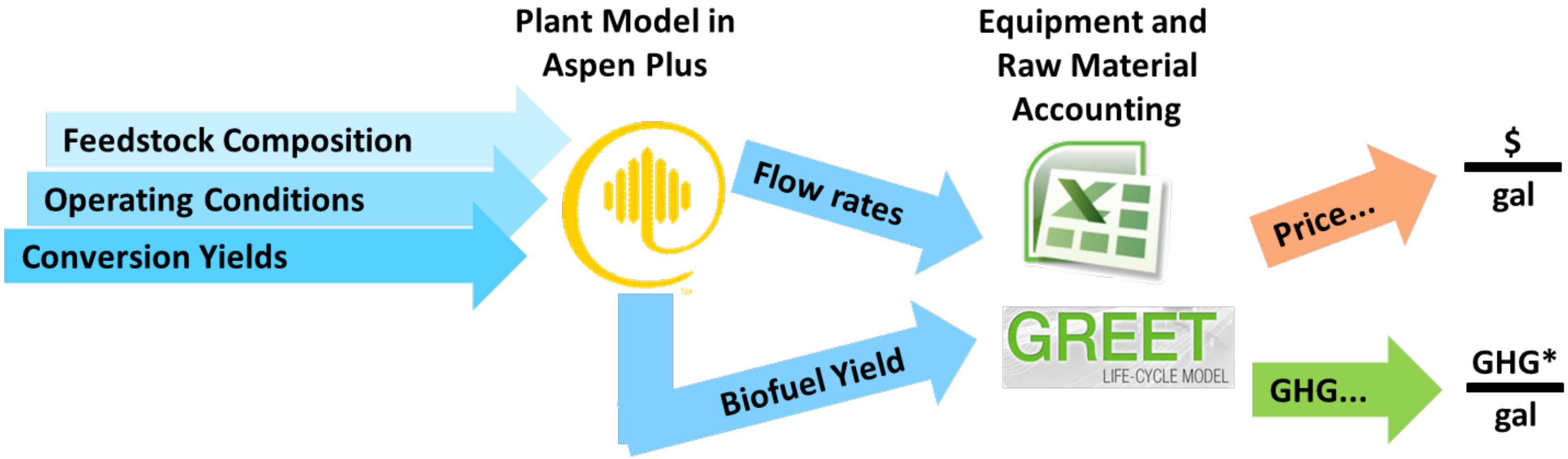
***SIMPLE PHENOLS***

phenol | cresol(s) | catechol



# Conversion Technology Assessment

- Techno-economic analysis (TEA)
  - Assess the technical and economic viability of new processes and technologies (MFSP)
- Life-cycle assessment (LCA)
  - Estimate the environmental impacts (GHGs)




*Biorefinery upstream and downstream processes not shown here.

# TEA Methodology & Assumptions

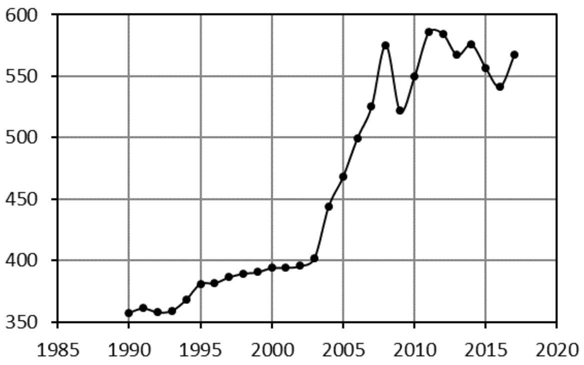
## Discounted Cash Flow Analysis Parameters

| | |
|---|---|
| **Plant life** | **30 years** |
| Discount rate | 10% |
| General plant depreciation | 7-year MACRS schedule[a] |
| Steam plant depreciation | 20-year MACRS schedule[a,b] |
| Federal tax rate | 35% |
| Financing | 40% equity |
| Loan terms | 10-year loan at 8% APR |
| Construction period | 3 years |
| First 12 months' expenditures | 8% |
| Next 12 months' expenditures | 60% |
| Last 12 months' expenditures | 32% |
| Working capital | 5% of fixed capital investment |
| Start-up time | 6 months |
| Revenues during startup | 50% |
| Variable costs incurred during startup | 75% |
| Fixed costs incurred during startup | 100% |
| | |

[a] https://www.irs.gov/pub/irs-pdf/p946.pdf

[b] For the case with no electricity selling, the steam plant is depreciated using the 7-yr basis instead of 20-yr basis.

**Chemical Engineering's Plant Cost Index**




$$Scaled\ Equipment\ Cost = Base\ Equipment\ Cost\left(\frac{Scaled\ Capacity}{Base\ Capacity}\right)^n$$

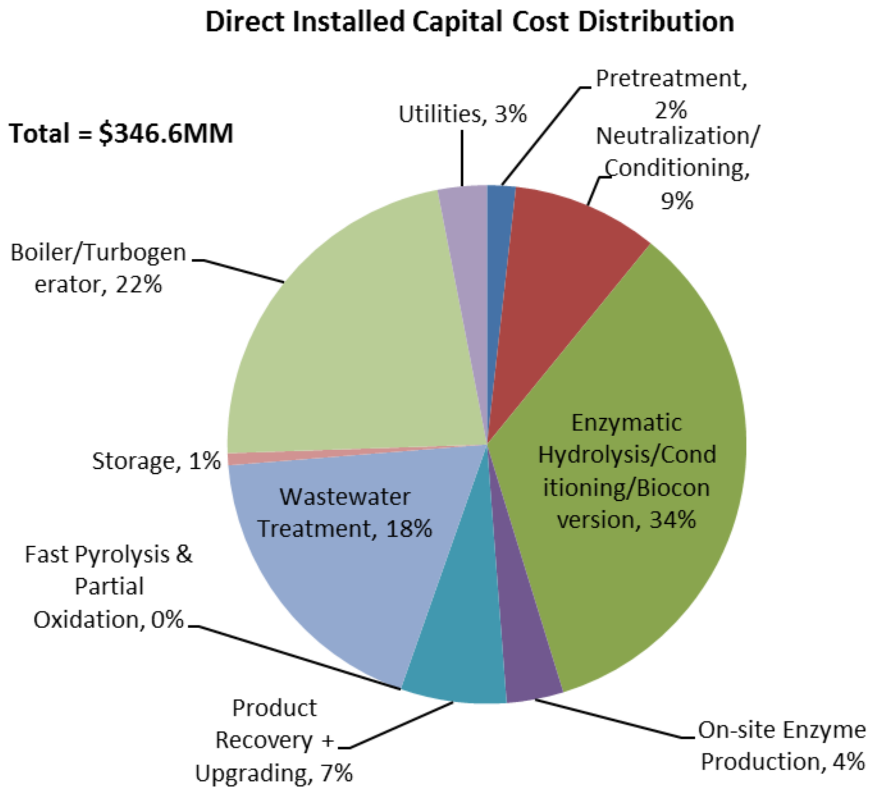
$$Total\ Installed\ Cost\ (TIC) = f_{installation} * Total\ Purchased\ Equipment\ Cost\ (TPEC)$$

$$Cost\ in\ 2014\$ = Base\ Cost\left(\frac{2014\ Cost\ Index\ Value}{Base\ Year\ Cost\ Index\ Value}\right)$$

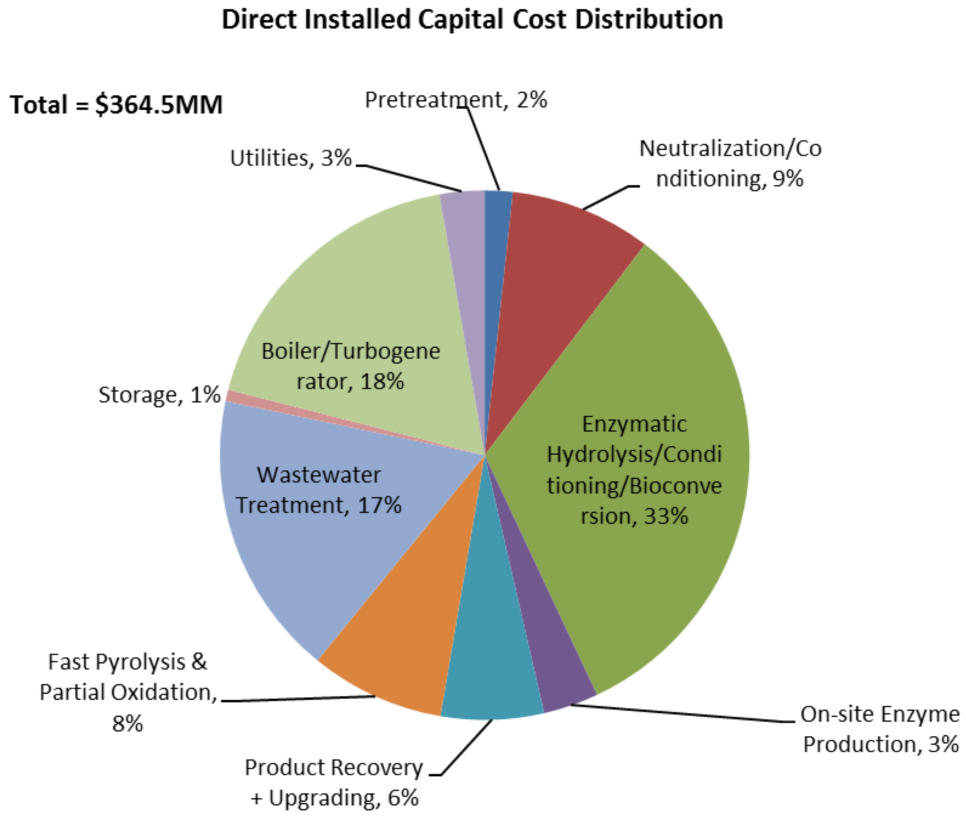
Costs in 2014$

# Capital cost breakout

Lignin to Heat & Power (no coproduct)




Lignin Valorization (Coproduct: phenols)



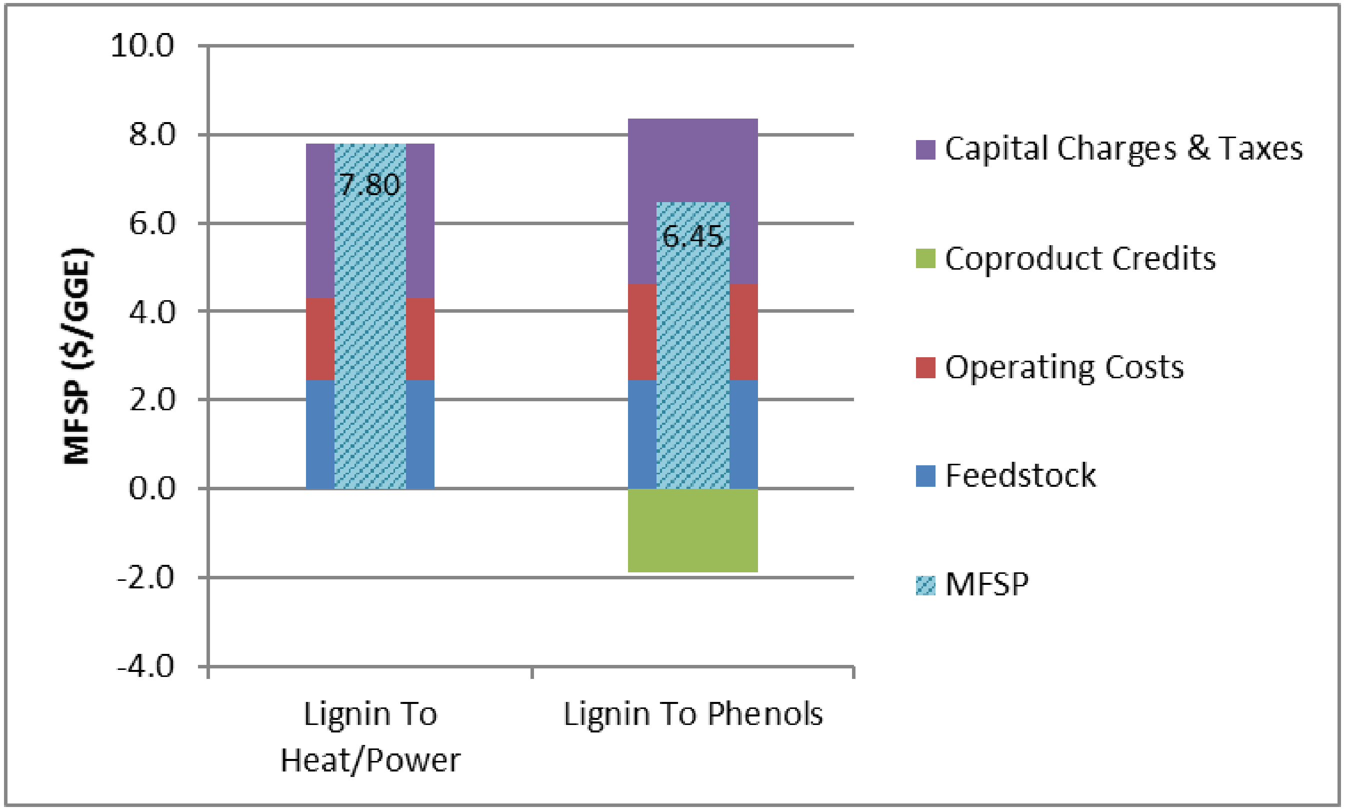

Costs in 2014$

# Preliminary TEA Results

*17% MFSP improvement from valorization of lignin*

Costs in 2014$

*Phenols coproduct value: $1,981/tonne (2010-2014 5-yr average from IHS)*

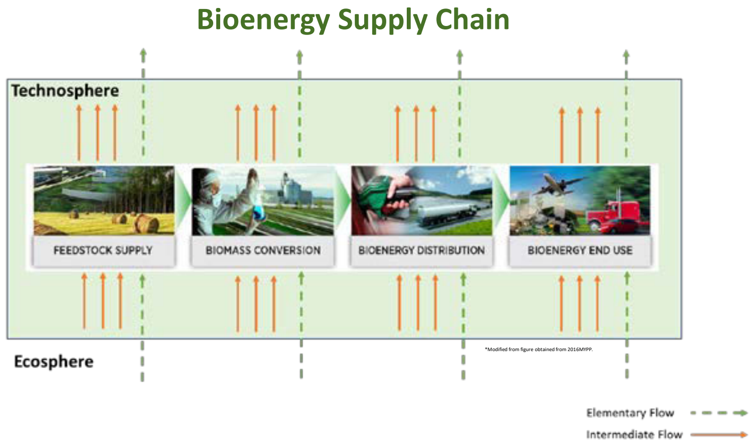



Note: The $7.80/GGE MFSP number for the pathway (via lipids) was presented in the DOE Bioenergy Technologies Office (BETO) 2017 Project Peer Review (March 7, 2017, Denver, CO) (https://www.energy.gov/sites/prod/files/2017/05/f34/Biochemical%20Platform%20Analysis%20Project_0.pdf, see slide 11).

# LCA Methodology & Assumptions

1. Goal
   - Preliminary life cycle GHG intensity assessment
   - Compare the base case, lignin used for heat and power generation, with the case with lignin valorization (producing coproduct)
   - Not intended to be used in comparative assertions

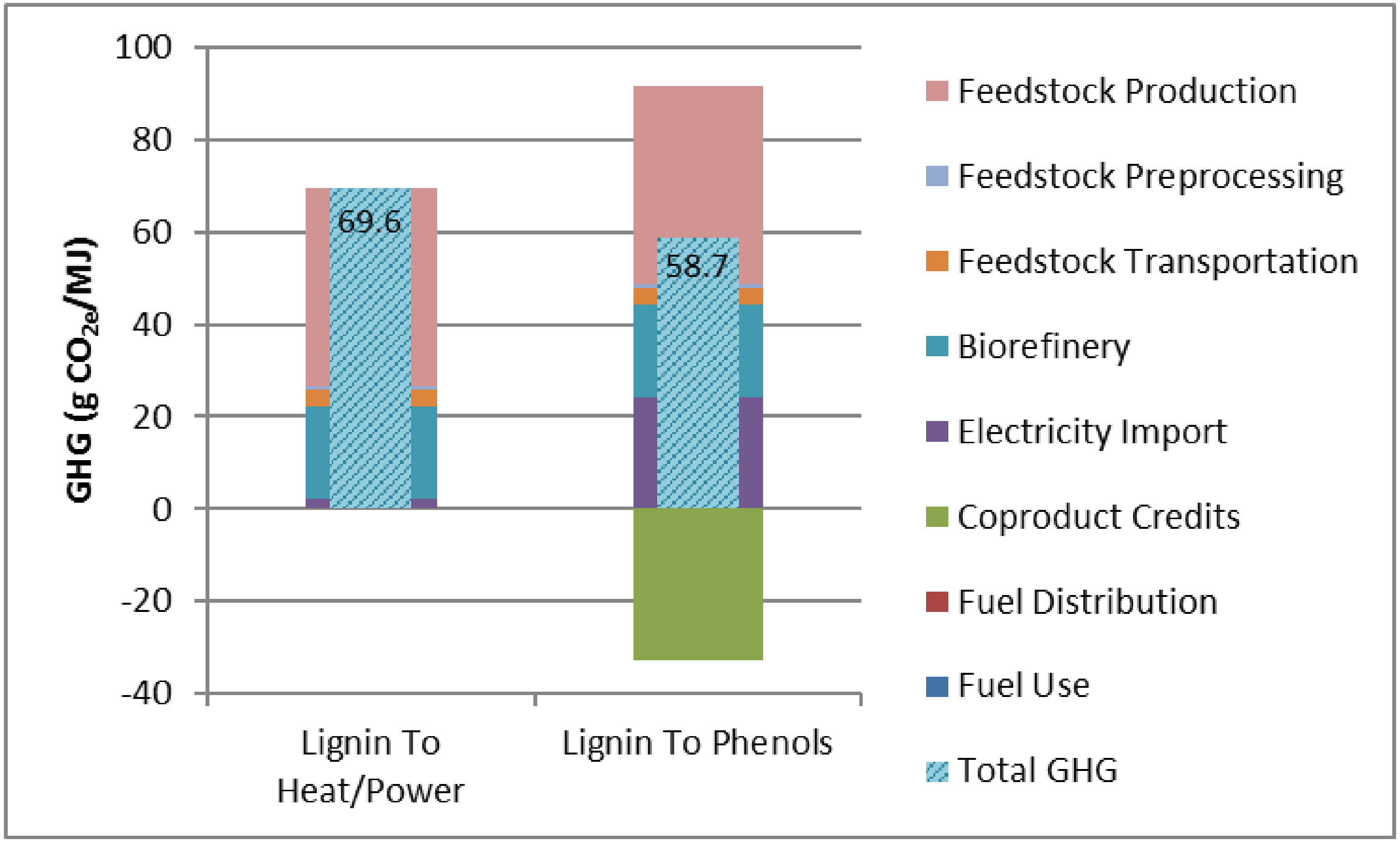
2. Scope
   - Functional unit: 1 MJ of RDB
   - System boundary: “field-to-wheel”
   - Allocation: coproduct displacement
   - Impact assessment method:
     - ✓ Single attribute LCA
     - ✓ IPCC 2013 GWP 100a




3. Life Cycle Inventory
   - Biorefinery – Aspen Plus process model
   - Upstream & downstream – GREET
   - Others – USLCI, EIO, Ecoinvent

# Preliminary LCA Results

*Lignin valorization potentially lowers life cycle carbon intensity (16% improvement)*




*Petroleum-based phenols (Hock process) GHG intensity: 4.14 kg CO2e/kg*

# LCA – Coproduct Allocation Sensitivity

Modeling and Analysis

Biofpr

**Life-cycle analysis of integrated biorefineries with co-production of biofuels and bio-based chemicals: co-product handling methods and implications**

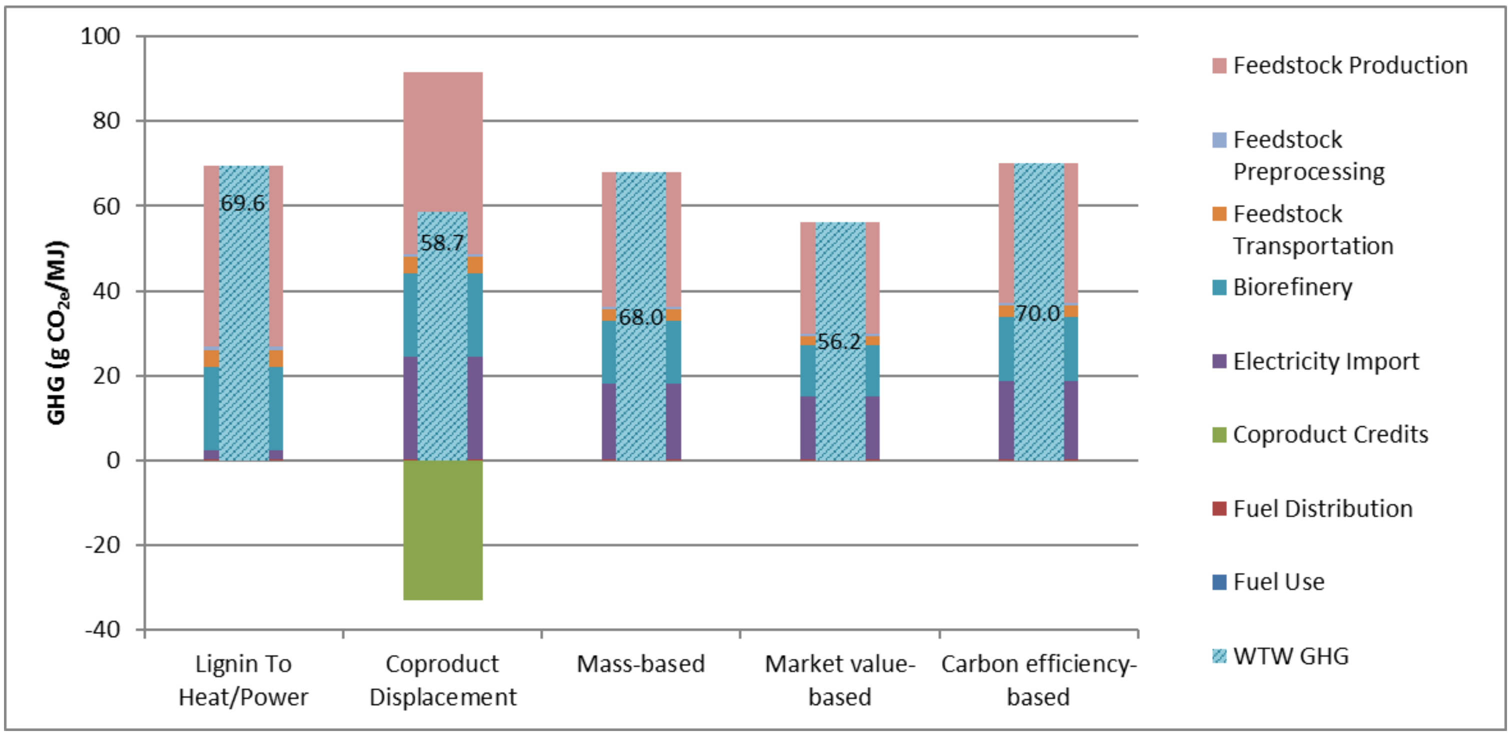
Hao Cai, Jeongwoo Han, Michael Wang, Systems Assessment Group, Energy Systems Division, Argonne National Laboratory, USA
Ryan Davis, Mary Biddy, Eric Tan, National Bioenergy Center, National Renewable Energy Laboratory IL, USA

Reference: Cai, et al., Biofuels, Bioprod. Bioref. 12, 815-833 (2018).

| Allocation Methods | Product / Coproduct | Units | Lignin To Heat & Power | Lignin To Coproduct | Allocation Factor |
|---|---|---|---|---|---|
| Mass | RDB[a] | kg/hr | 8603 | 8603 | 74.2% |
| | Coproduct | kg/hr | 0 | 2994 | 25.8% |
| Market value[b] | RDB | MM$/yr | 74.21 | 74.21 | 61.3% |
| | Coproduct | MM$/yr | 0.00 | 46.77 | 38.7% |
| Carbon efficiency | RDB | % | 19.8% | 19.8% | 76.4% |
| | Coproduct | % | 0% | 6.1% | 23.6% |

[a] RDB: Renewable Diesel Blendstock

[b] System-level allocation. RDB at $3.00/GGE. Coproduct (phenols) at $1981/tonne.



# Summary

- NREL has developed a vapor phase selective oxidation process for the conversion of insoluble lignin streams from the biological biofuels production into phenols.

- As illustrated using an NREL's biological conversion of C5/C6 sugars to renewable diesel blendstock via lipid upgrading, lignin valorization has improved the economics by 17%.

- Lignin valorization has also had the potential to lower the life cycle carbon intensity of the biofuel (16% improvement) when coproduct (phenols) is handled using displacement approach (a.k.a system expansion).

- Coproduct displacement is the default coproduct handling approach under the current policy framework that allows the biorefinery to be credited for producing chemical coproducts with fewer GHG emissions than their petroleum counterparts.

- Coproduct handling approach sensitivity analysis has revealed that the life-cycle GHG emissions readily vary with the coproduct handling method. This should be examined at the interpretation phase of the LCA study.

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