

# Converting Biomass to Liquid Hydrocarbon Fuels



**Catalysis and Biomass  
Feedstocks Workshop**

**Council for Chemical Research**

**Thomas D. Foust**

**Director,**

**National Advanced Biofuels  
Consortium**

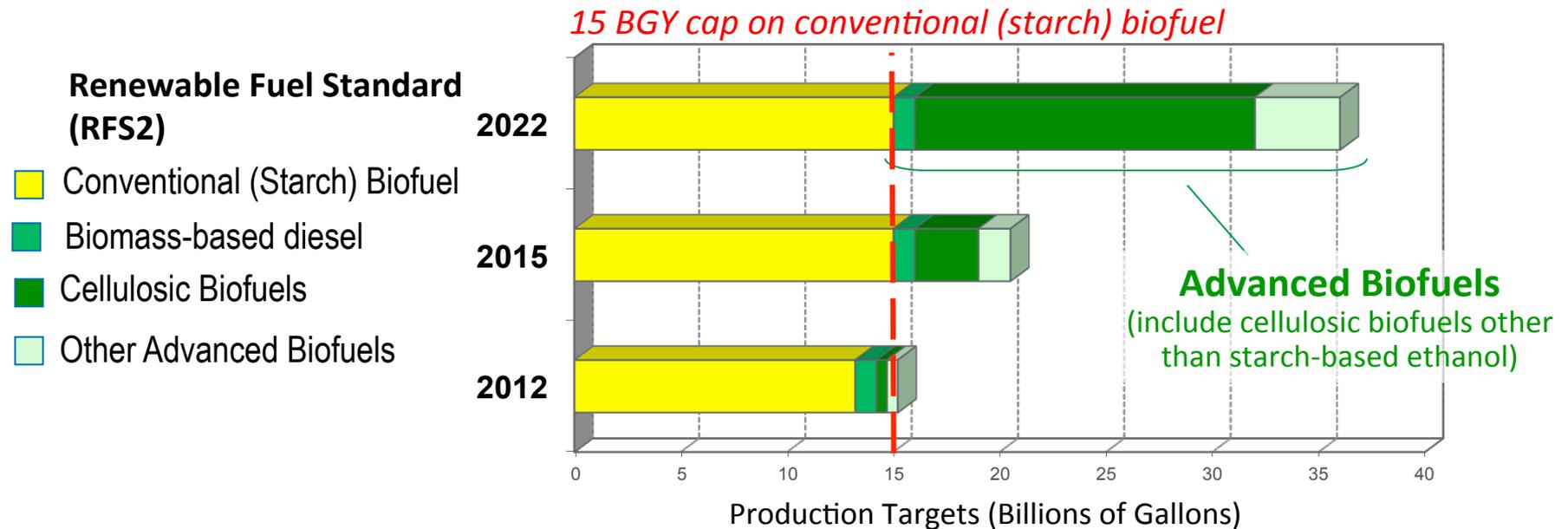
**September 21, 2011**

# Overview

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- Future directions of transportation fuel needs
- Conversion options and initial assessment of potentials
- Barrier areas and research needs
- Path forward

# EISA Mandated Biofuel Production Targets



**EISA** defines **Cellulosic Biofuel** as “renewable fuel derived from any cellulose, hemicellulose, or lignin that is derived from renewable biomass and that has lifecycle greenhouse gas emissions...that are *at least 60 percent less* than baseline lifecycle greenhouse gas emissions.” The EPA interprets this to include cellulosic-based diesel fuel.

**EISA** defines **Advanced Biofuel** as “renewable fuel, other than ethanol derived from corn starch, that has lifecycle greenhouse gas emissions...that are *at least 50 percent less* than baseline lifecycle greenhouse gas emissions.” This includes biomass-based diesel, cellulosic biofuels, and other advanced fuels such as sugarcane-based ethanol.

# U.S. Transportation Fuel Needs

**Gasoline (cars & trucks)**



**137 bgy**

**Diesel (on-road, rail)**



**43 bgy**

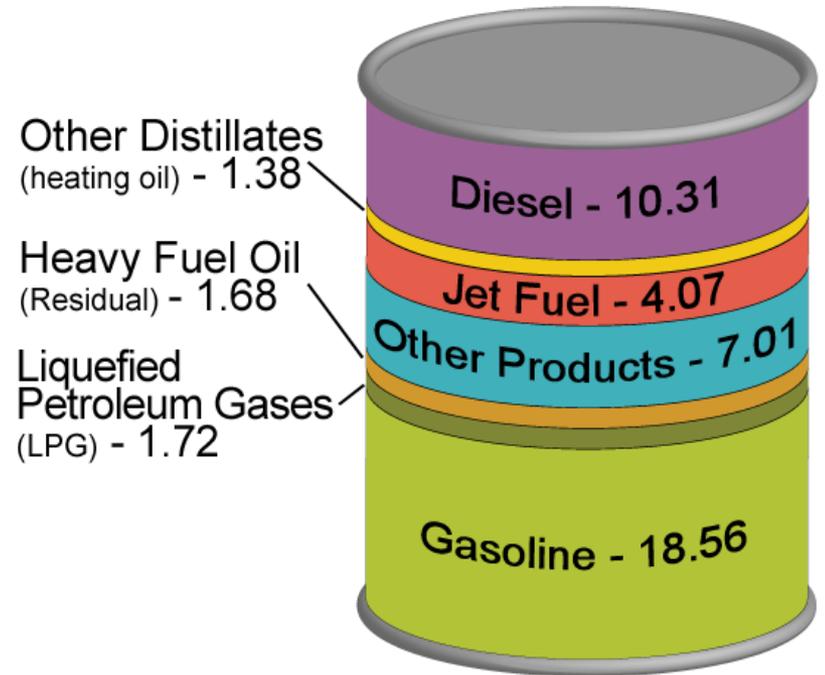
**Aviation (jet fuel)**



**23 bgy**

	2008	2030
Motor gasoline	137	126
Diesel	43	71
Jet fuel	23	30

Products in a Barrel of Crude (gal)



Source: Energy Information Agency

# Long-Term Role of Ethanol

## Ultimate ethanol market - 20 -25 BGY

- EPA has approved E15 as substantially similar to gasoline
- E85 sales gaining slightly –still very small as overall percentage
- E20 future uncertain – EPA will most likely take a wait and see posture on results of E15
- Strong sentiment that VETC will not be renewed beyond 2011
  - Impact on ethanol production volumes uncertain

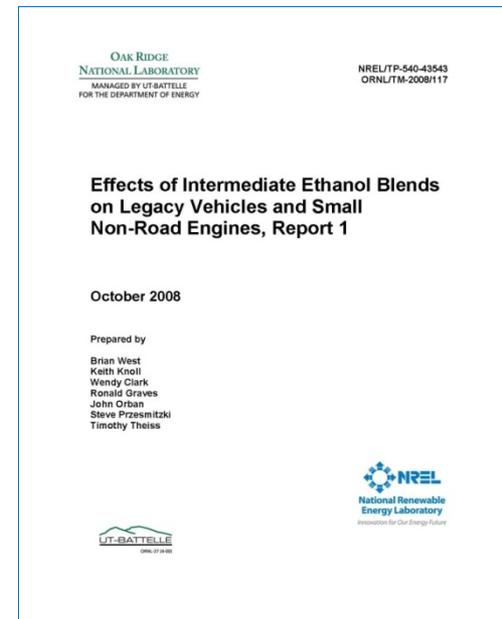
## Ethanol Production

### Corn

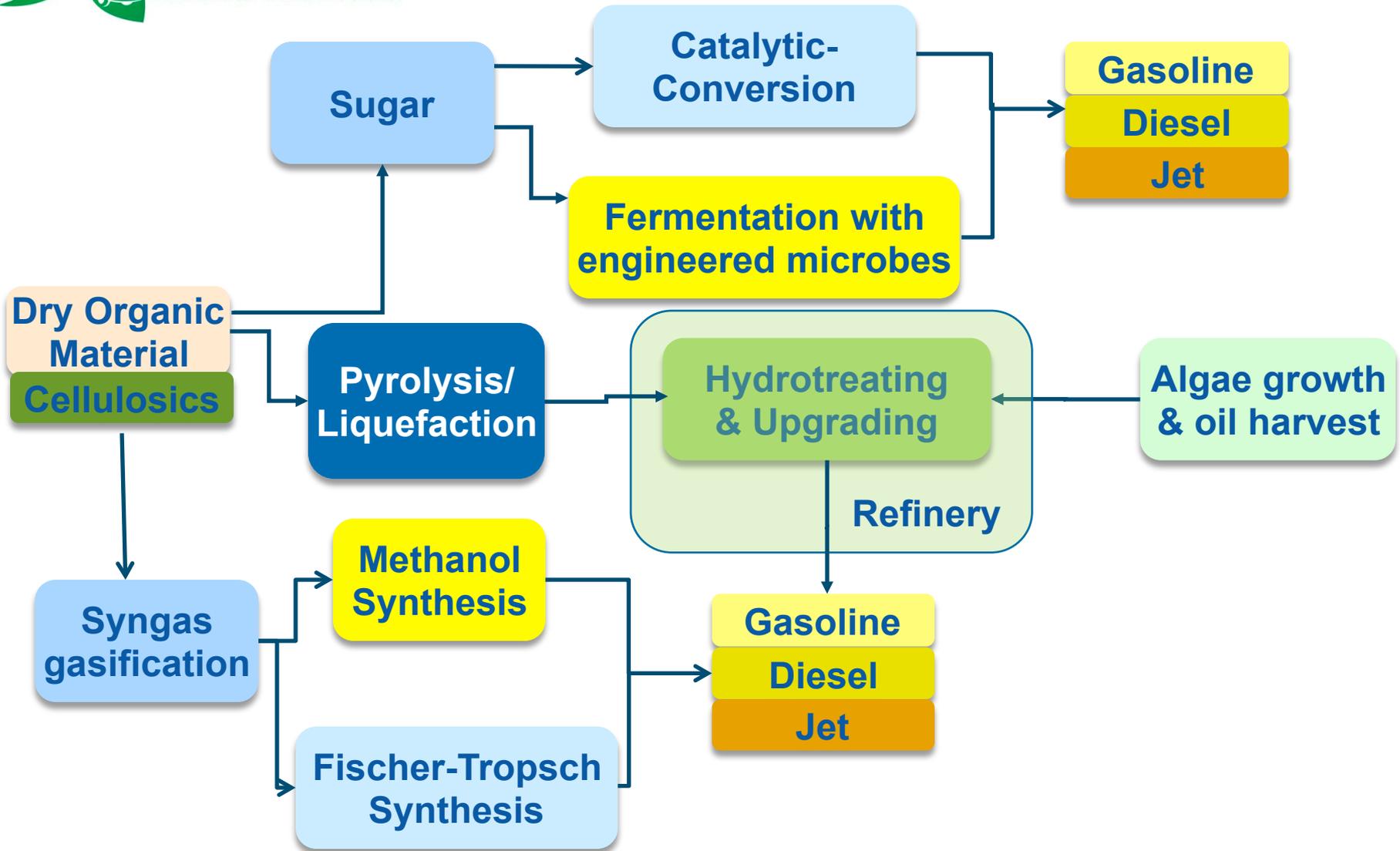
- 2010 production - 13.2 BGY
  - Nameplate – 13.5 BGY
  - Construction/Expansion – 0.5 BGY
  - Total – 14.0 BGY

### Lignocellulosic

- Currently being piloted by a number of organizations-  
DuPont, Poet, Abengoa



# Advanced Biofuel Conversion Routes



# National Advanced Biofuels Consortium

**Project Objective** – Develop cost-effective technologies that supplement petroleum-derived fuels with advanced “drop-in” biofuels that are compatible with today’s transportation infrastructure and are produced in a sustainable manner.

**ARRA Funded:**

- 3 year effort
- DOE Funding \$35.0M
- Cost Share \$15.1M

**Total**      **\$50.1M**

## Consortium Leads

National Renewable Energy Laboratory  
Pacific Northwest National Laboratory

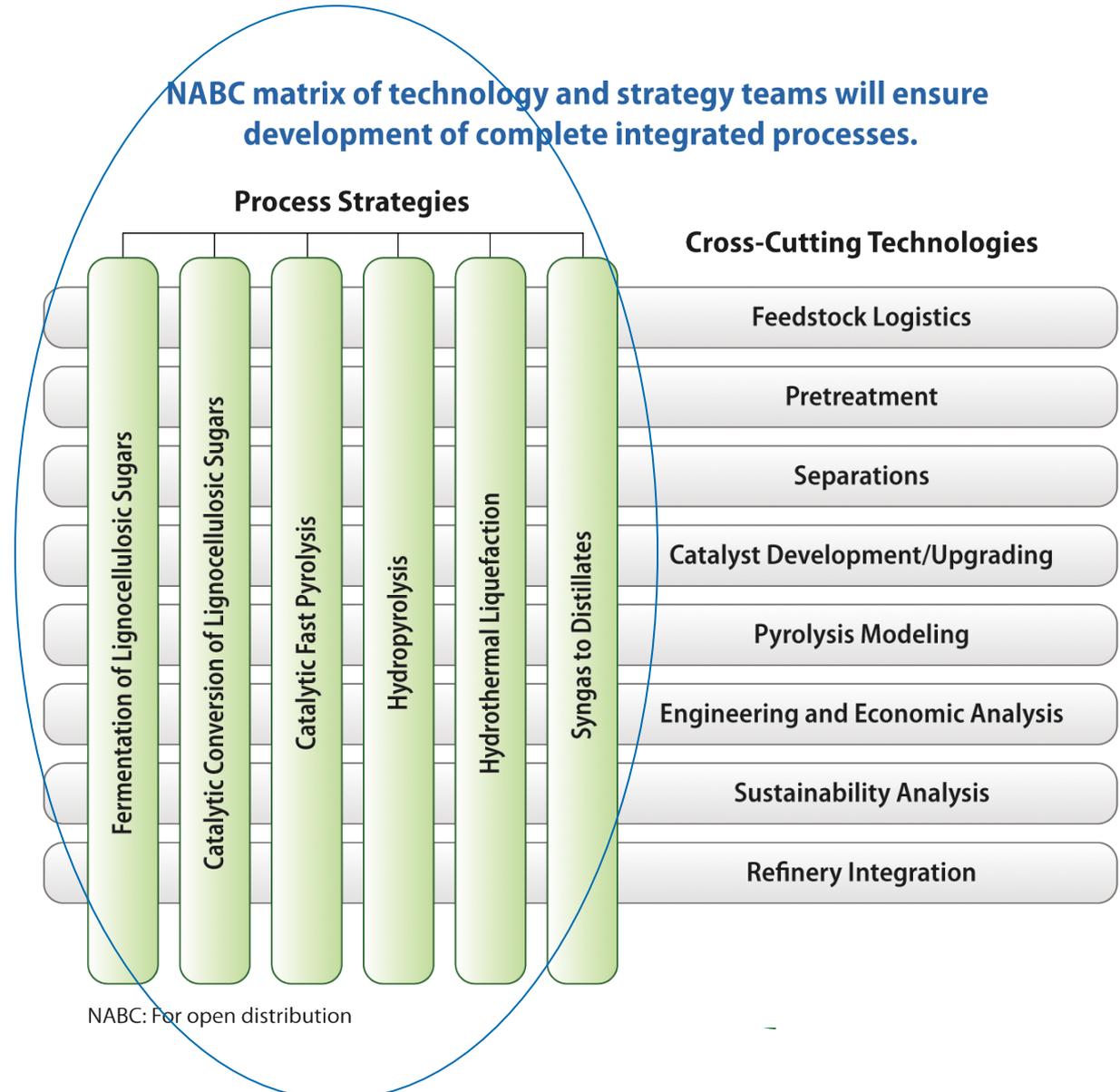
## Consortium Partners

Albemarle Corporation	Los Alamos National Laboratory
Amyris Biotechnologies	Pall Corporation
Argonne National Laboratory	RTI International
BP Products North America Inc.	Tesoro Companies Inc.
Catchlight Energy, LLC	University of California, Davis
Colorado School of Mines	UOP, LLC
Iowa State University	Virent Energy Systems
	Washington State University

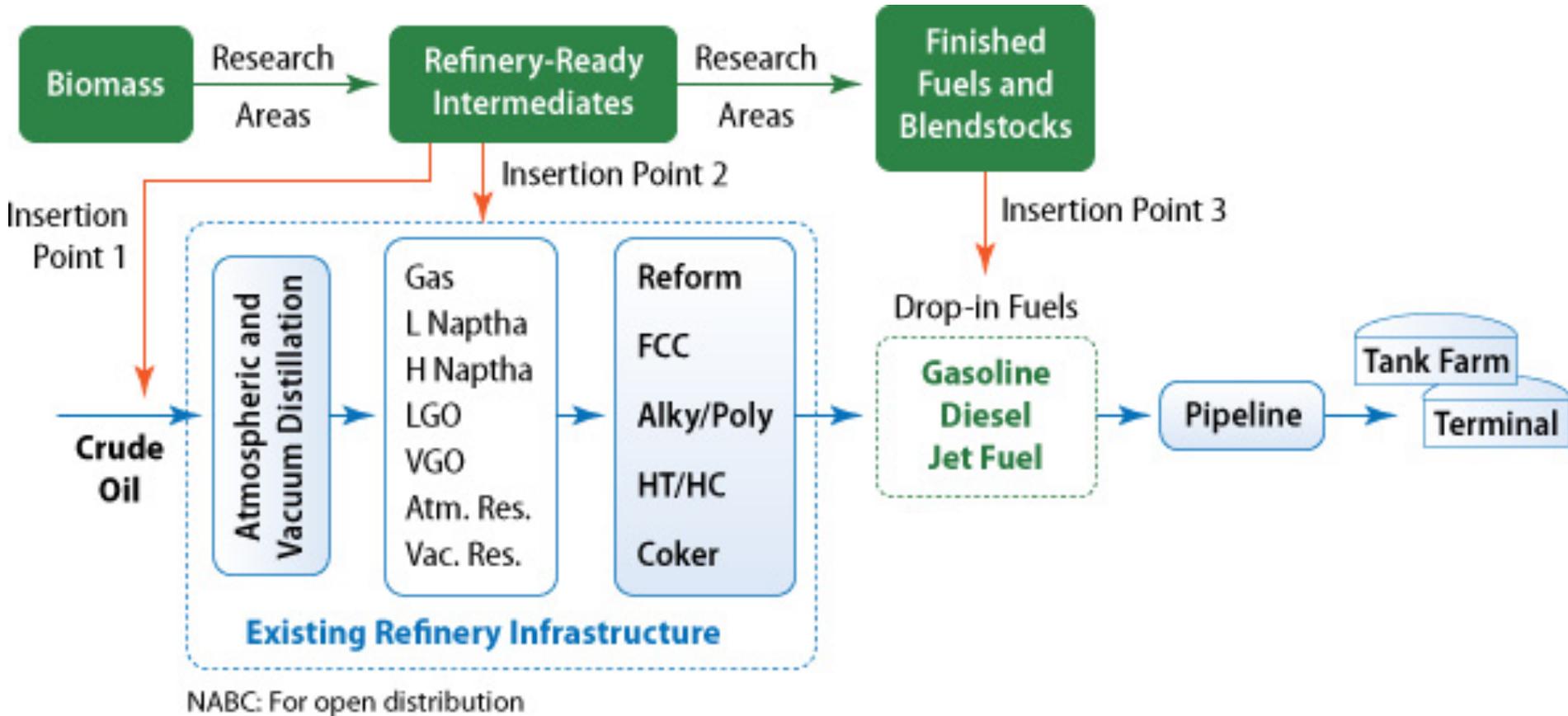


# NABC Research Focus

Converting biomass into infrastructure-compatible materials



# Refinery Integration



- Three possible insertion points
- Develop new technologies that use today's infrastructure

# Down-selection matrix

	(C1) Fuel / Intermediates quality	(C2) Technical readiness	(C3) Sustainability	(C4) Process Efficiency	(C5) Capital and operating costs	(C6) Catalyst and organism robustness	(C7) Fuel Toxicity (Benzene)
CLS							
FLS							
CFP							
HYP							
HTL							
S2D							

Evaluation Results will be ranked as follows:



# Down-select Results

## Strategies moving into Stage II

- Catalysis of Lignocellulosic Sugars
- Fermentation of Lignocellulosic Sugars

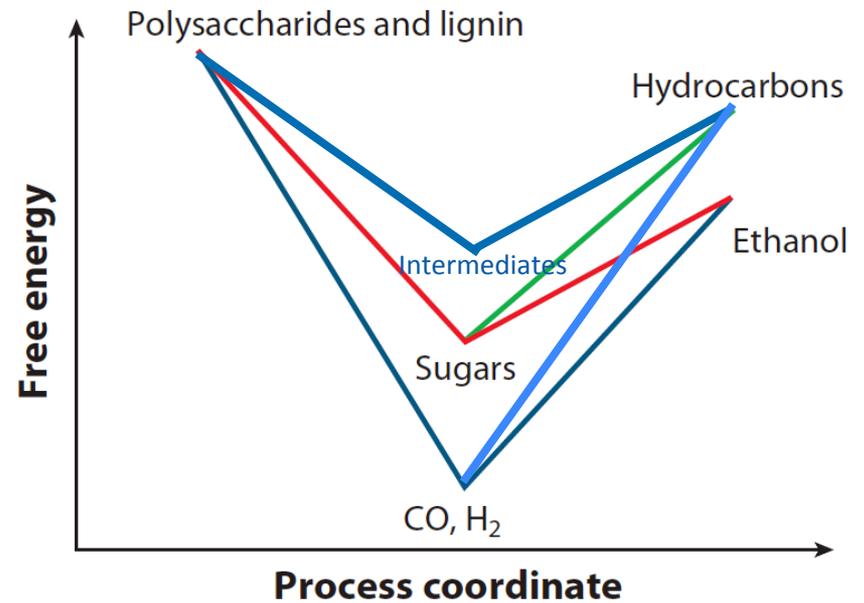
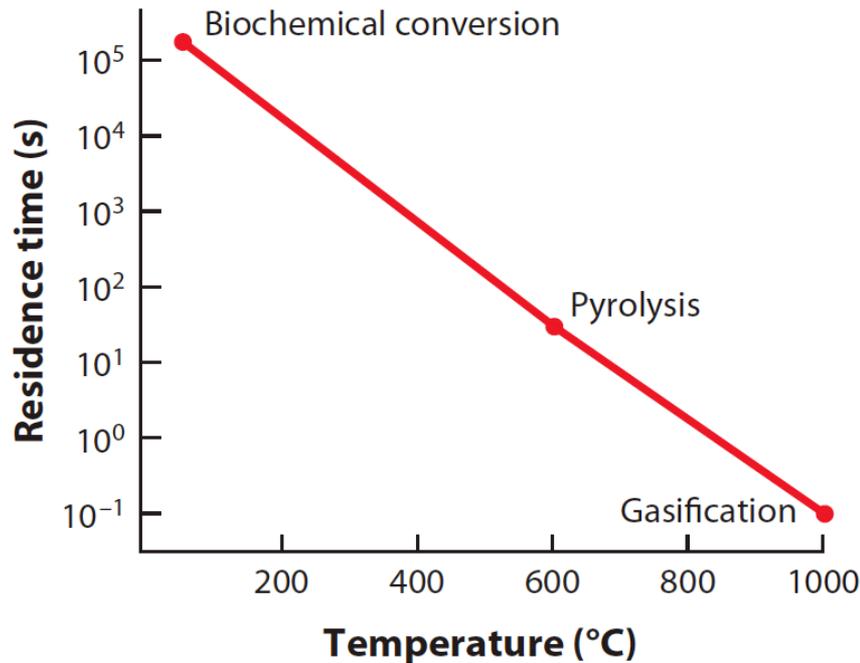
## Strategies missing key data that will be given a three month extension

- Hydrothermal Liquefaction
  - Need to address pumping, reactor design /cost issues and scalability issues.
- Catalytic Fast Pyrolysis
  - Need to verify consistent results and address data quality concerns

## Strategies not moving into Stage II

- Syngas to Distillates
  - Need more R&D on proof of concept
- Hydropyrolysis
  - Unable to generate data that can be replicated
  - Sufficient data to address feasibility not generated
  - High hydrogen use

# Thermodynamics and kinetics of biomass conversion



## Energy Regimes

High

- Gasification -Syngas

Intermediate

- Fast Pyrolysis, Catalytic Fast Pyrolysis, Hydropyrolysis –complex mixture
- Liquefaction- aqueous – mono-oxygenates, organic -polyphenolics

Low

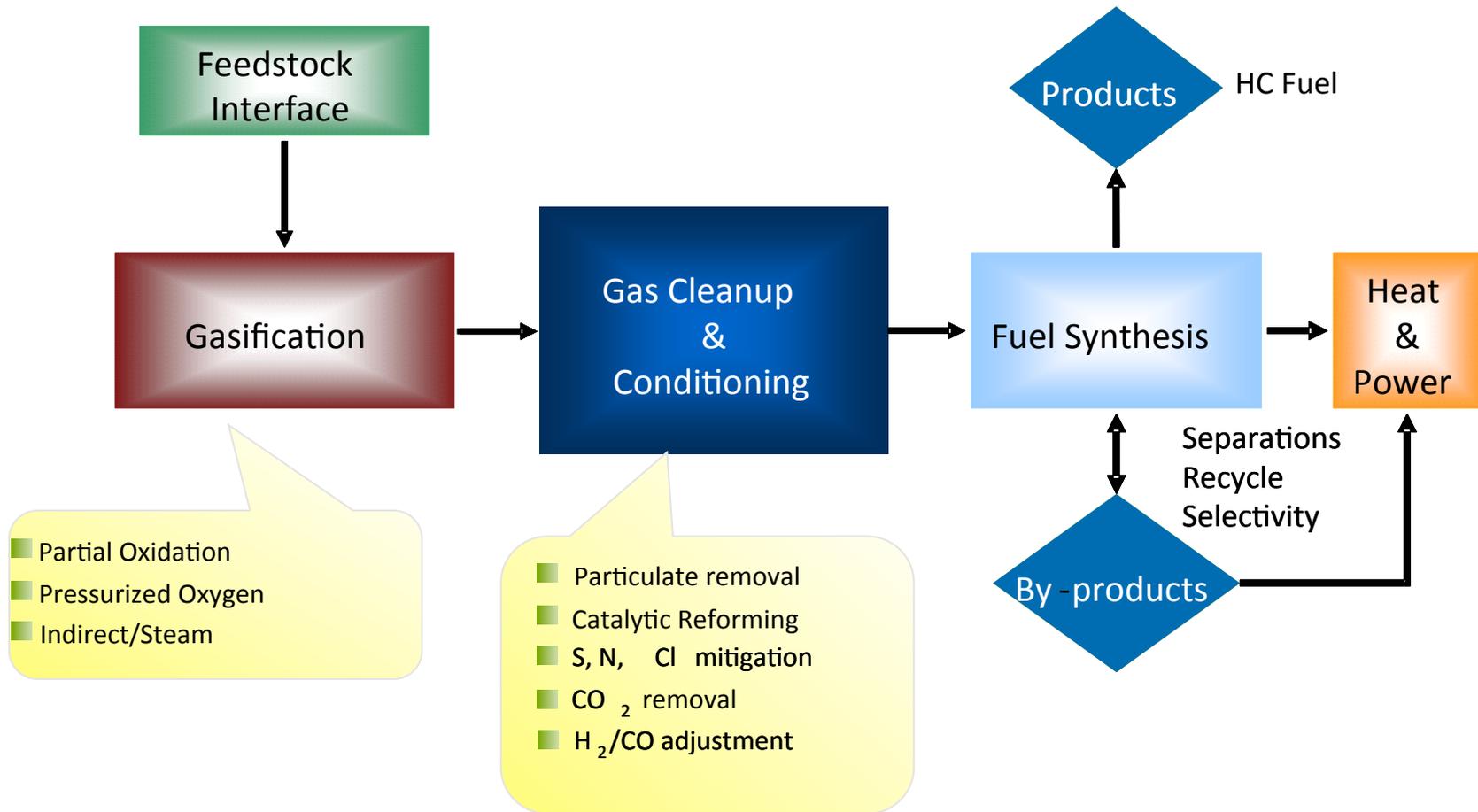
- Sugars –Carbohydrate
- ?? - Lignin

# High Energy Route - Gasification

- ❑ Technology fairly well developed
- ❑ Classes of gasifiers
  - ❑ **Air Blown Gasification** (updraft or downdraft)
    - low cost and thermally efficient, product gas not well suited for fuel synthesis – high  $N_2$  content
  - ❑ **Indirect Gasification** – good thermal efficiency, syngas not diluted with  $N_2$  – product gas relatively high in tars
  - ❑ **Direct Gasification** – Good product gas, lower in tars, - high cost of  $O_2$ , lower thermal efficiency, syngas high in  $CO_2$
  - ❑ **Entrained Flow Gasification** – Excellent product gas, essentially no tars – high cost of  $O_2$ , low thermal efficiency, higher capital cost because of increased complexity

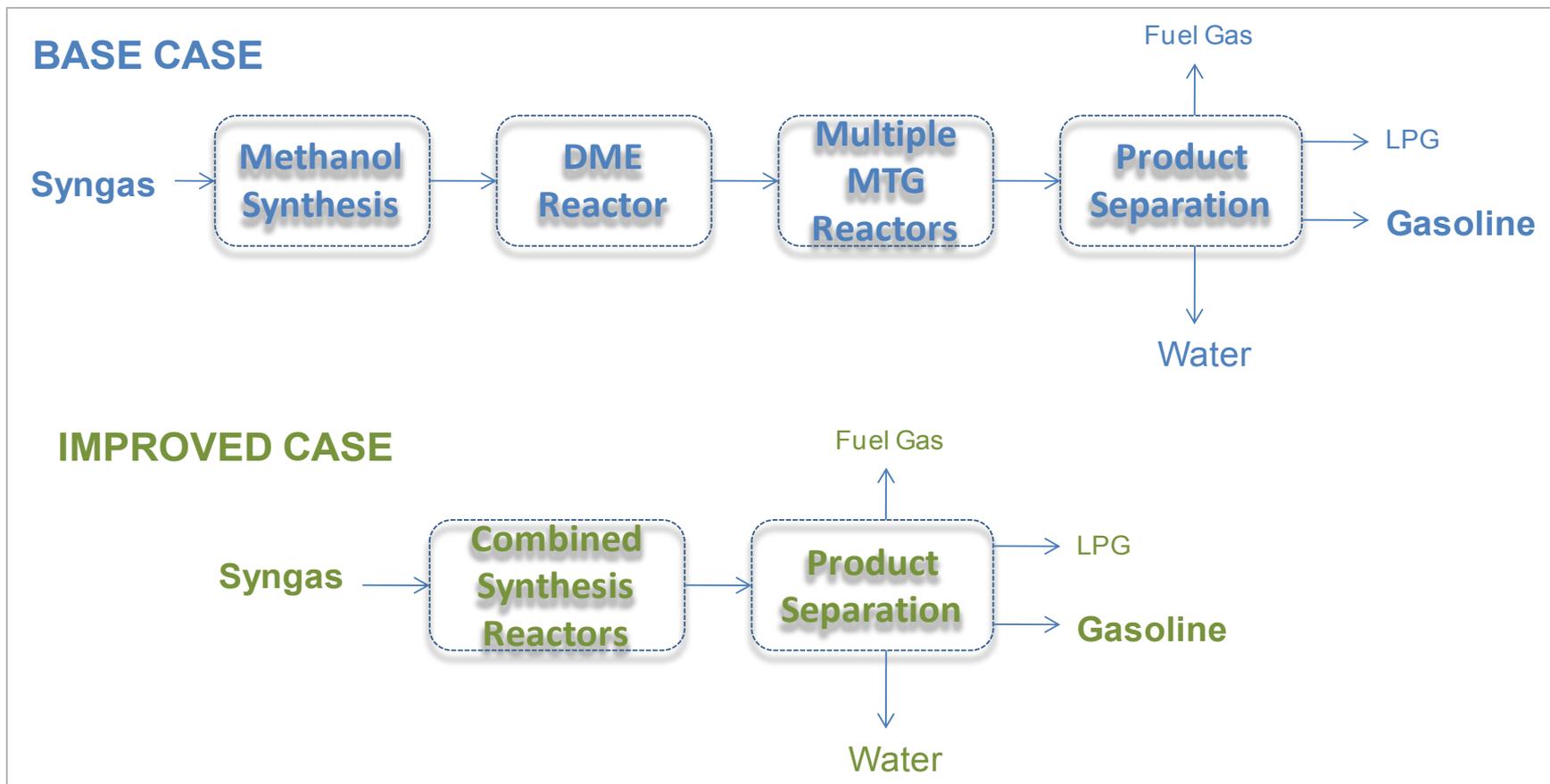


# Gasification Route to Hydrocarbon Fuel



# Challenge - Fuel Synthesis is Process/Capital Intensive

Simplify process as shown  
Results did not meet targets



# Intermediate Energy Route - Fast Pyrolysis

## Process:

- 500 °C atm, dry, finely divided, < 1 sec
- Inert atmosphere
- Non-catalytic

## Product:

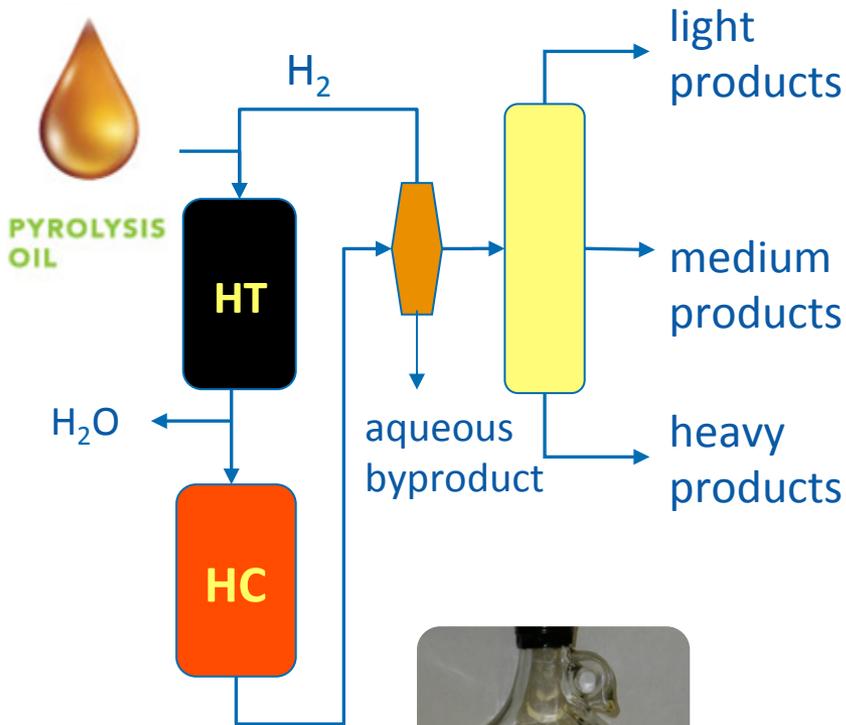
- Medium Btu oil (8,000 Btu/lb)
- High water content and acidity
- Not miscible with hydrocarbons
- Low thermal stability



<http://www.envergentech.com/index.php>

Biomass Material	Yield (wt%)	Gross Caloric Value (MJ/kg)	Higher Heating Value (Btu/lb)
Hardwood	70-75	17.2 - 19.1	7,400 - 8,000
Softwood	70-80	17.0 - 18.6	7,300 - 8,000
Hardwood Bark	60-65	16.7 - 20.2	7,180 - 8,680
Softwood Bark	55-65	16.7 - 19.8	7,180 - 8,500
Corn Fiber	65-75	17.6 - 20.2	7,570 - 8,680
Bagasse	70-75	18.9 - 19.1	8,100 - 8,200
Waste Paper	60-80	17.0 - 17.2	7,300 - 7,400

# Fast pyrolysis oil is converted to fuels in a 2-step process



	Hydroprocessed Bio-oil (from Mixed Wood)		Petroleum Gasoline
	Min	Max	Typical
Paraffin, wt%	5.2	9.5	44.2
Iso-Paraffin, wt%	16.7	24.9	
Olefin, wt%	0.6	0.9	4.1
Naphthene, wt%	39.6	55.0	6.9
Aromatic, wt%	9.9	34.6	37.7
Oxygenate, wt%		0.8	

The product carbon recovery based on biomass was about 35%

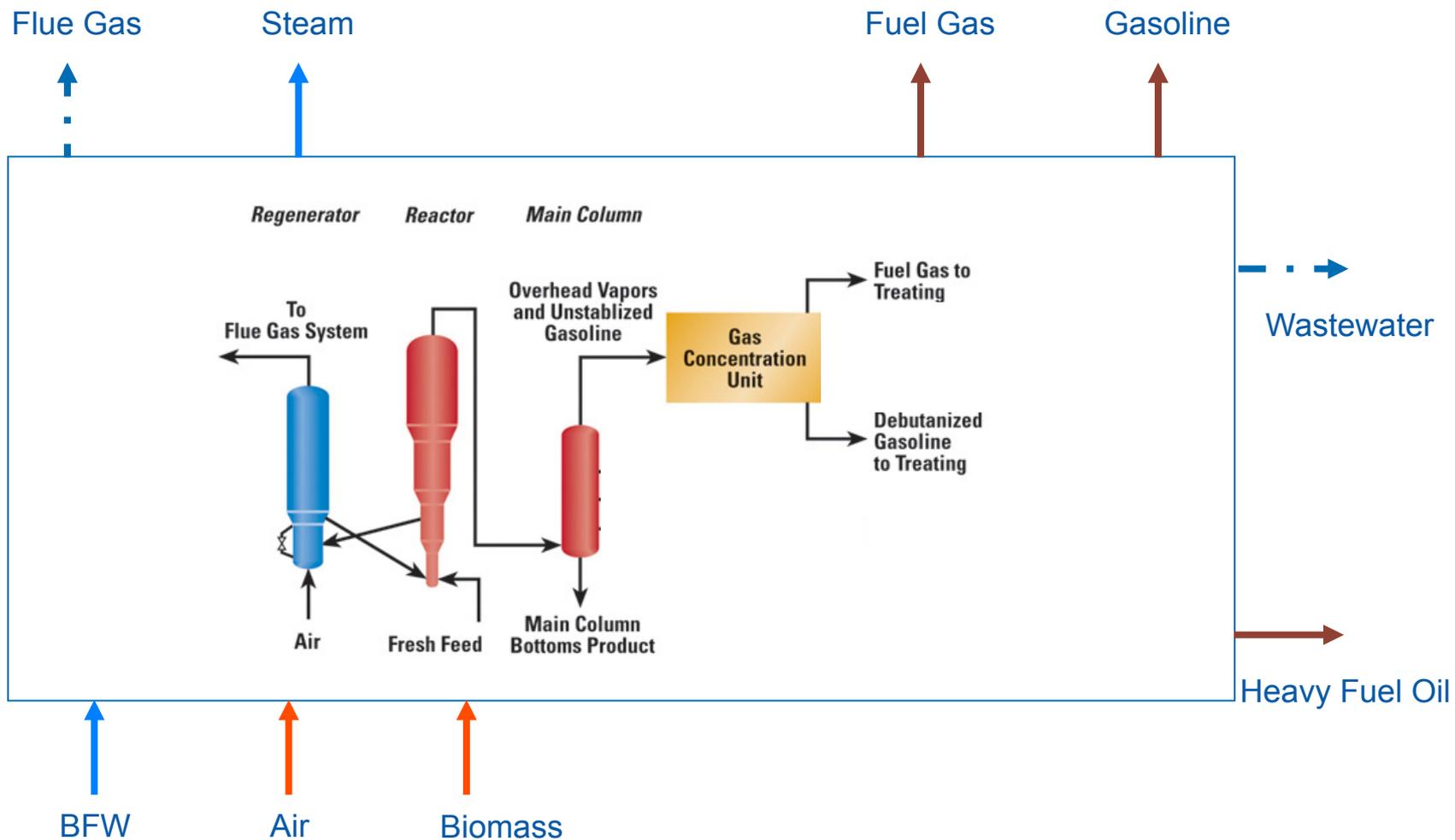
Process is capital intensive

Logistics issue since pyrolysis oil is highly corrosive and unstable

Process may not be scalable or replicable for large volume fuel production

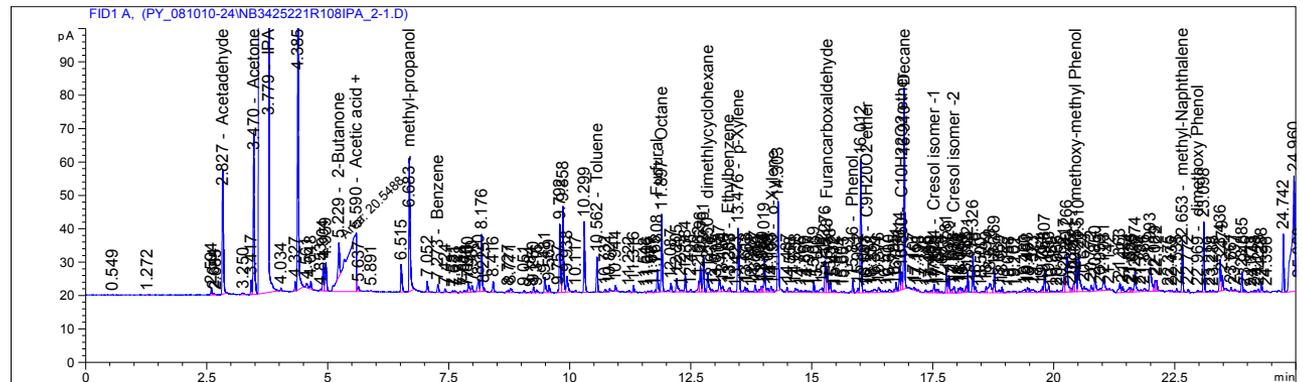
Holmgren, J. et al. NPRA national meeting, San Diego, March 2008.

# Catalytic Fast Pyrolysis



# CFP/HYP Catalyst Impact

## Standard Fast Pyrolysis



# Hydropyrolysis

## Process Conditions

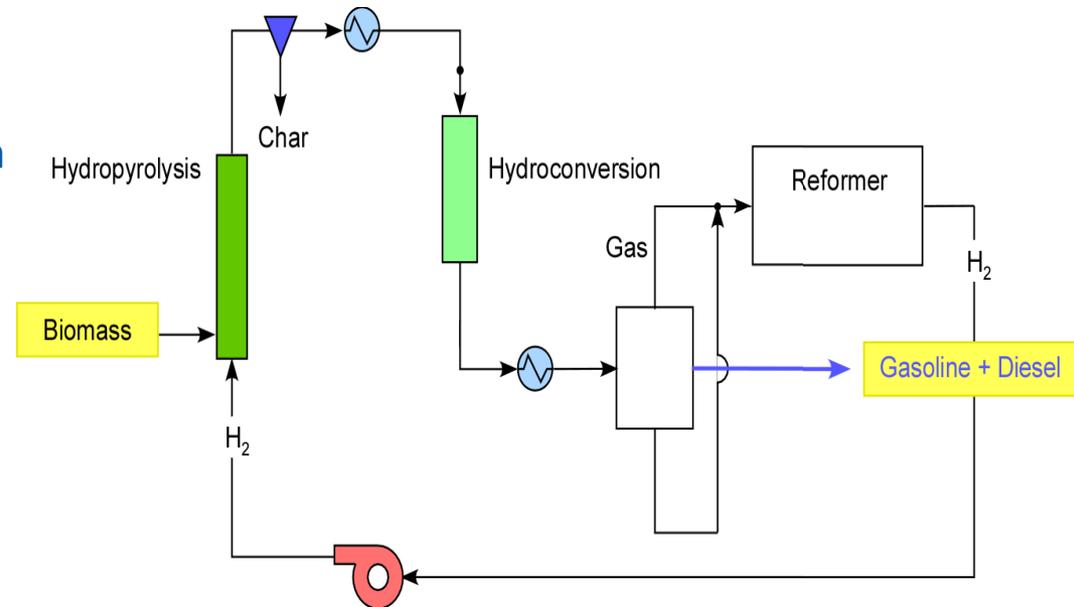
$T = 375$  and  $400^{\circ}\text{C}$ ;  $P_{\text{H}_2} = 42.9$  psig  
(14.4%) at 300 psig

In the absence of a catalyst, hydrogen partial pressure has no effect on biomass pyrolysis

Catalyst has significant impact on liquid product composition

High water content indicates significant hydrodeoxygenation

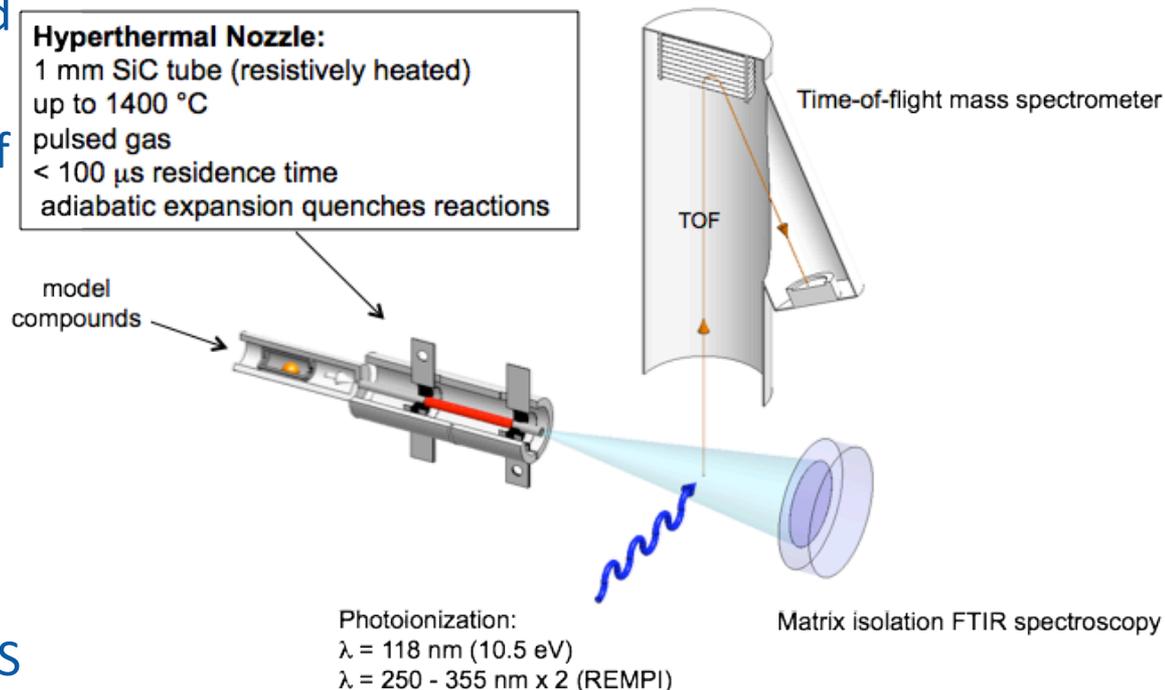
Time and resources did not allow an optimization of the results



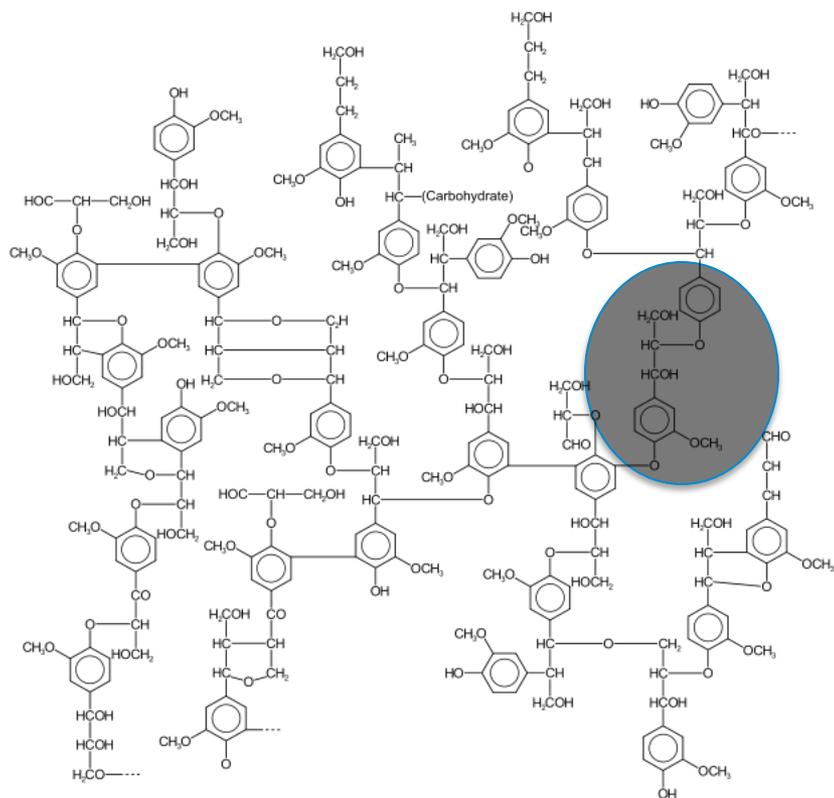
# New methods to characterize pyrolysis intermediates

## Hyperthermal nozzle

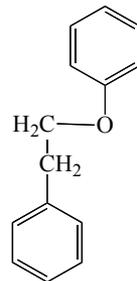
- Compounds rapidly heated and quenched adiabatically
- Enables direct measurement of radicals and intermediates
- Results can be directly compared to QM calculations
- Bond dissociation energies
- Transition states
- Vibrational frequencies
- Measure products with TOF-MS or MIS



# Realistic Linkages



Activation Energies (DFT)  
kcal mol<sup>-1</sup>



retro-ene	55
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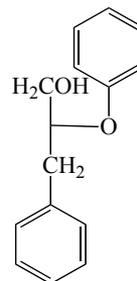
Maccoll	63
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C-O	70
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C-C	77
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*concerted  
elimination*

*radical  
mechanism*

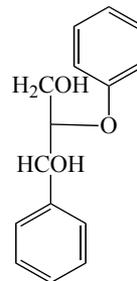


retro-ene	50
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Maccoll	64
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C-O	72
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C-C	77
-----	----



retro-ene	50
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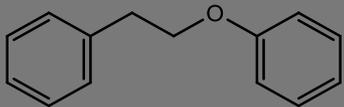
Maccoll	66
---------	----

Grobe	63
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C-O	72
-----	----

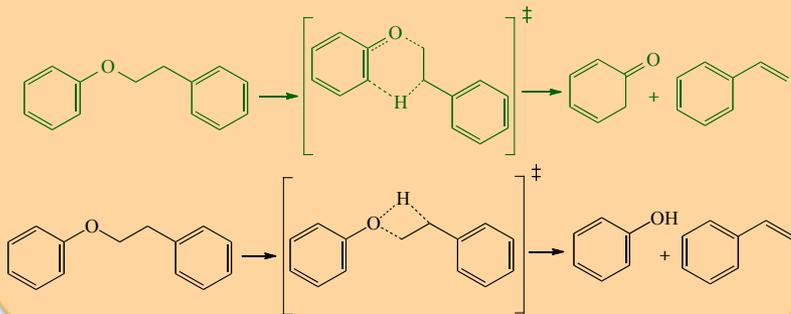
C-C	77
-----	----

# Concerted elimination dominates radical reactions

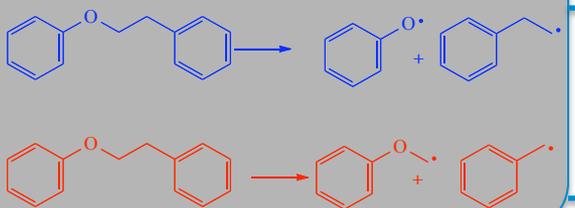


2-phenethylphenyl ether  
 $\beta$ -O4 linkage  
~50% of linkages in lignin

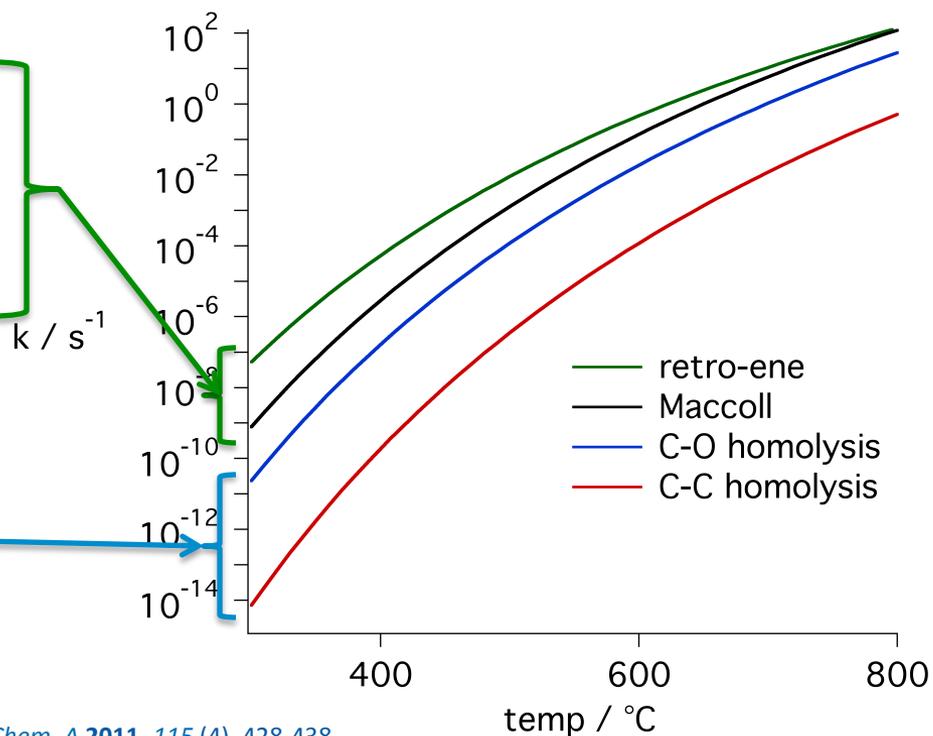
## Concerted Elimination



## Radical Reactions



Rate Constants from Quantum Mechanics  
CBS-QB3  
Consistent with Experimental Measurements



Jarvis et al., *J. Phys. Chem. A* **2011**, *115* (4), 428-438.

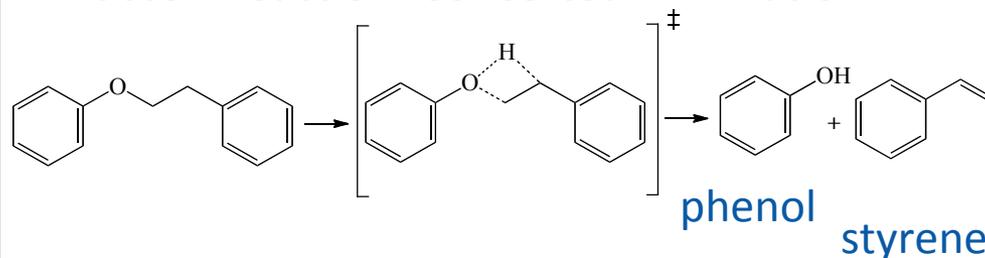
# Concerted Elimination

Concerted elimination can produce **stable compounds**

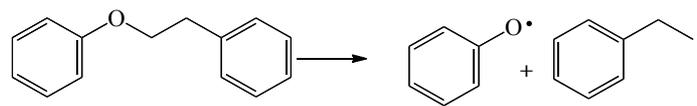
Radicals are nonspecific reactants – can lead to **condensation reactions** – high char and coke

**Need catalysts that promote concerted eliminations**

## Maccoll Reaction: Concerted Elimination



## C-O Homolytic Bond Scission

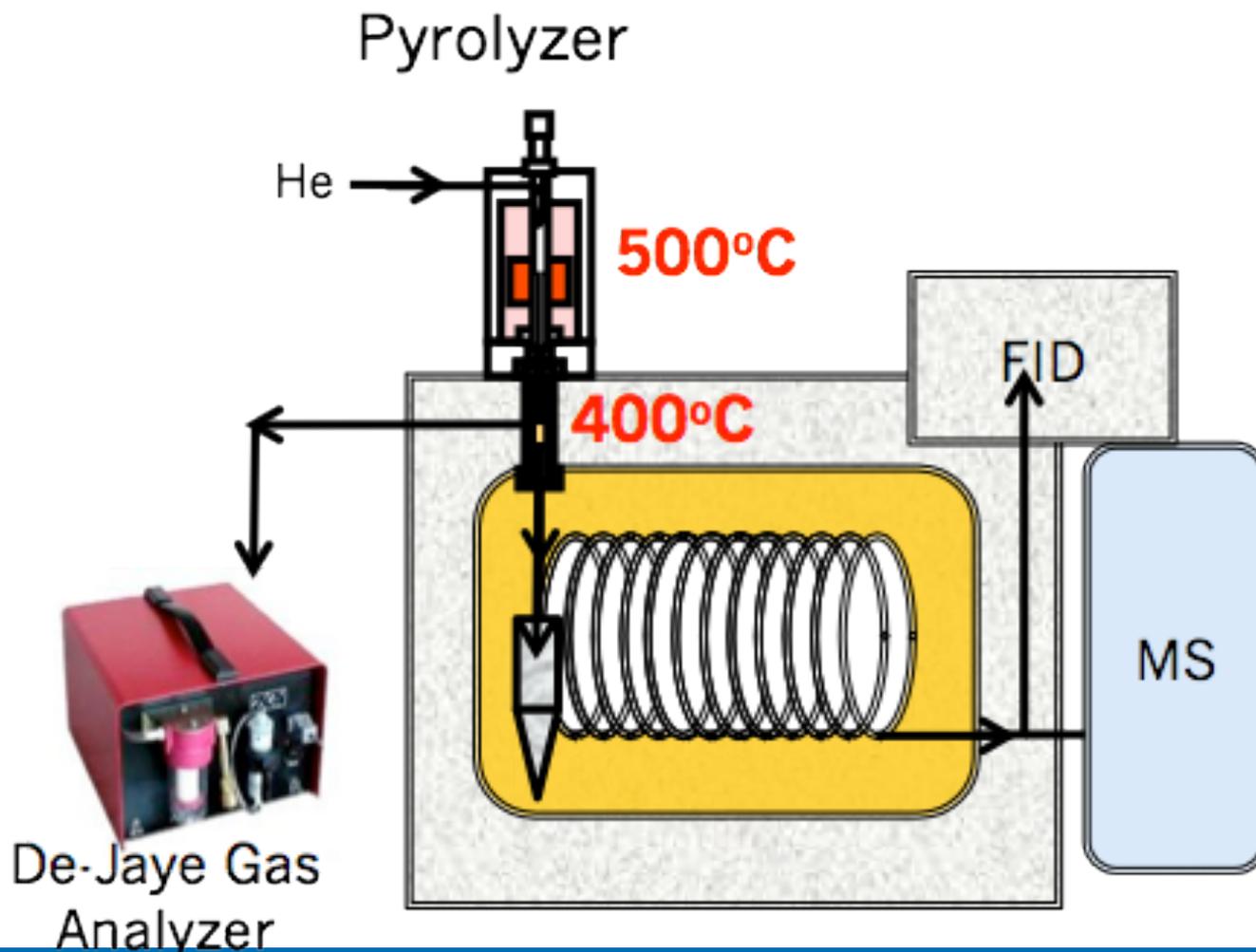


phenoxy radical

phenylethyl radical

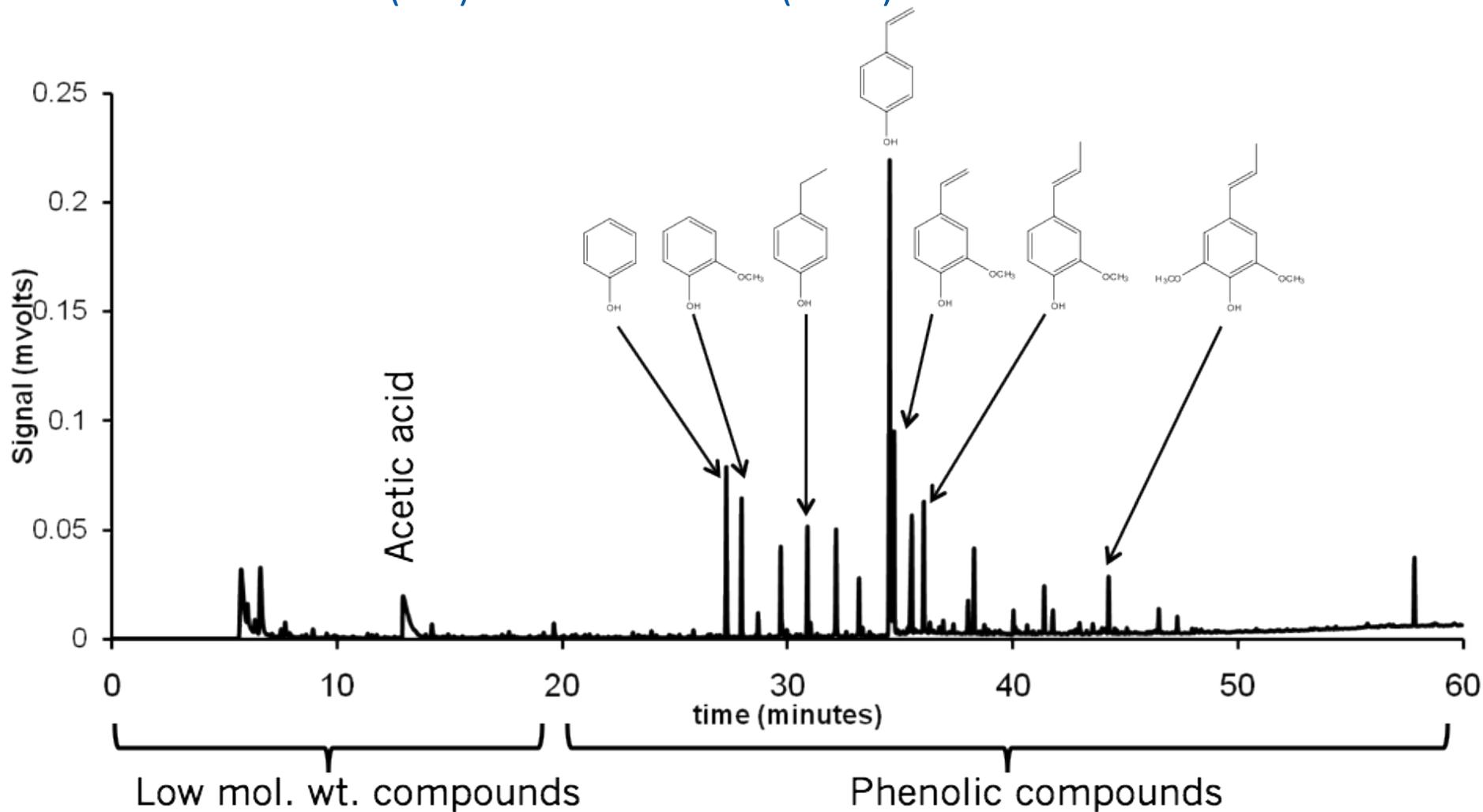
# Lignin pyrolysis microreactor

- Work from Brent Shanks (ISU) and Bob Baldwin (NREL)
- Pyrolysis with GC-MS analysis capabilities



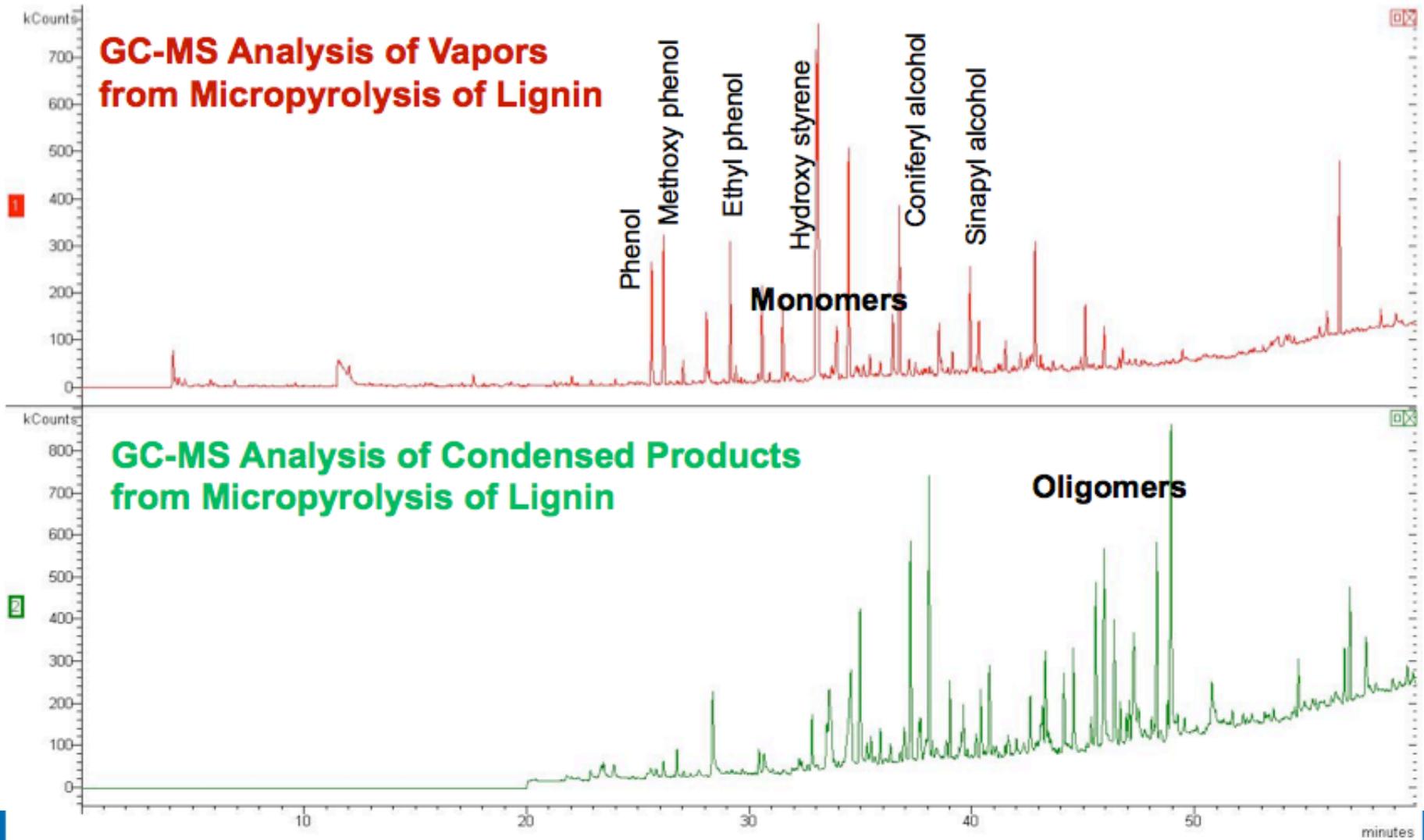
# GC-MS for pyrolysis vapors

From Brent Shanks (ISU) and Bob Baldwin (NREL)



# GC-MS data for vapors and condensed products

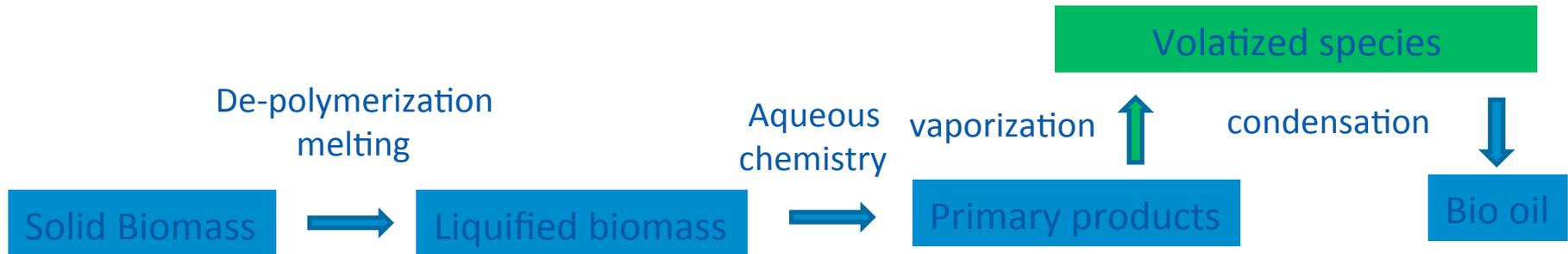
- Work from Brent Shanks (ISU) and Bob Baldwin (NREL)
- Examination of pyrolysis vapor and condensate



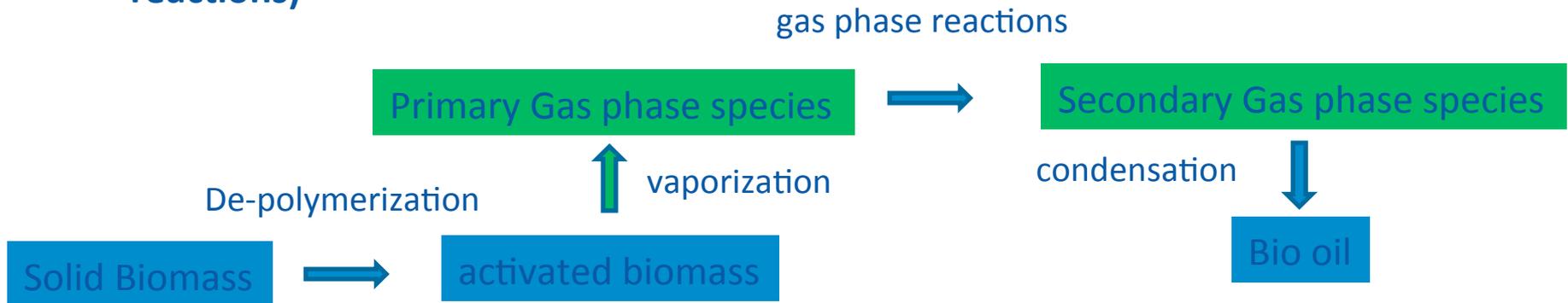
# Question: Gas Phase or Condensed Phase?

Pyrolysis chemistry might be controlled by either:

- Primarily ionic reactions in the condensed phase



- Gas phase reactions of initially formed products (bond fissions, radical reactions)



Successful modeling of biomass pyrolysis requires knowledge of which chemistry dominates

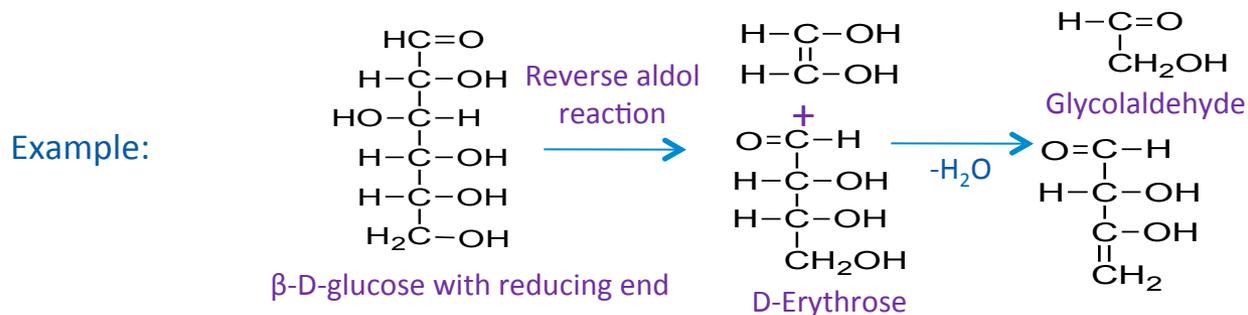
# Evidence suggests that condensed phase reactions more important in pyrolysis of cellulose and lignin

## Experimental evidence by Iowa State University:

- Change of carrier gas flow rate (varied residence times) by ~ factor of 3 does not change the product distribution in lignin
- Levoglucosan (major product in cellulose pyrolysis) does not react at 500°C on experimental time scale

## Mechanistic evidence by Northwestern University:

- Reaction pathways for all major products observed in the Iowa State cellulose pyrolysis experiments
- Dominant reaction pathways are acid or OH catalyzed ionic reactions (e.g. retro-Aldol reactions)



**Q.E.D. → Free radical chemistry (typical for gas phase) not needed to explain primary products of pyrolysis**

# Methodology to test importance of gas phase reactions in pyrolysis of cellulose and lignin

## Computational evidence from CSM:

✓ **Approach:** Calculate rate expressions of possible gas phase reactions and determine whether they could be relevant at typical biomass pyrolysis conditions

Gaussian  
(commercial  
software)

Electronic Structure Calculations



Molecular Properties

**Methods: CBS-QB3**

**Statistical Mechanics, HIR**

**c-TST w/ Eckart Tunneling**

**QRRK/MS**

In-house  
software

Thermodynamic Properties

Add to or Validate

“Core” Thermodynamic Database

Provide fit data

Group Additivity Database

TST Rate Expressions

Add to or Validate

“Core” Kinetic Database

Provide fit data

Rate Estimation Rules

“Fall-Off” Parameters

Add to or Validate

“Core” Kinetic Database

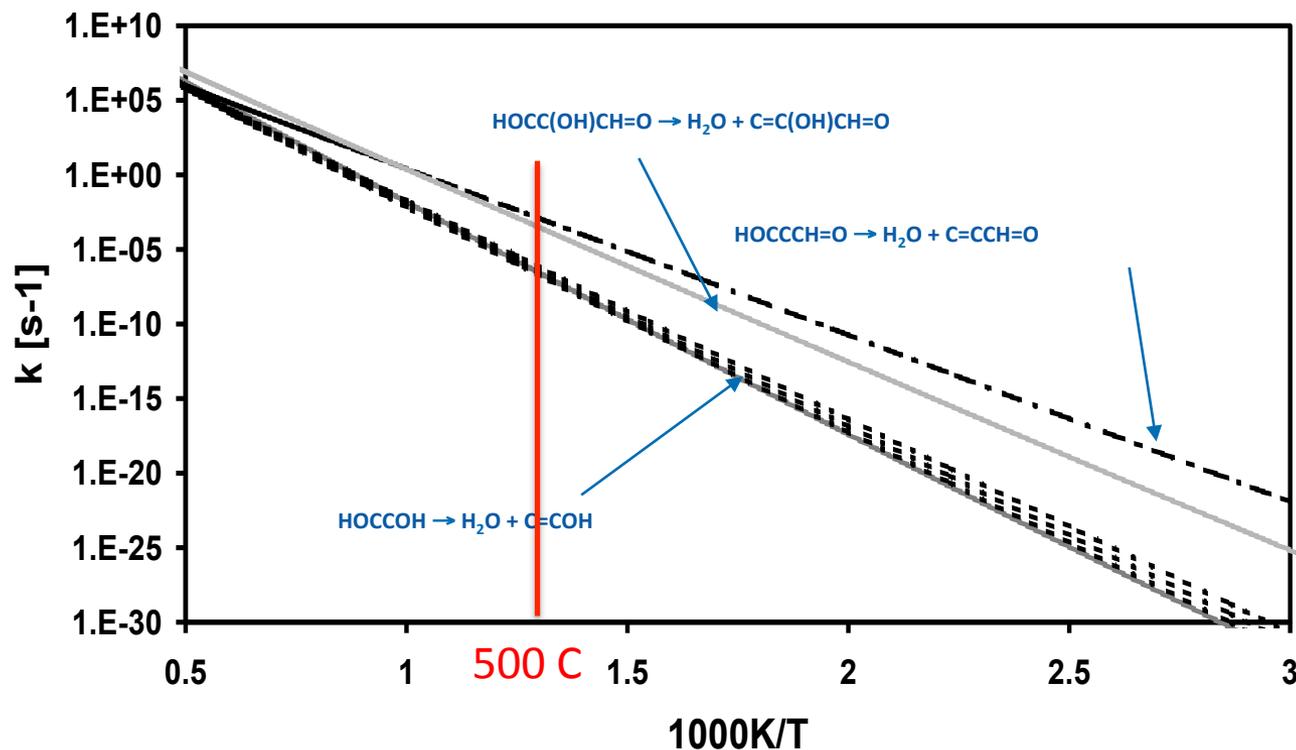
Provide test set

Automated Fall-Off Analysis

**Outcome →  $k(T,P)$  expressions**

# Calculated rate constants for H<sub>2</sub>O formation via gas phase reactions are too slow to contribute at 500°C.

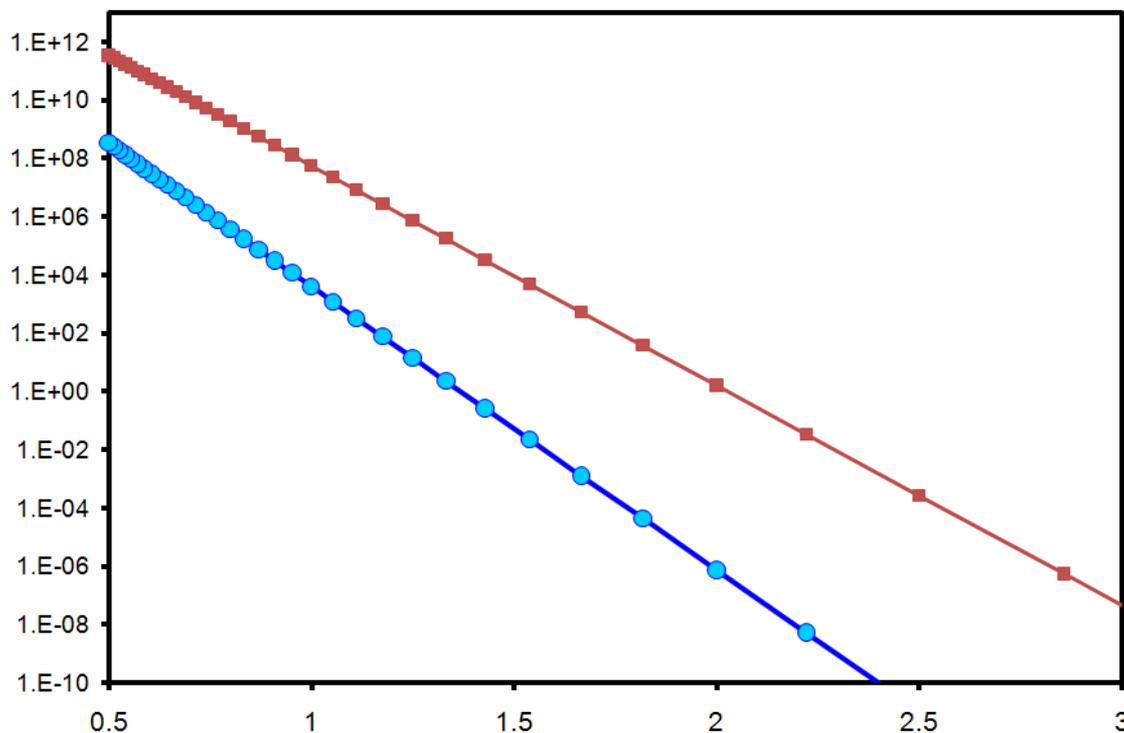
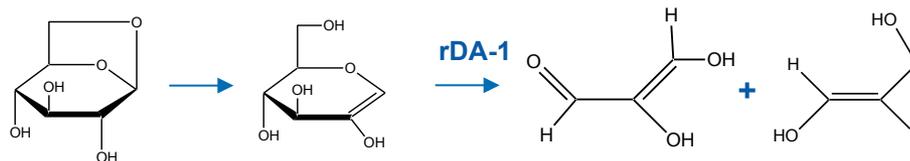
Example: H<sub>2</sub>O formation via elimination from poly-functional alcohols



Calculated rate constants for molecular elimination of water from hydroxy aldehydes (“sugars”) are so slow that they do not contribute even at gasification temperatures (1000K)

# Calculated rate constants for gas phase reactions of cellulose fragments also too slow to form smaller oxygenates

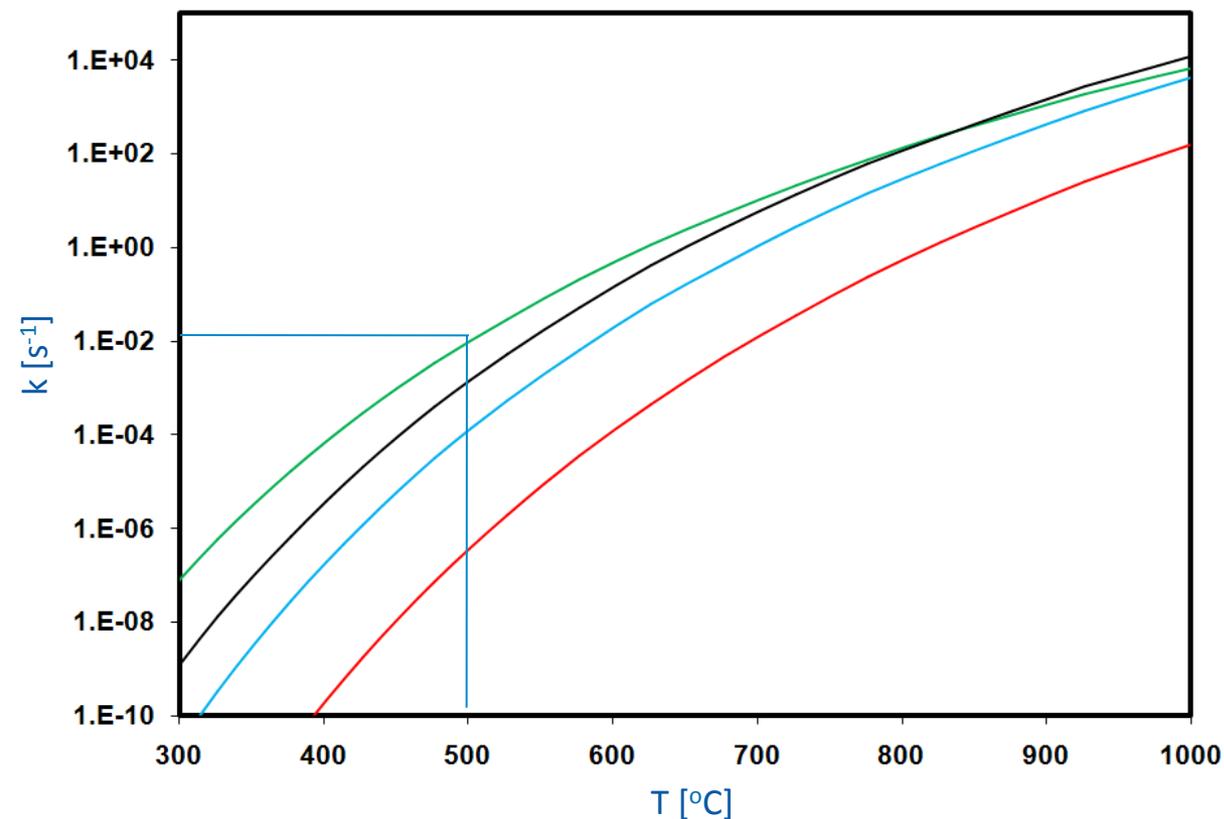
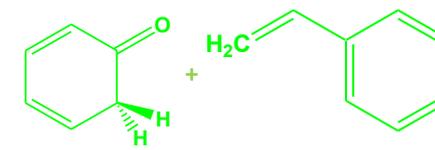
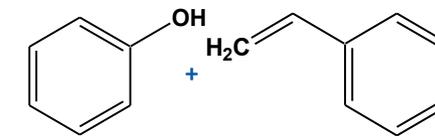
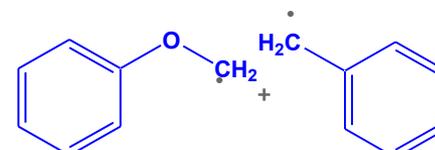
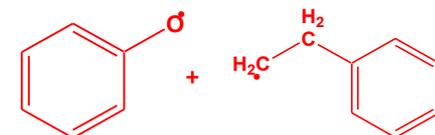
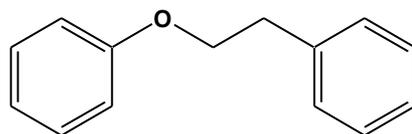
Example: Retro-Diels-Alder reaction:



Calculated gas-phase rate constant much slower than that suggested by condensed phase rate rule

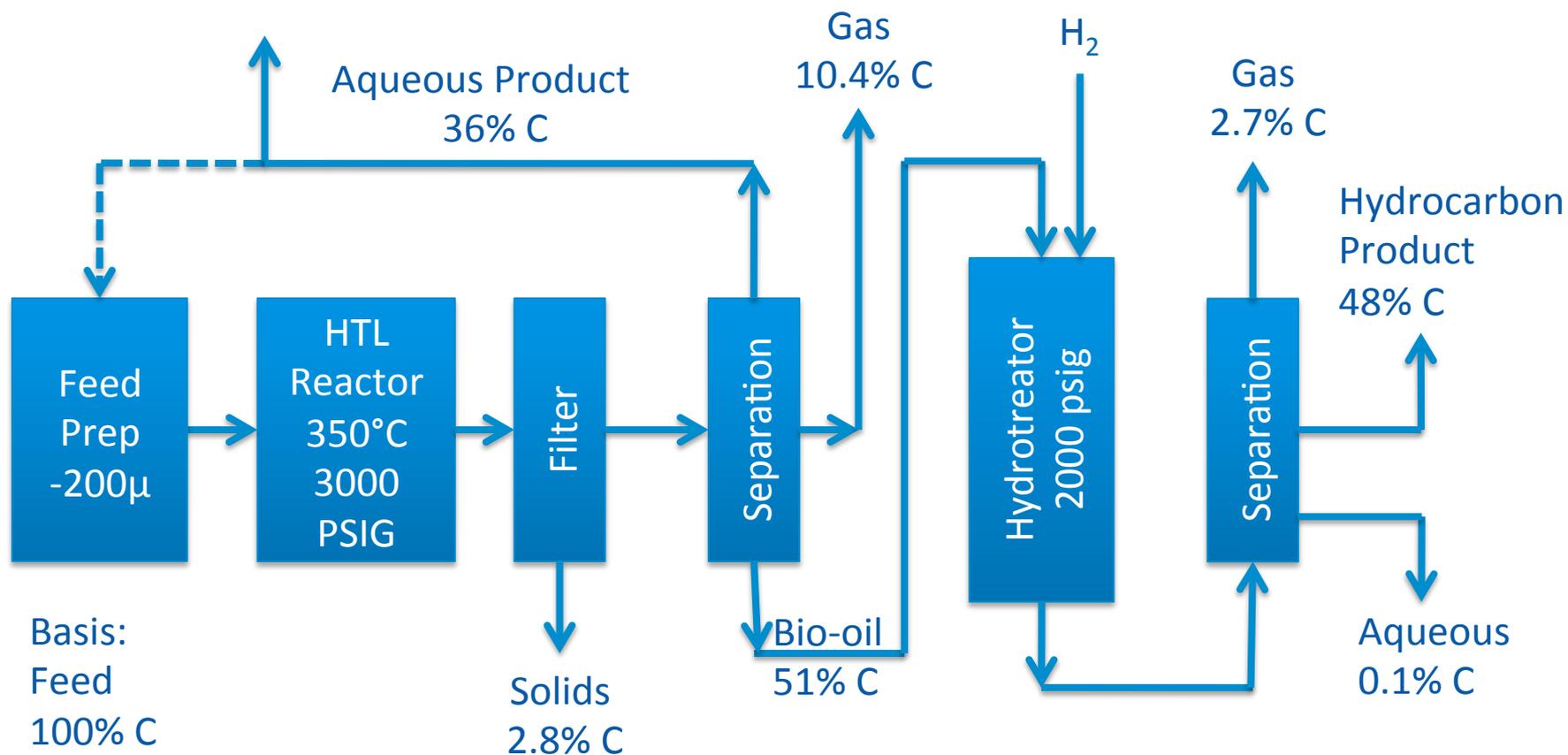
# Similar Conclusions for Lignin

Example: Decomposition of lignin model compound Phenethyl phenyl ether (PPE)



Again, calculated rate expressions too slow to contribute on fast pyrolysis timescale

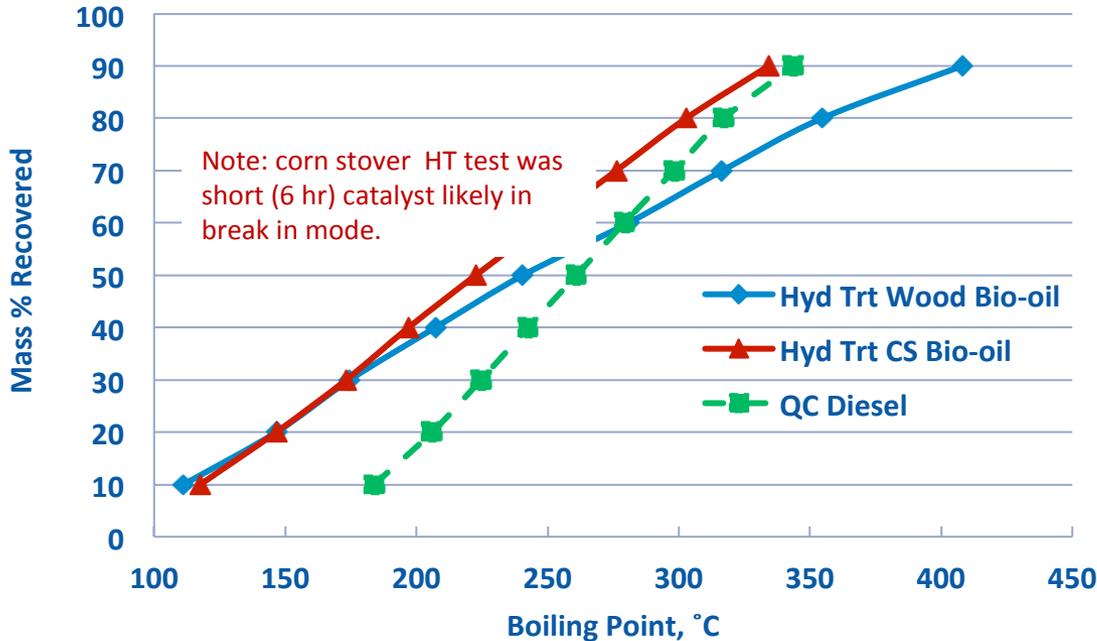
# Hydrothermal Liquefaction



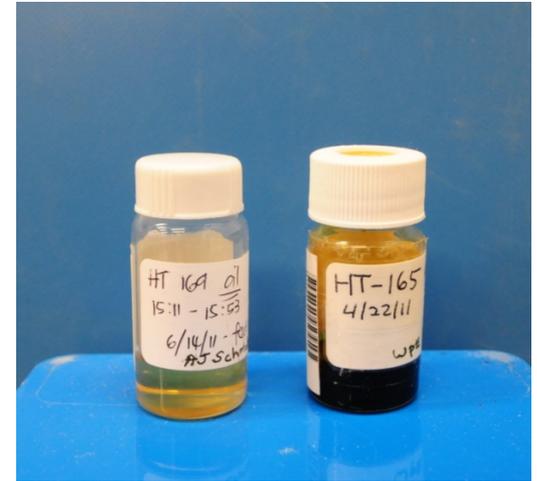
- Overall carbon yield to hydrotreated product is 50%

# Products and Issues

## Hydrotreated Bio-Oil SimDis D2887 Results



➤ ~30% gasoline and ~50% diesel range

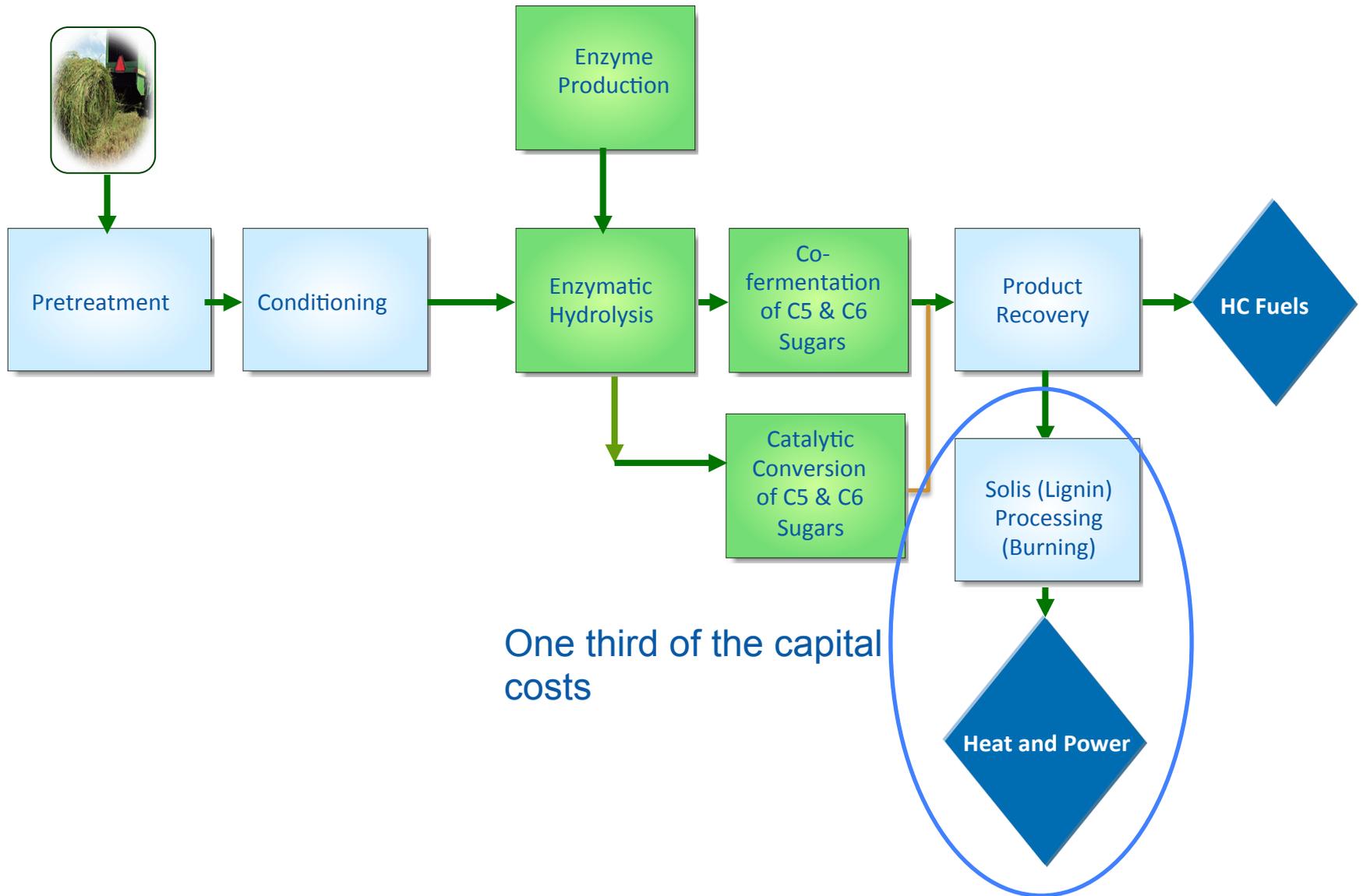


Hydrotreated Products



Challenge: Pumping High Suspended Solids Slurry to High Pressure

# Low Energy Route

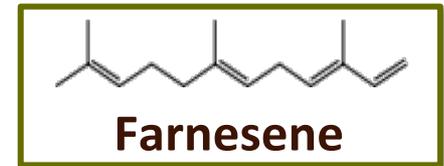
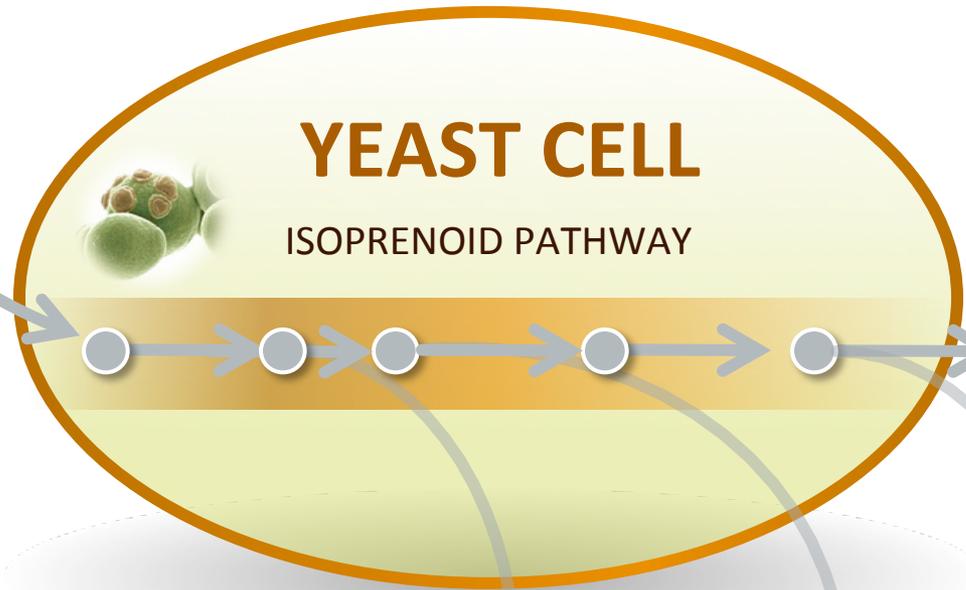


One third of the capital costs

# Modified yeast to produce diesel fuel



SUGAR SOURCE



Isoprenoid-based Diesel  
Fuel



ISOPRENE

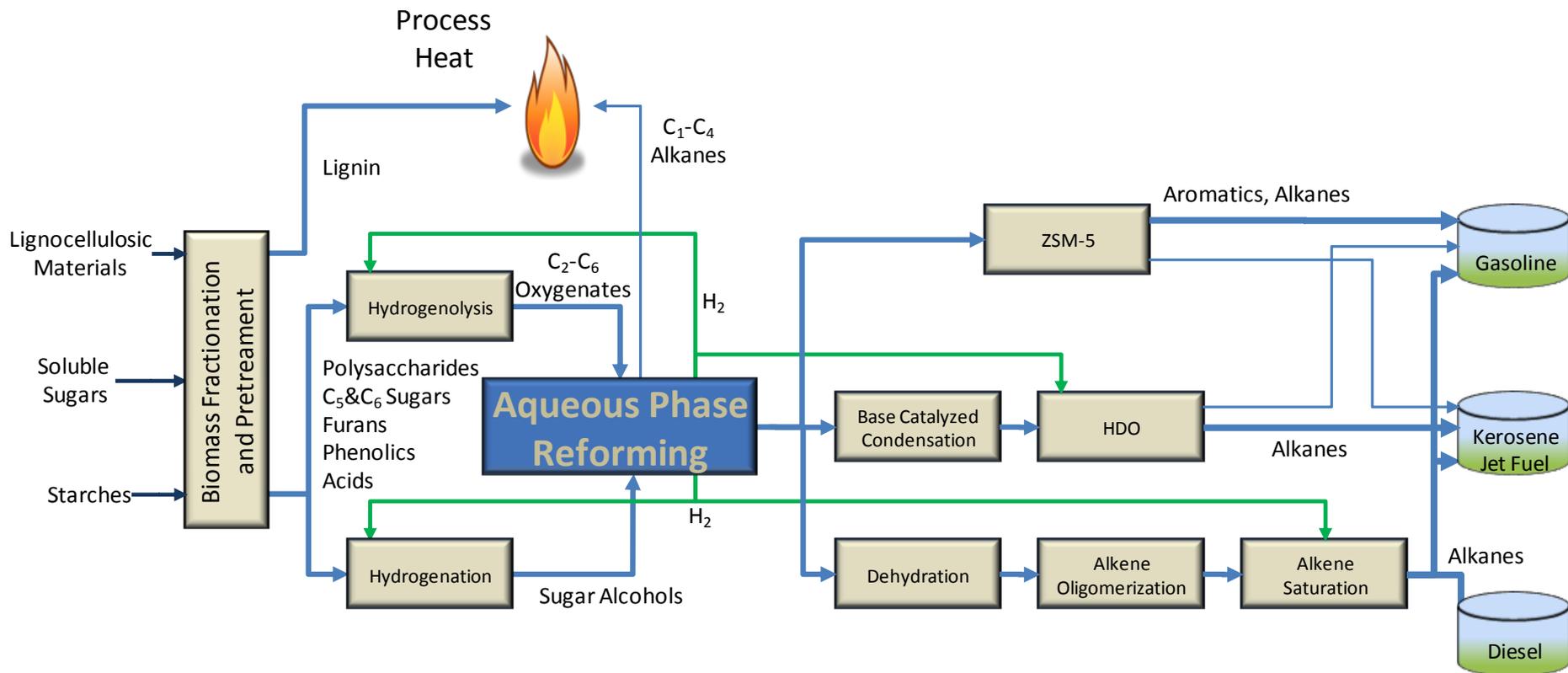


PINENE  
(JET FUEL)



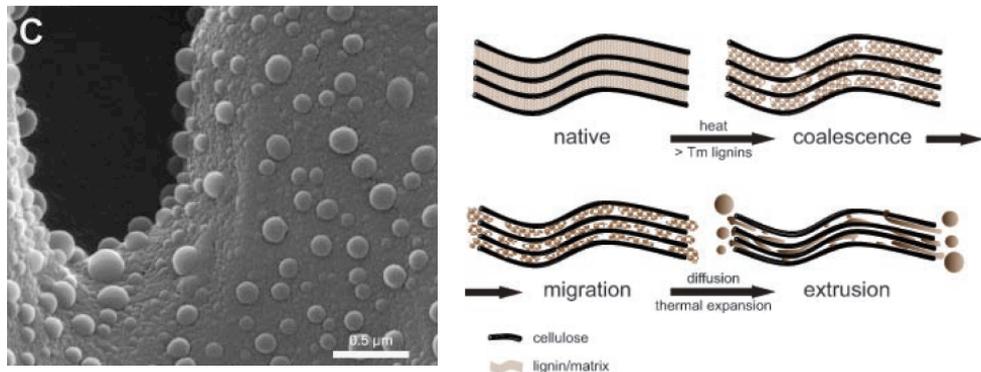
ANTI-MALARIAL  
DRUG

# Virent Technology Overview



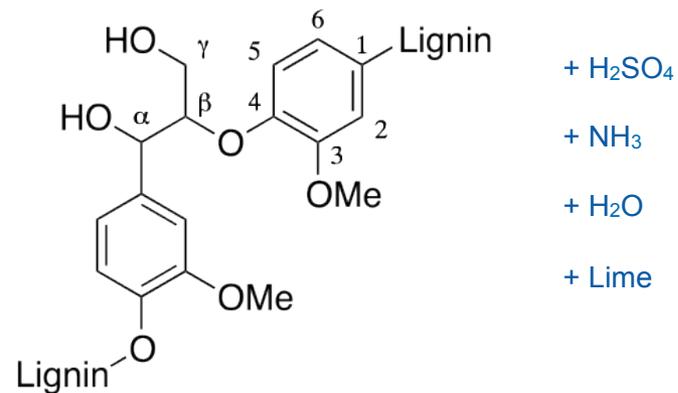
# Can higher value be extracted from lignin via low energy approaches

## Effect of pretreatment on lignin



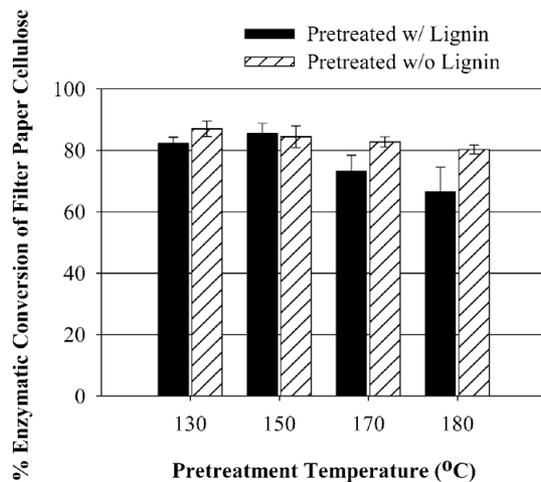
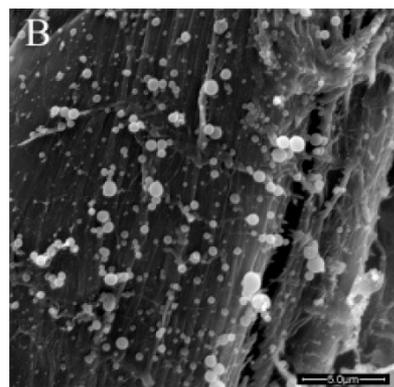
Donohoe et al., Biotech. Bioeng., 101, 2008

## Pretreatment chemistry on lignin models



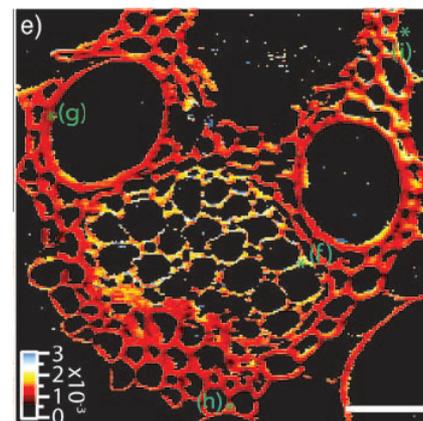
Sturgeon, Kim, et al., in progress

## Lignin effects on enzyme activity



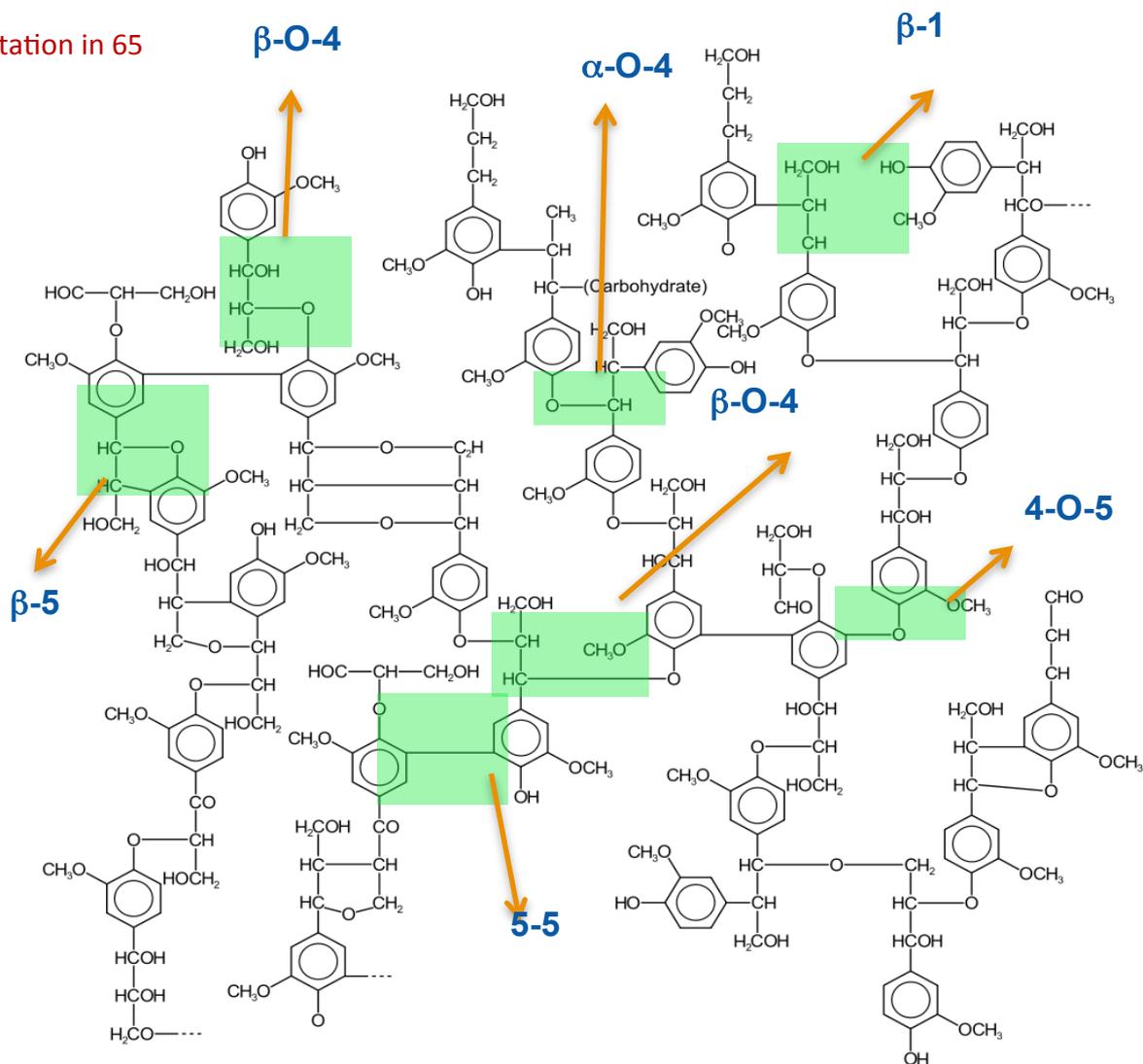
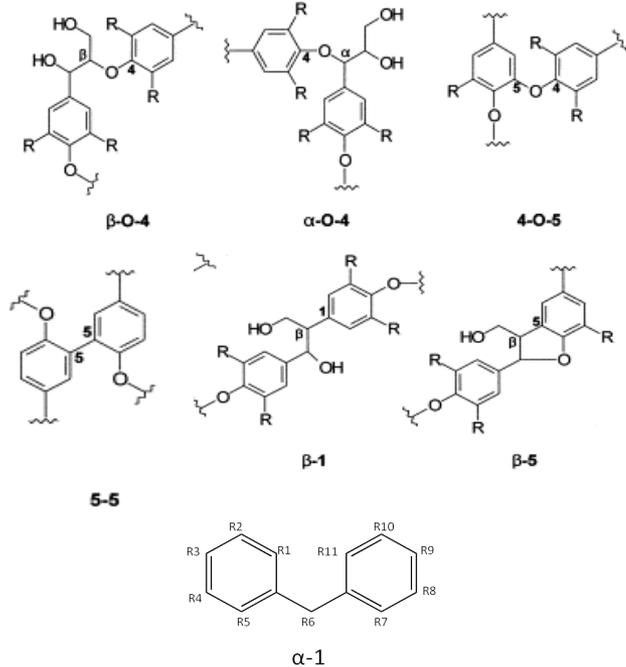
Selig et al., Biotech. Prog., 23, 2007

## Lignin in genetically modified plants



Saar et al., Bioenergy Res., 3, 2010

- a) Density Functional Calculations of bond fragmentation in 65 distinct Lignin Model Compounds
- b)  $^{13}\text{C}$  NMR of Lignin /  $^{13}\text{CO}_2$ :



# Computed bond distances and respective bond dissociation energies (BDE) of the ether linkages and carbon-carbon linkages of different classes of lignin model compounds at M06-2X/6-311++G(d,p) level

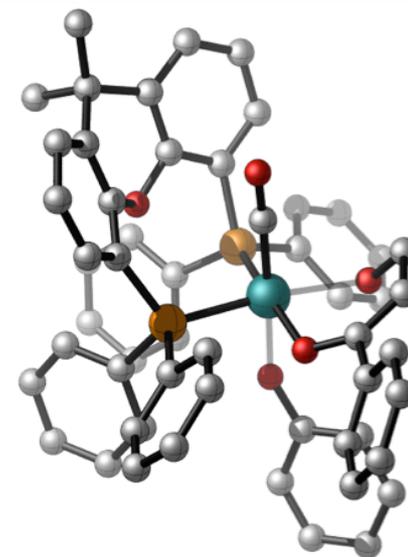
	Bond Distances (Å)		BDE ZPE corrected (kcal/mol)	
	C-C	O-C	C-C	O-C
<b>β-O-4</b>				
L1	1.531	1.431	75	66.38
L2	1.531	1.429	75.46	67.33
L3	1.53	1.427	75.71	64.61
L4	1.531	1.429	75.48	67.04
L5	1.53	1.429	75.58	67.1
L6	1.523	1.424	76.4	68.35
L7	1.53	1.427	75.74	64.3
L8	1.536	1.432	79.09	56.54
L9	1.526	1.412	77.75	59.88
L10	1.54	1.423	76.99	72.3
L11	1.524	1.426	76.25	68.71
L12	1.524	1.425	80.07	55.96
L13	1.523	1.423	76.11	65.91
L14	1.525	1.425	79.75	55.75
L15	1.537	1.438	78.8	53.94
L16	1.523	1.416	76.09	68.45
L17	1.533	1.422	72.05	69.35
L18	1.525	1.41	78.13	59.64
L19	1.523	1.428	77.08	64.39
L20	1.522	1.429	77.73	62.24
L21	1.523	1.428	78.45	61.37
<b>α-O-4</b>		O-C		O-C
L22		1.428		50.24
L23		1.421		56.43
L24		1.412		57.28
L25		1.422		56.24
L26		1.43		51.32
L27		1.428		48.31
L28		1.421		56.34
L29		1.432		50.62
L30		1.429		48.45
L31		1.427		48.89
<b>4-O-5</b>		O-C		O-C
L32		1.375		82.54
L33		1.382		77.74

	Bond Distances (Å)		BDE ZPE corrected (kcal/mol)	
	C-C		C-C	
<b>β-1</b>				
L34	1.541		65.29	
L35	1.546		67.54	
L36	1.541		68.83	
L37	1.541		66.62	
L38	1.54		68.59	
L39	1.543		64.7	
L40	1.542		69.14	
L41	1.541		68.87	
L42	1.546		68.54	
L43	1.338		165.8	
L44	1.339		162.1	
L45	1.546		67.83	
L46	1.541		68.53	
<b>α-1</b>	C-C		C-C	
L47	1.518		91.59	
L48	1.516		92.56	
L49	1.517		93.33	
L50	1.518		90.94	
L51	1.518		86.27	
L52	1.516		92.74	
L53	1.518		90.26	
<b>β-5</b>	C-C		C-C	
L54	1.461		125.5	
L55	1.462		127.1	
L56	1.462		127.6	
L57	1.461		125.2	
<b>5-5</b>	C-C		C-C	
L58	1.484		117.3	
L59	1.485		117.3	
L60	1.484		117	
L61	1.488		118.4	
L62	1.485		117.5	
L63	1.485		114.9	
L64	1.484		115.4	
L65	1.483		116.5	

# Low energy catalytic lignin deconstruction

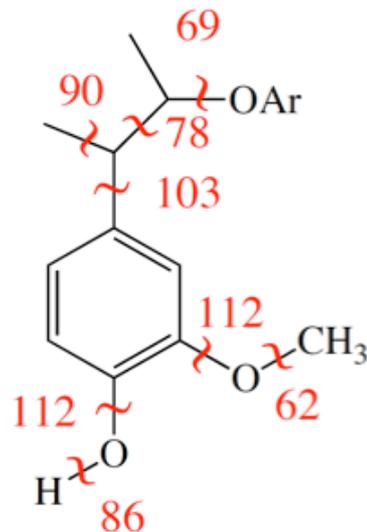
## Catalyst design for lignin deconstruction

- Computational/experimental approach
- Model lignin libraries
- Computational results for a known catalyst

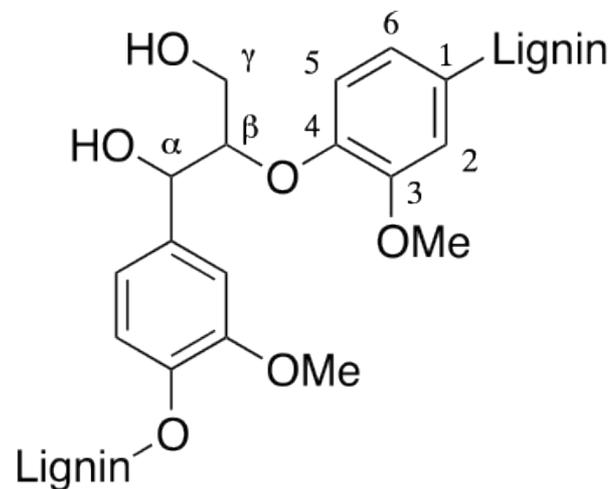


## Primary target linkage for lignin deconstruction

### Bond dissociation energies (kcal/mol)

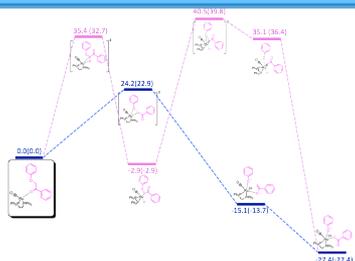


### Target linkage B-O-4



# Computational and experimental approach for lignin deconstruction

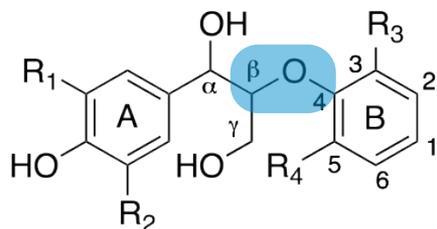
Quantum calculations



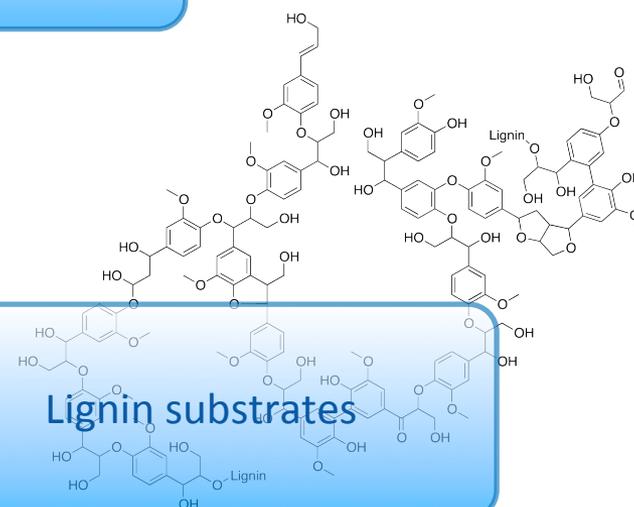
Rate measurements

NMR, GCMS, LCMS

New catalysts for lignin deconstruction



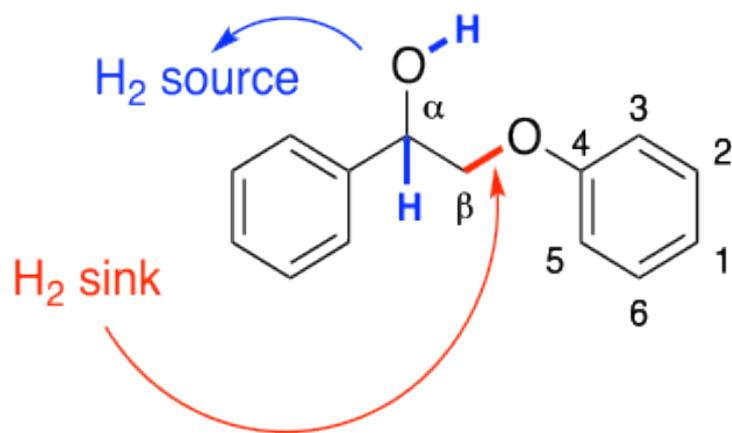
Model substrates



Lignin substrates

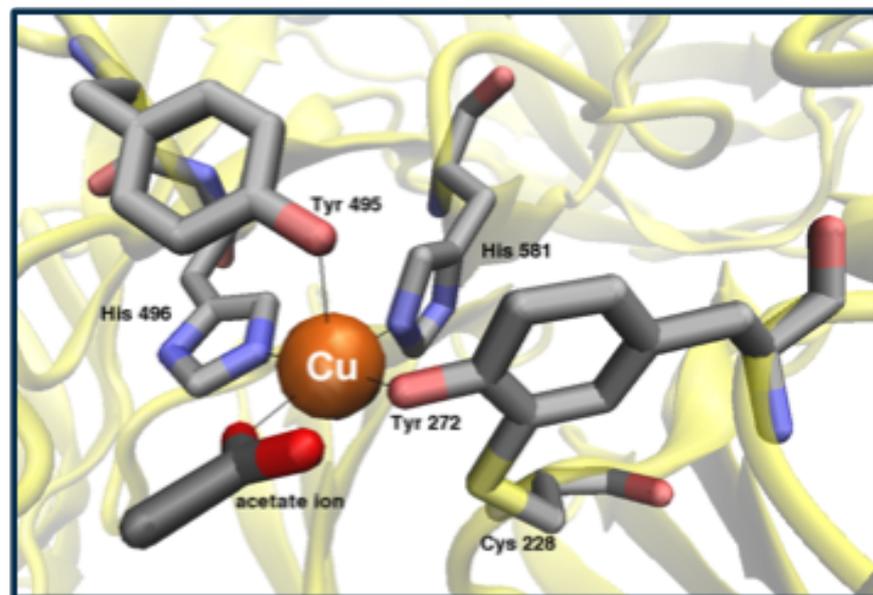
# Catalytic routes under investigation

Reductive routes



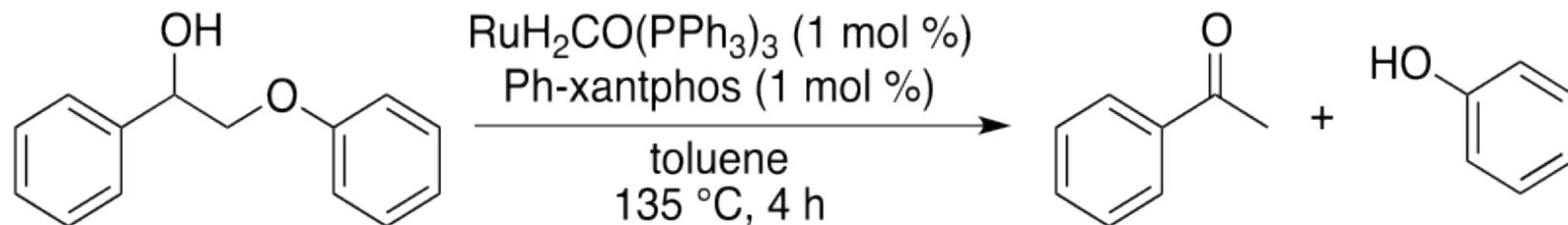
Nichols et al., JACS, 132, 2010

Oxidative routes



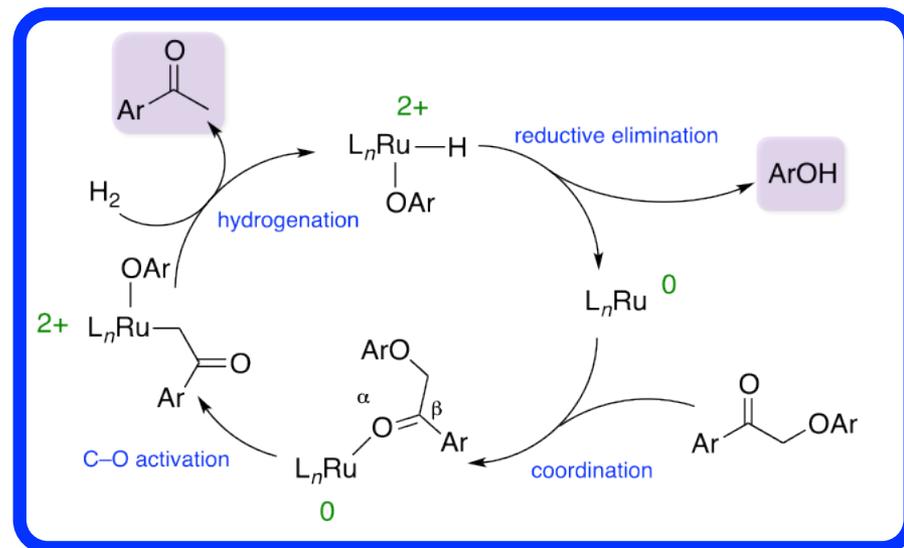
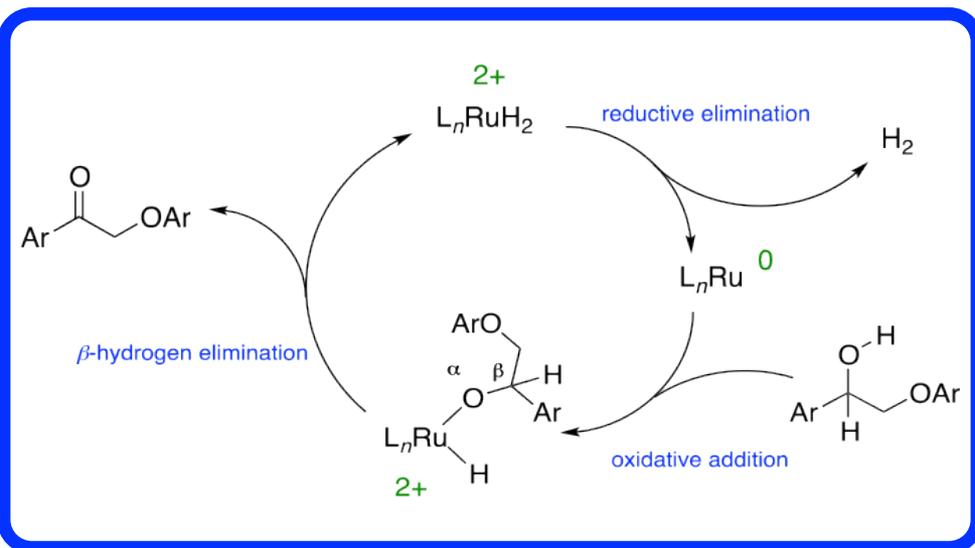
Ito et al., Nature, 350, 1991

# Methodology example: Application to a ruthenium catalyst

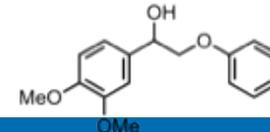
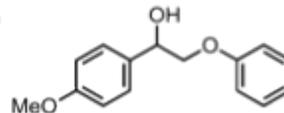
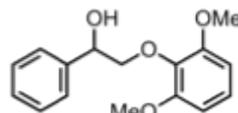
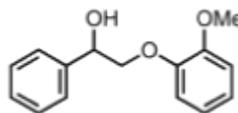
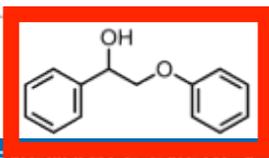
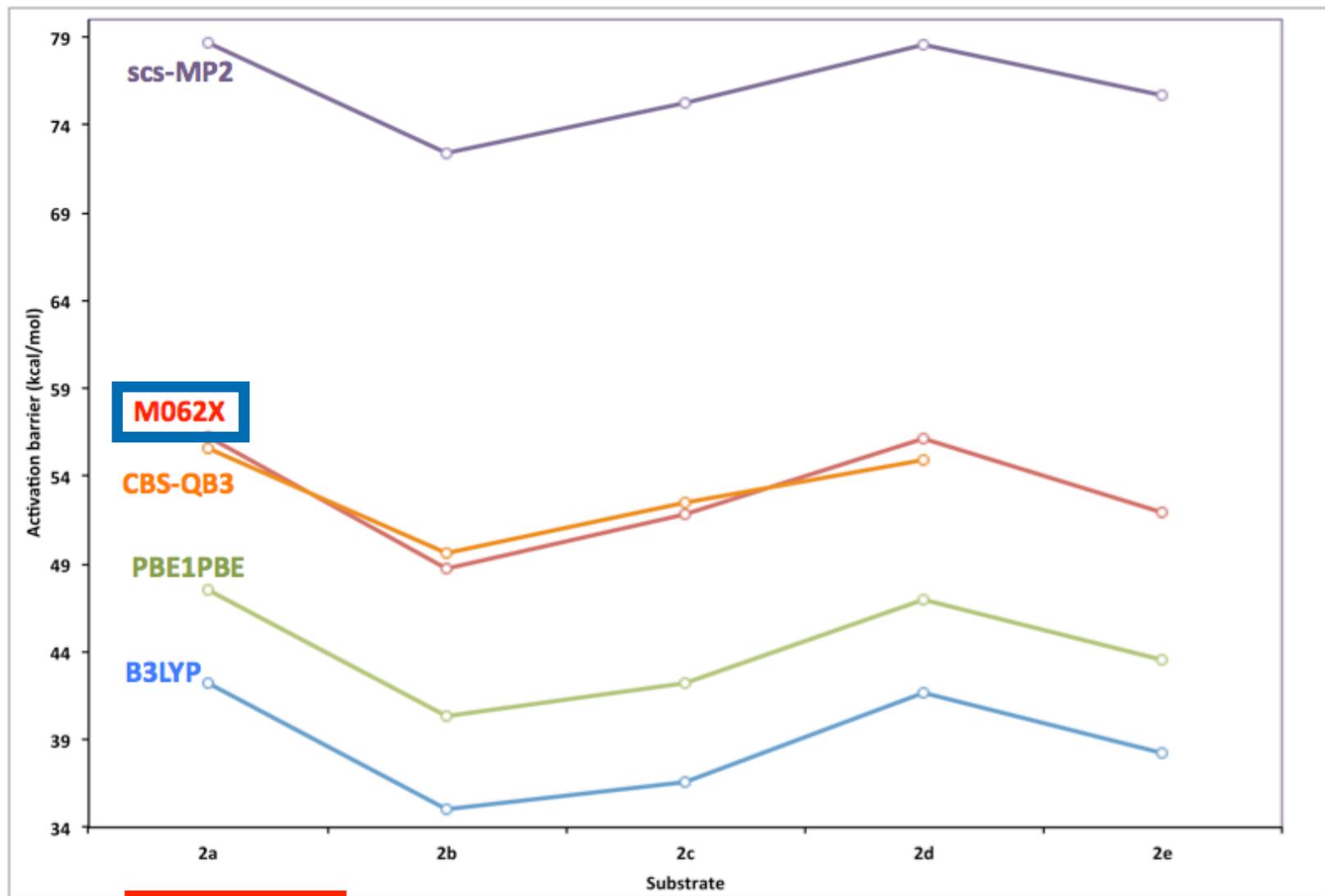


Oxidation

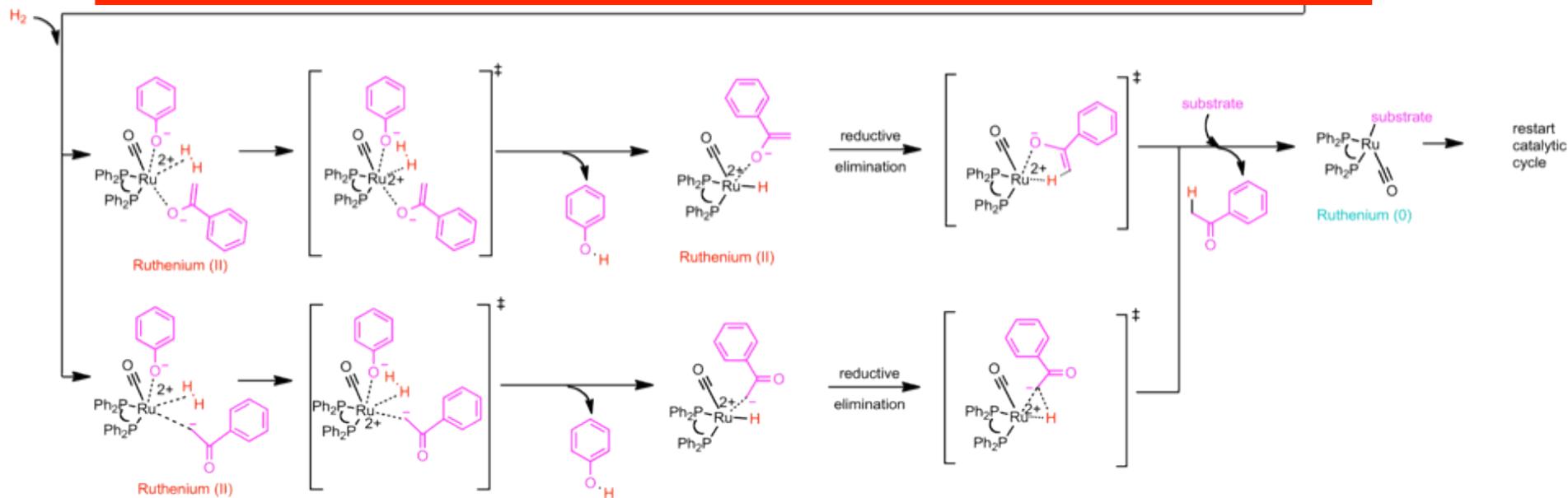
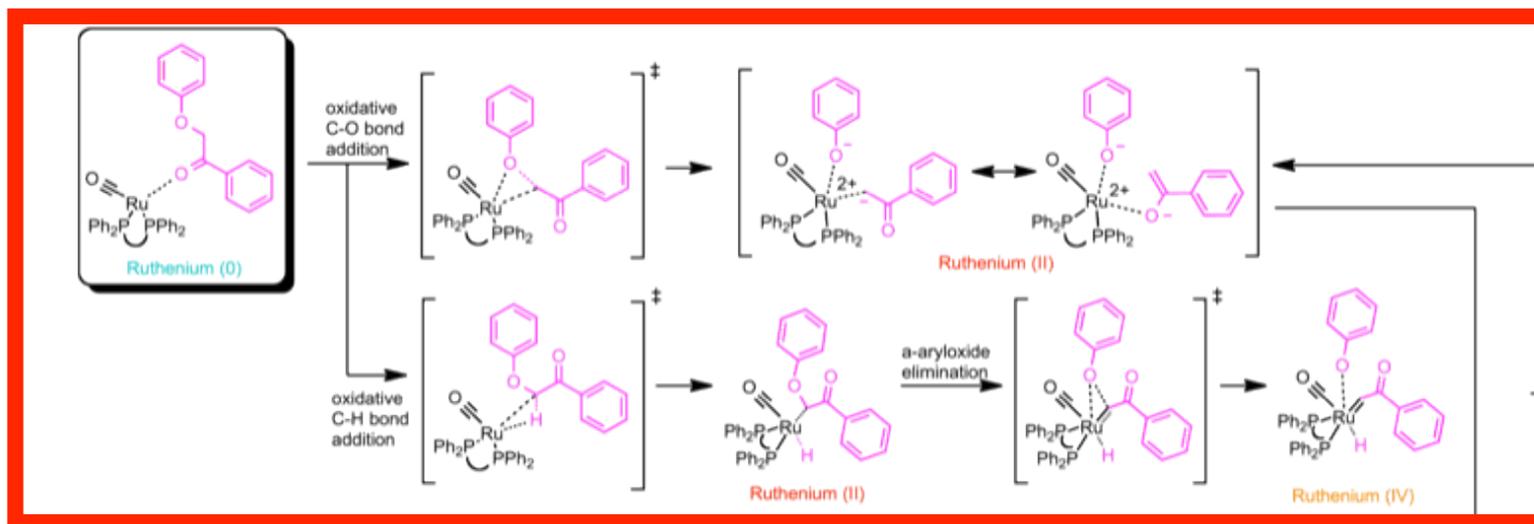
Reduction



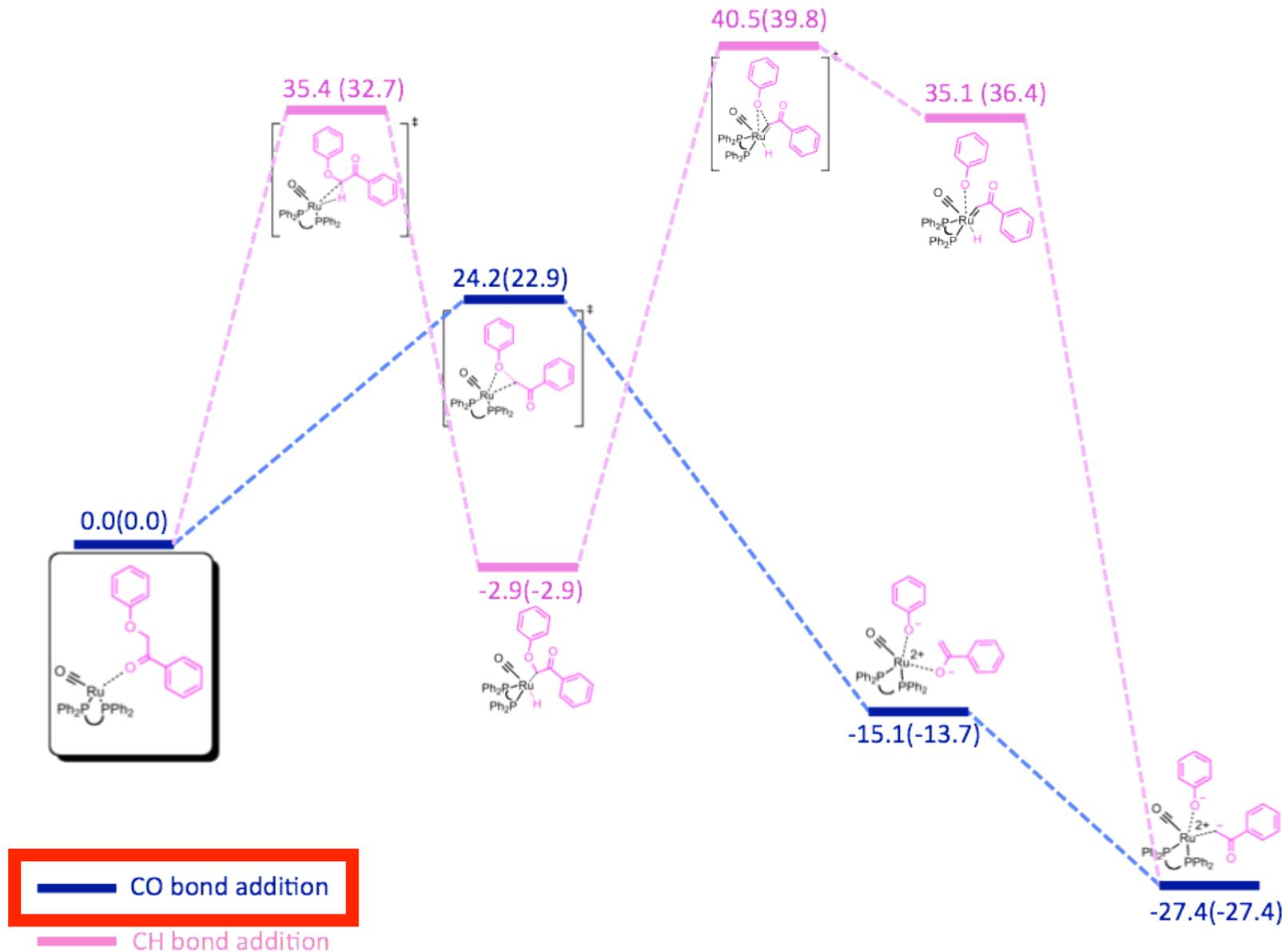
# Method validation against CBS-QB3 calculations for model compounds



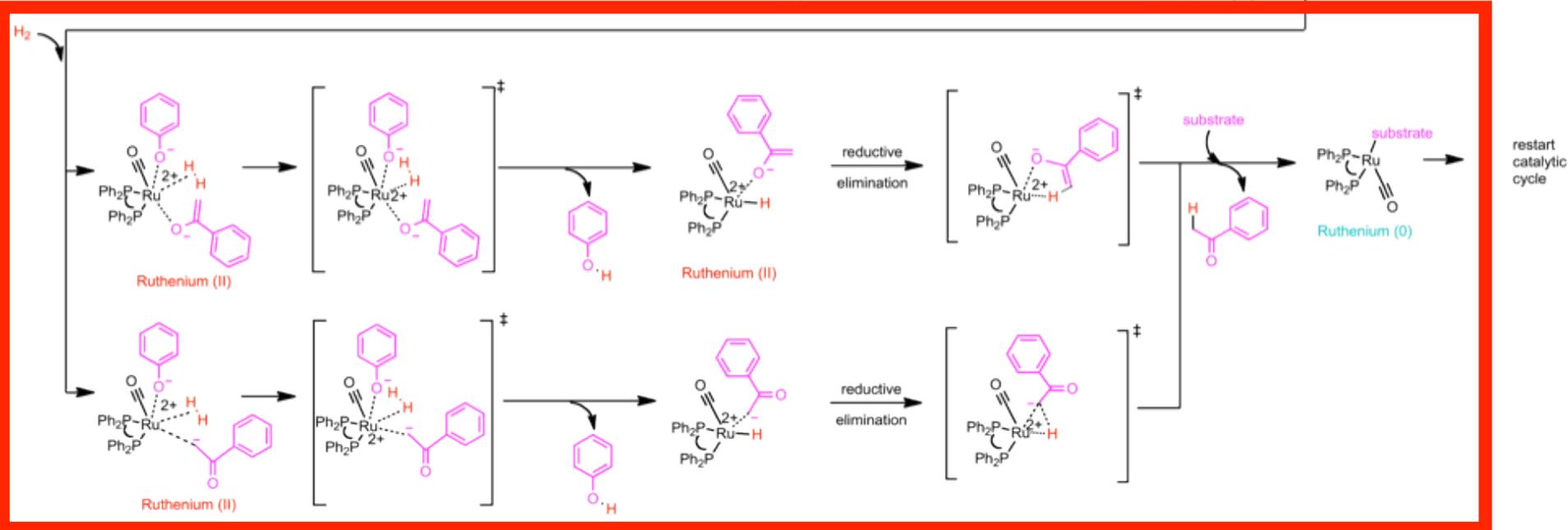
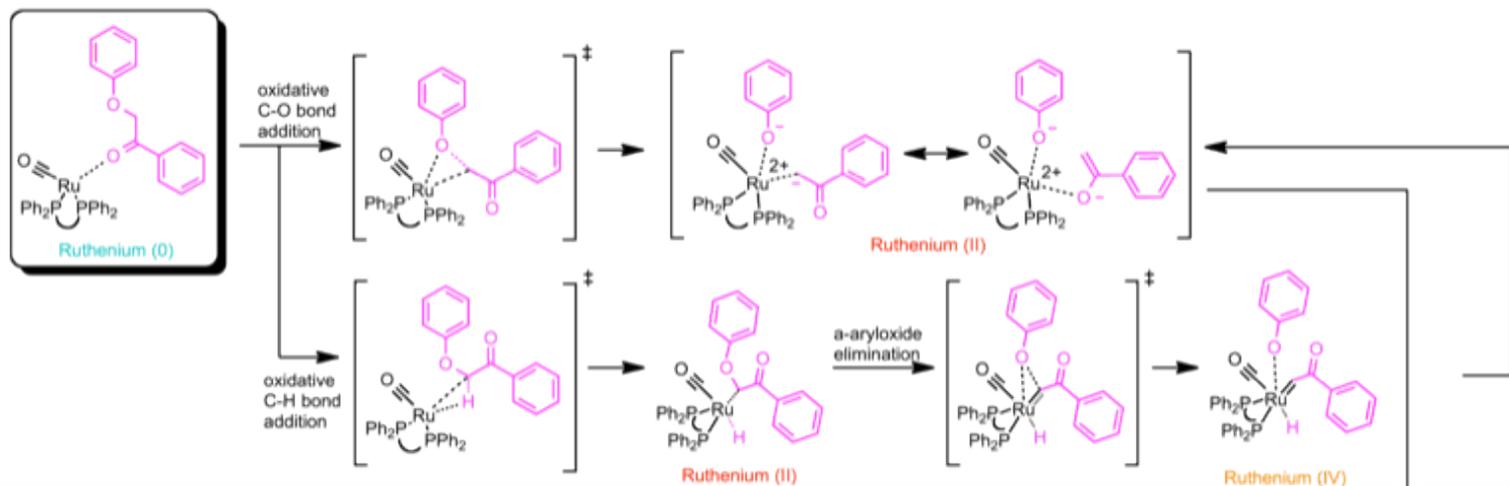
# Proposed mechanistic cycle for Ru-xantphos catalyst



# Two potential pathways for aryl-ether cleavage

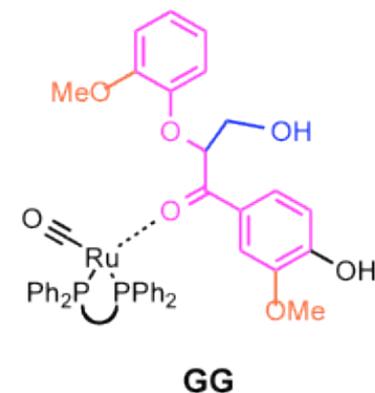
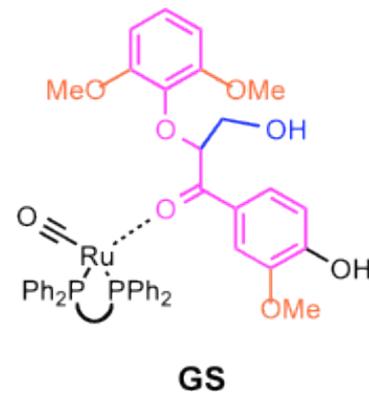
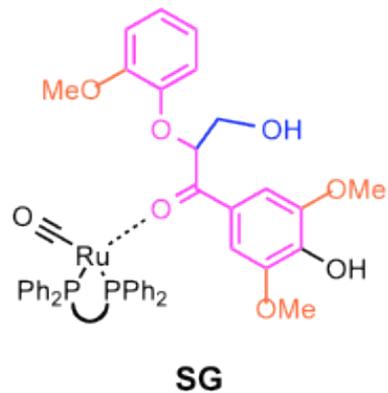
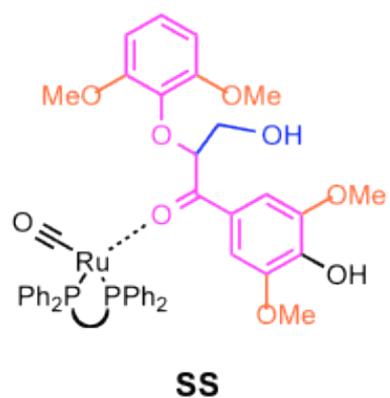
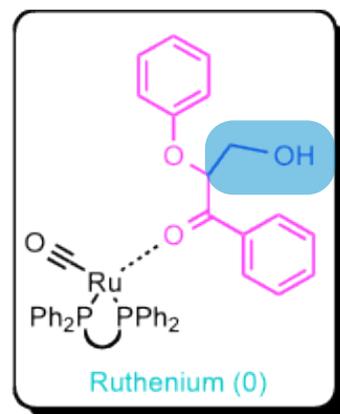
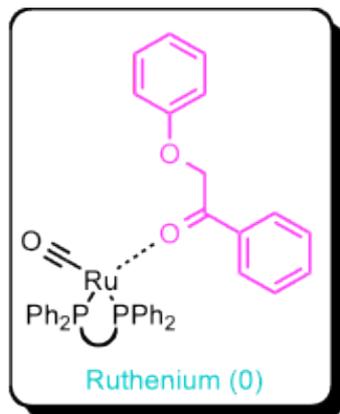


# Proposed mechanistic cycle for Ru-xantphos catalyst

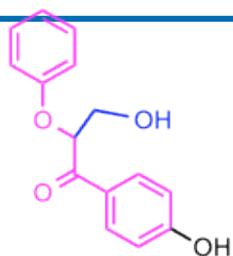




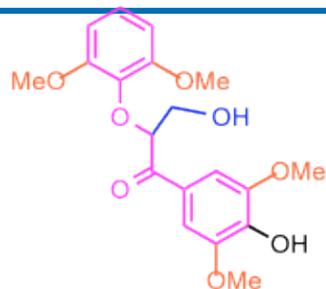
# Effect of substrate on the catalytic cycle



# Dimers for computational and experimental screening



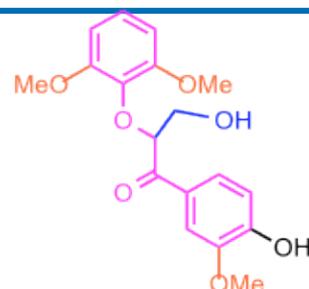
HH



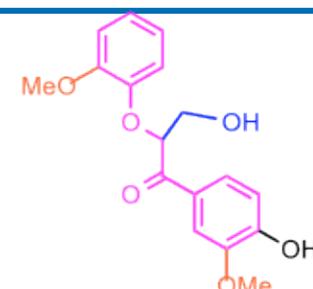
SS



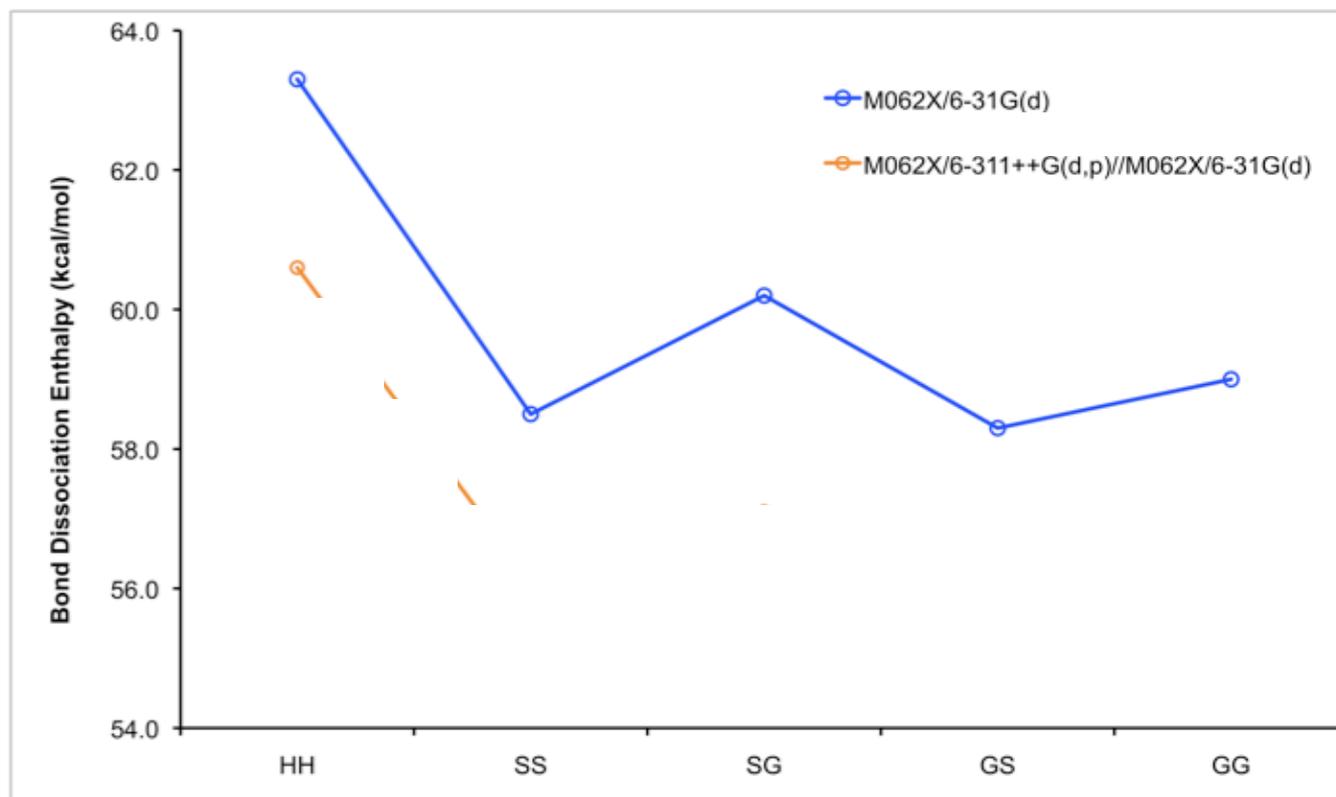
SG



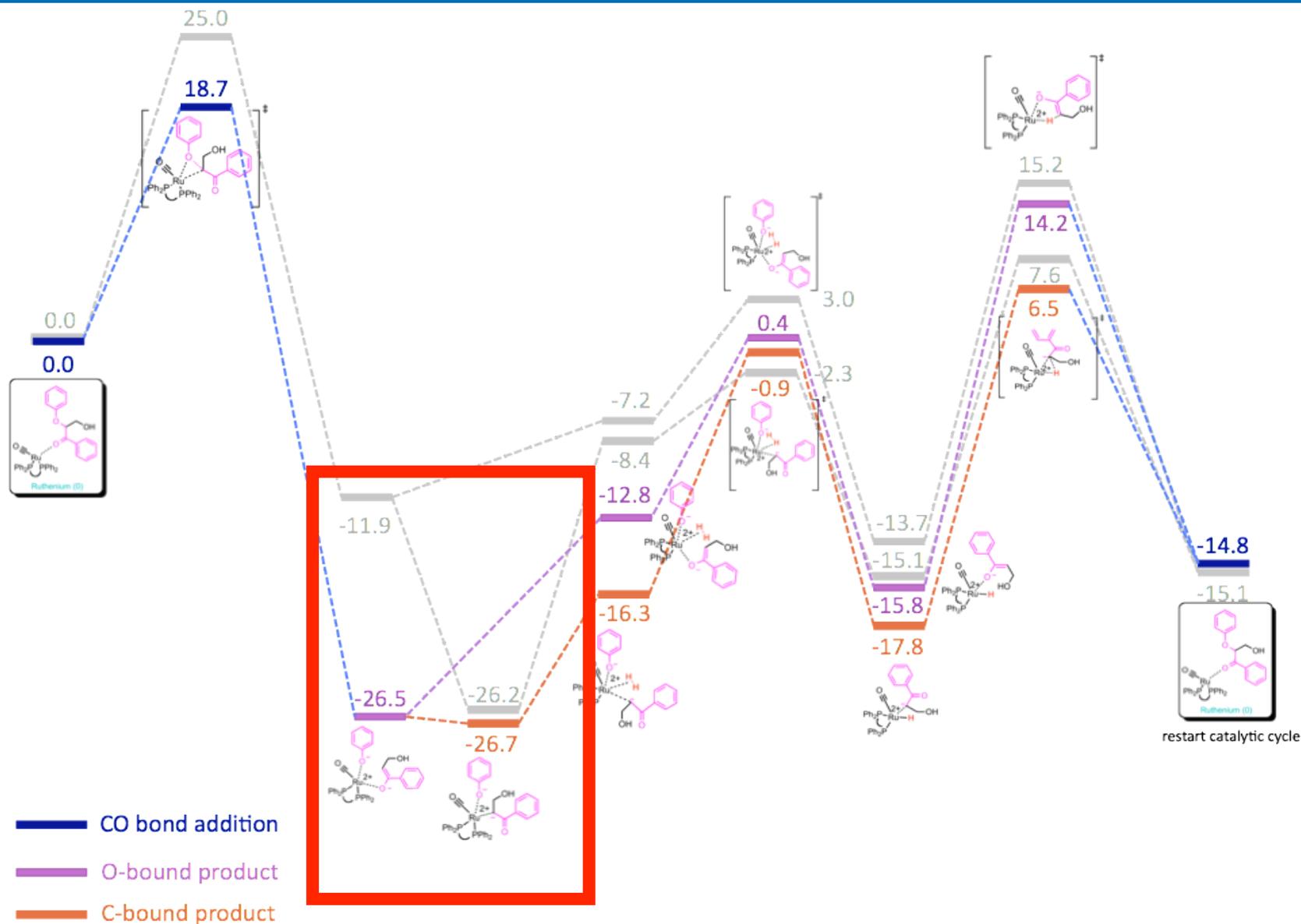
GS



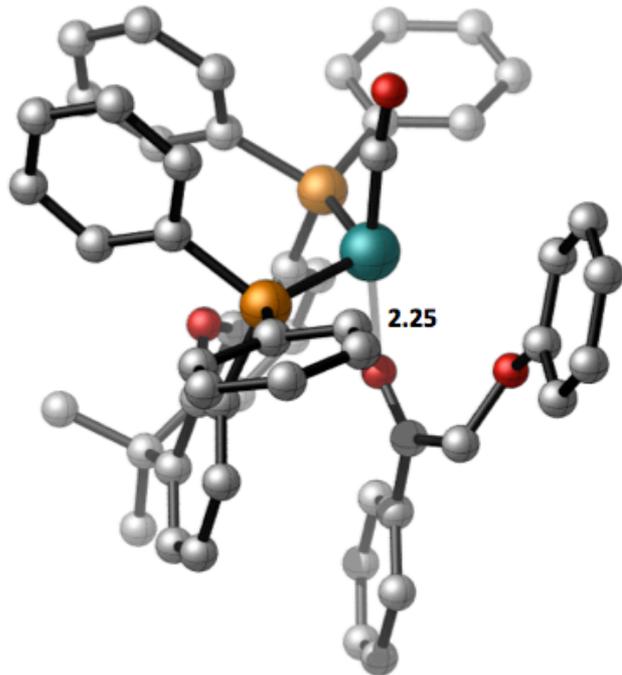
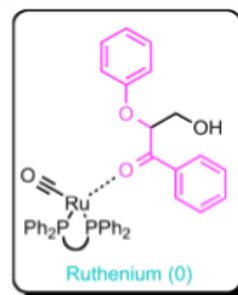
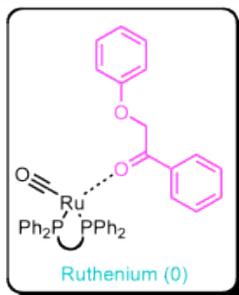
GG



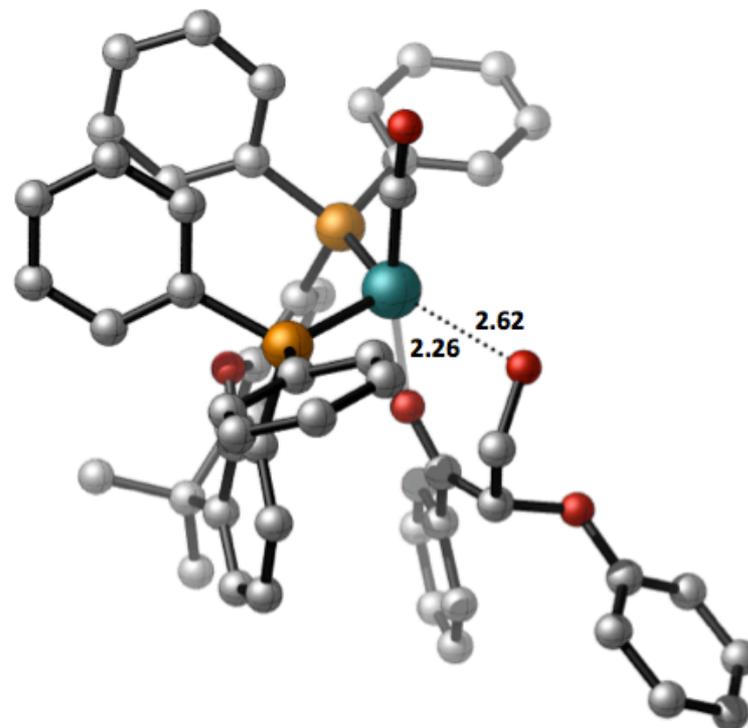
# Full catalytic cycle for both substrates



# Starting configurations of Ru-xantphos catalyst with 2 substrates

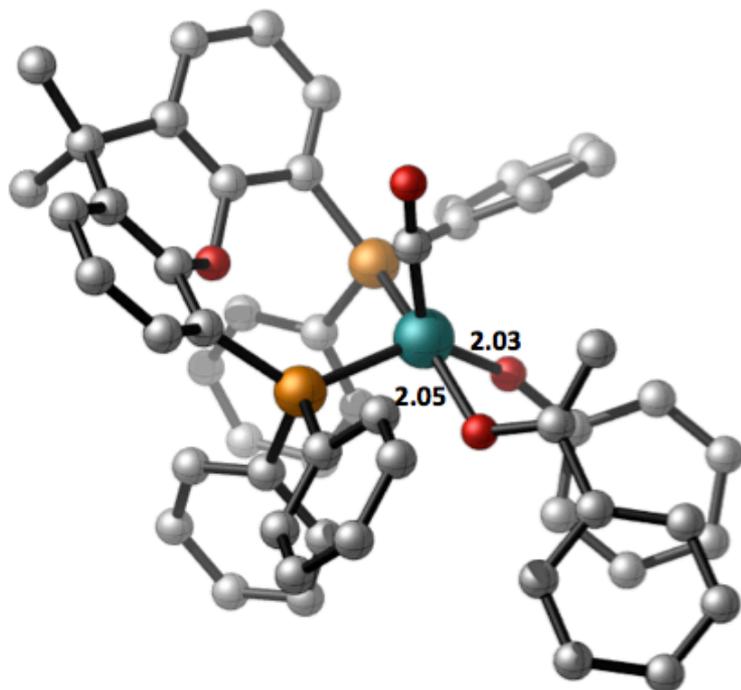
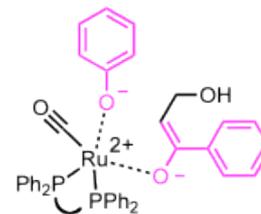


0.0 (0.0)

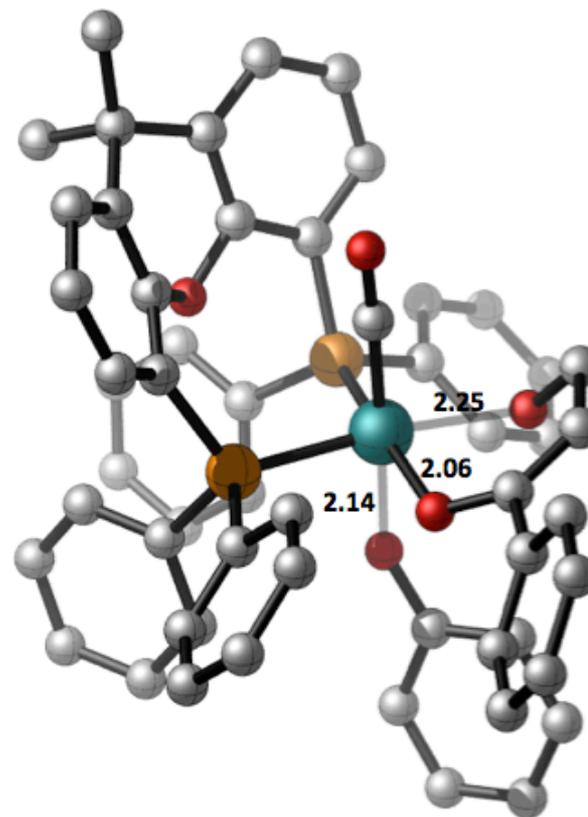


0.0 (0.0)

# O-bound product for HH is more stable because Ru is 6-coordinated

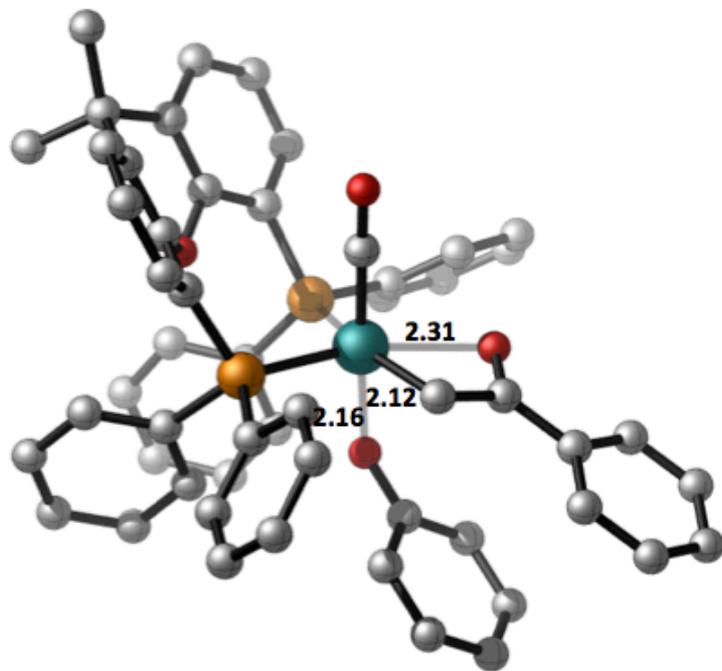
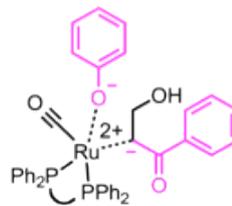
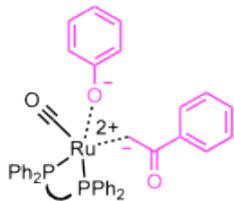


-15.1 (-13.7)

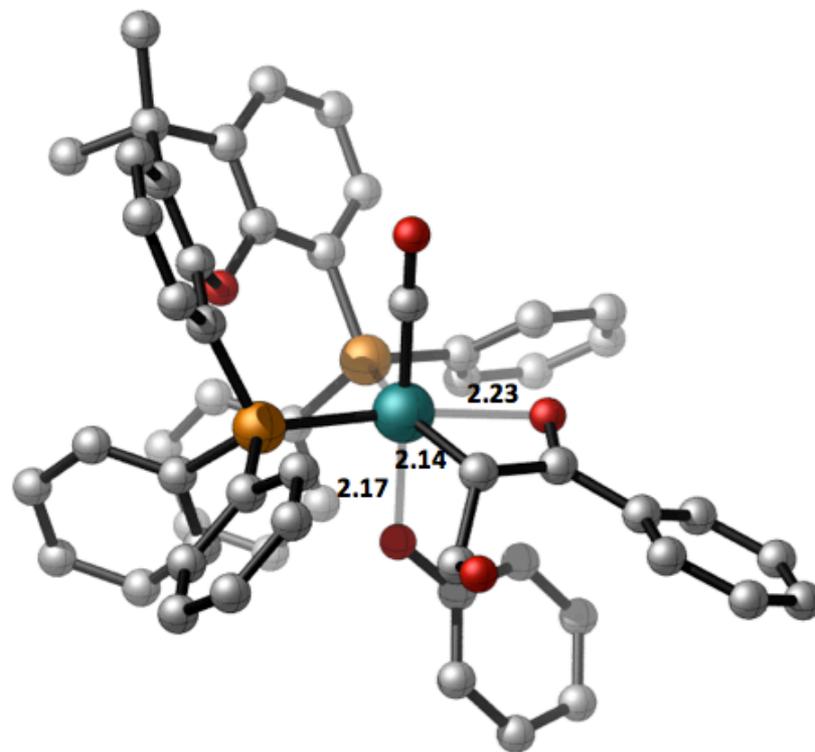


-27.1 (-26.6)

# No significant effect for the C-bound product



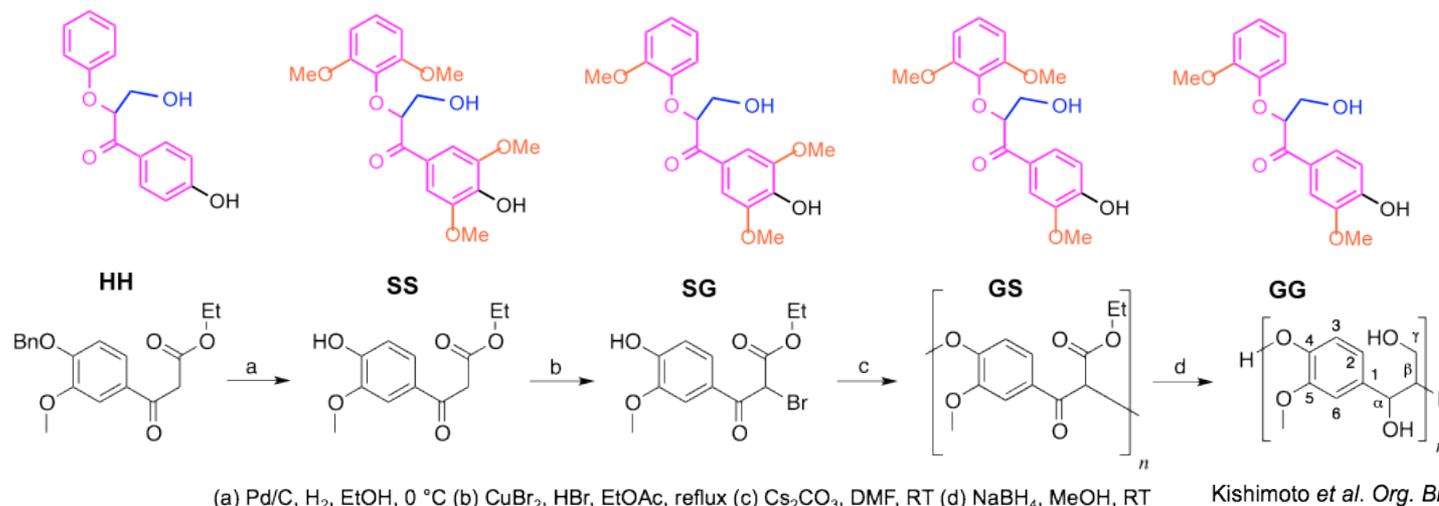
-27.4 (-27.4)



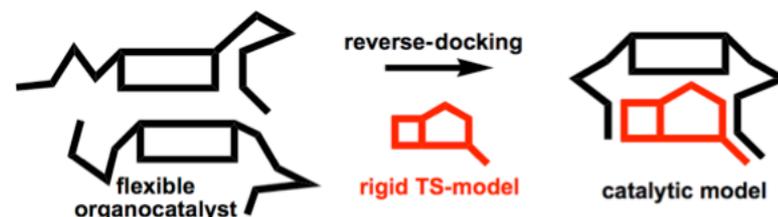
-29.5 (-27.2)

# Current work on catalyst design for lignin deconstruction

- Conducting computational and experimental work with new catalysts
- Screening of Ru-xantphos catalyst with 5 model dimers and lignin polymers

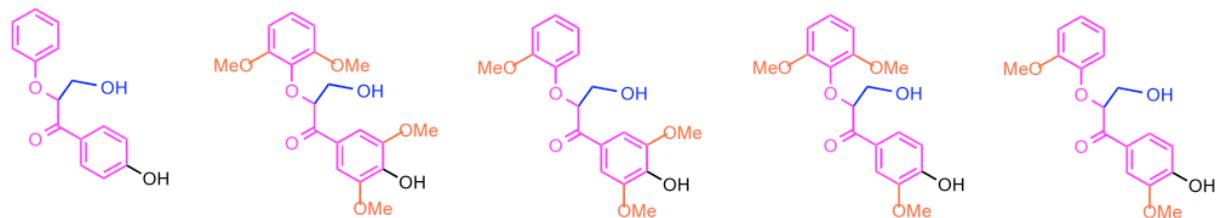


- Mechanistic cycles such as these provide insight into:
  - Ligand design and metal selection
  - Electronic structure of transition states
- Combine transition states with HTP ligand screening
- Challenges: designing methods for monitoring catalytic activity on real lignin



# Looking forward on substrates

Model dimers



HH

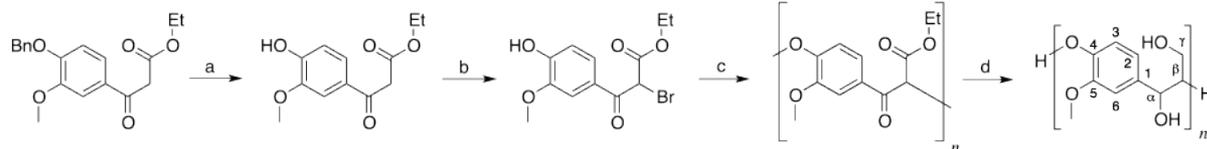
SS

SG

GS

GG

Model homopolymers



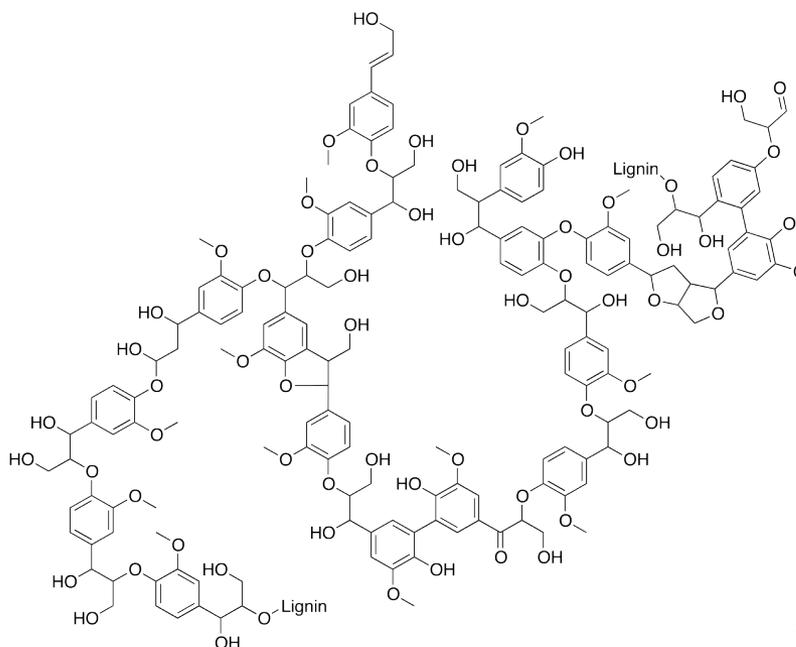
(a) Pd/C, H<sub>2</sub>, EtOH, 0 °C (b) CuBr<sub>2</sub>, HBr, EtOAc, reflux (c) Cs<sub>2</sub>CO<sub>3</sub>, DMF, RT (d) NaBH<sub>4</sub>, MeOH, RT

Kishimoto *et al. Org. Biomol. Chem.*, 2006.

Model heteropolymers

Native/GM lignin

Treated lignins



Chen and Dixon, *Nat. Biotech.*, 2007

# Conclusions and path forward

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Significant potential for HC fuels from biomass

- Intermediate and low energy routes look the most promising
  - Intermediate Energy Routes
    - Catalytic Pyrolysis Routes
      - » Better understanding of underlying chemistry and mechanisms
    - Liquefaction Routes
      - » Significant engineering challenges
  - Low Energy Routes
    - Better value at lower capital costs for lignin

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# Questions?

***Biomass for Advancing America***