Efficient Conversion of Lignin into a water-soluble polymer by a Chelator-Mediated Fenton Reaction: Optimization of H2O2 & Performance as a Dispersant

SAND2017-11813PE

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and
JBEI – Deconstruction Division

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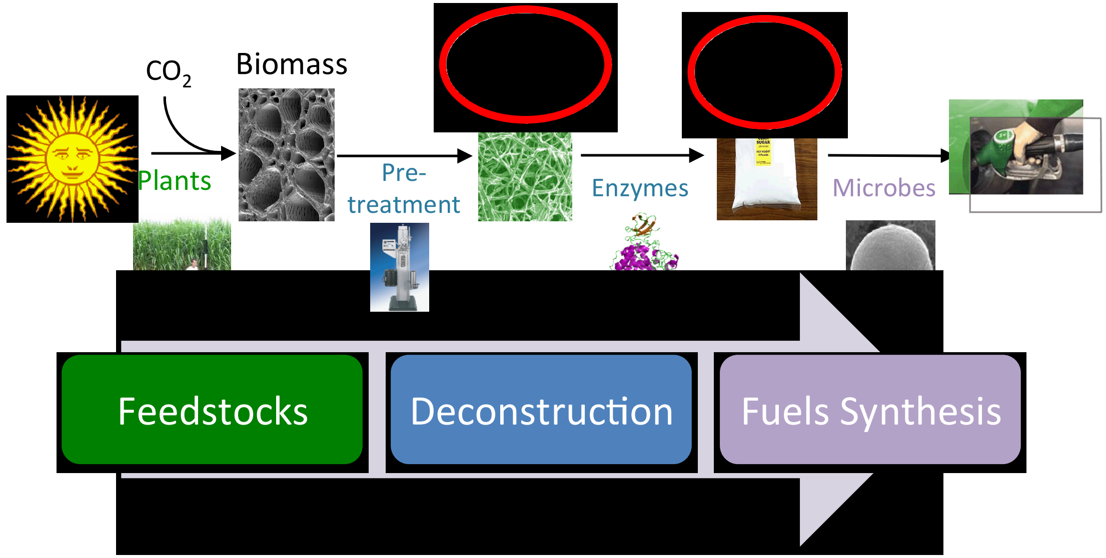
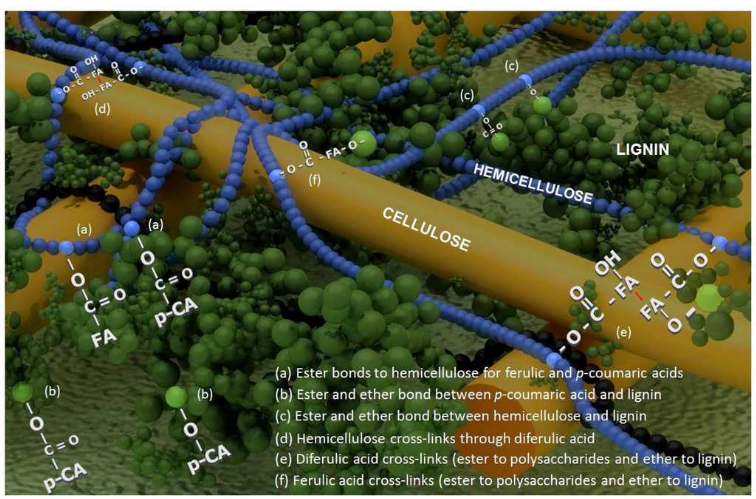
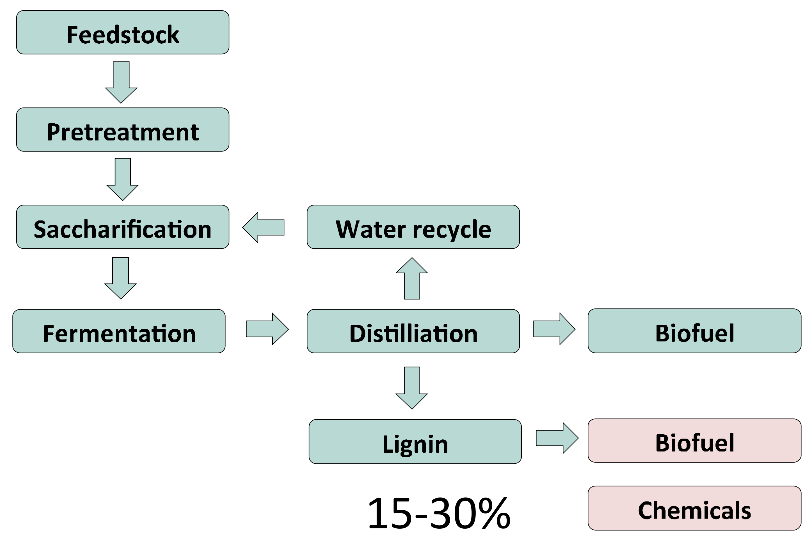
LIGNIN VALORIZATION



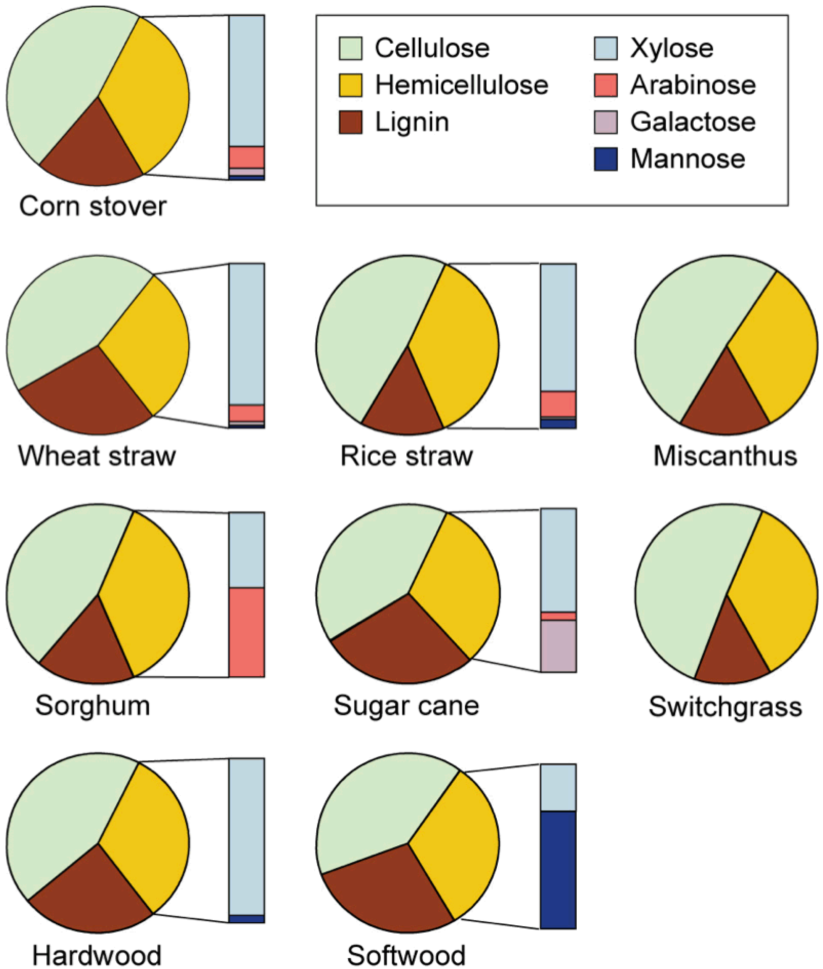
What about lignin?

Int. J. Mol. Sci. 14, 6960, **2013**





LIGNIN VALORIZATION



Economics:
critical to use
all carbon!

Cellulose	40-50%
Hemicellulose	20-30%
Lignin	**15-30%**

LIGNIN VALORIZATION

monomers

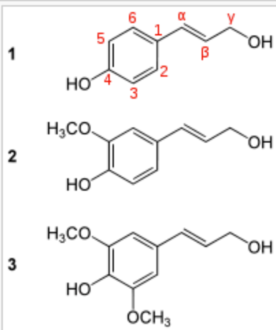
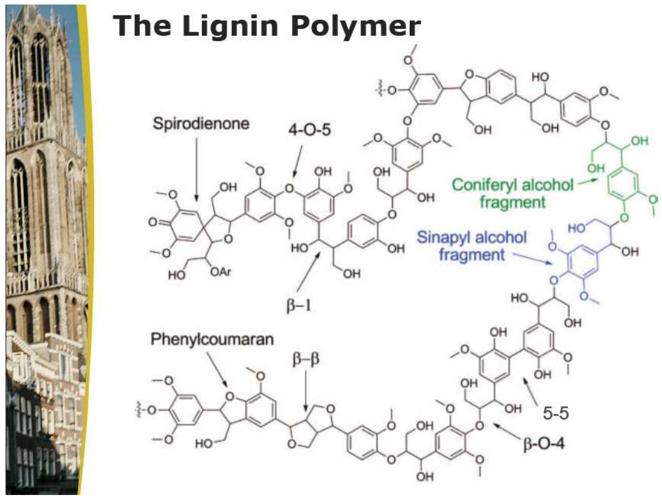
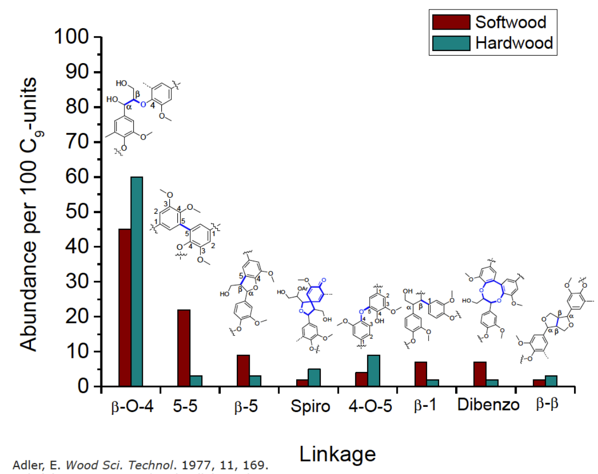


Fig. 3: The three common monolignols: paracoumaryl alcohol (1), coniferyl alcohol (2) and sinapyl alcohol (3)



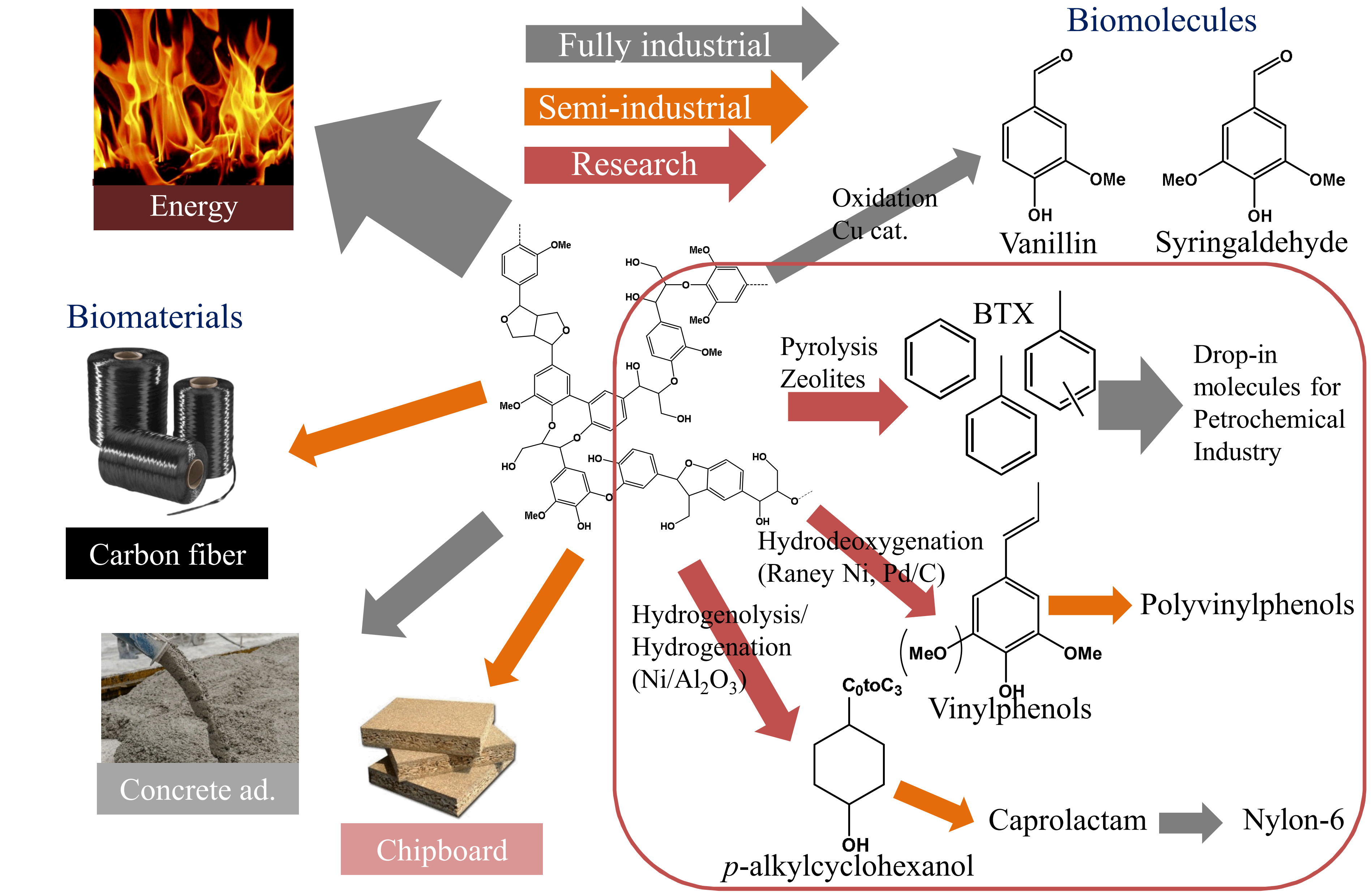
The Lignin Polymer



Adler, E. *Wood Sci. Technol.* 1977, 11, 169.
Sakakibara, A. In *Wood and Cellulose Chemistry*, 1991.

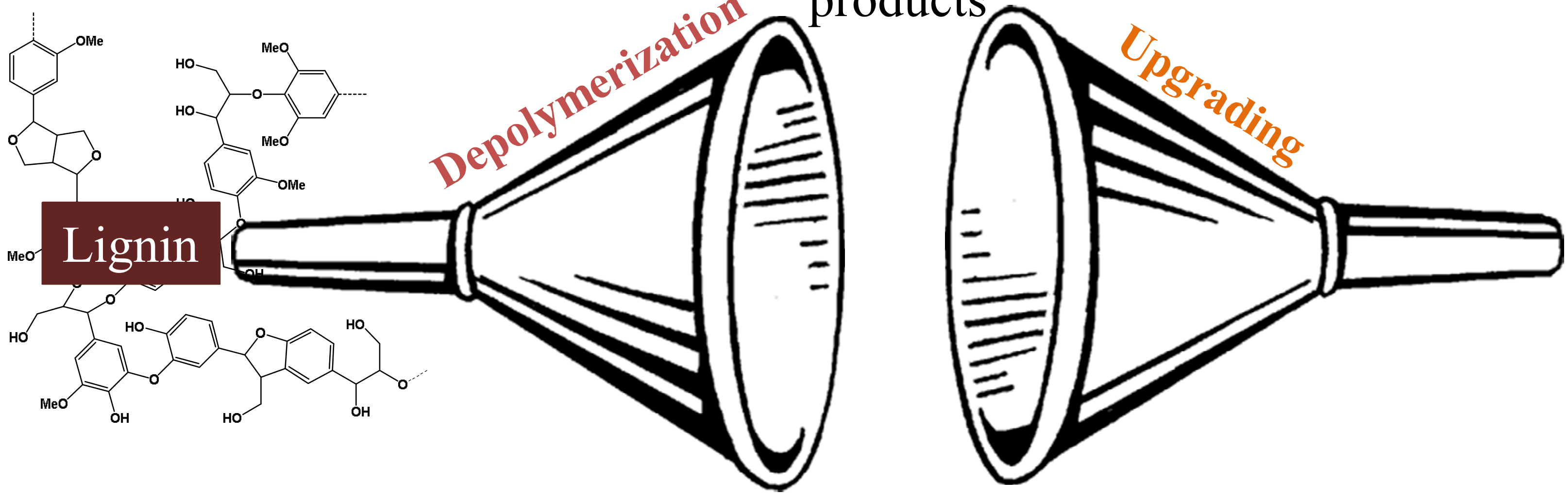
Lignin is chemically complex. Varies with source, method for isolation.

LIGNIN CURRENT AND FUTURE APPLICATIONS



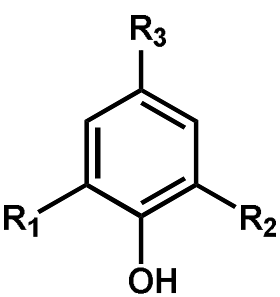
Lignin Depolymerization and Upgrading

Over 100 monomers products



Drop-in Molecules (e.g. BTX)

R_3 from H to propyl



H-type units
- Phenols ($R_1 = R_2 = H$)

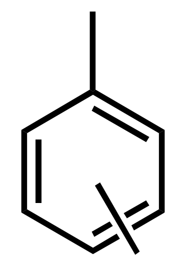
G-type units
- Guaiacols ($R_1 = OMe$, $R_2 = H$)
- Catechols ($R_1 = OH$, $R_2 = H$)

S-type units
- Syringols ($R_1 = R_2 = OMe$)
- Methoxycatechol ($R_1 = OH$, $R_2 = OMe$)
- Pyrogallols ($R_1 = R_2 = OH$)

Dealkylation

Deoxygenation

Demethoxylation

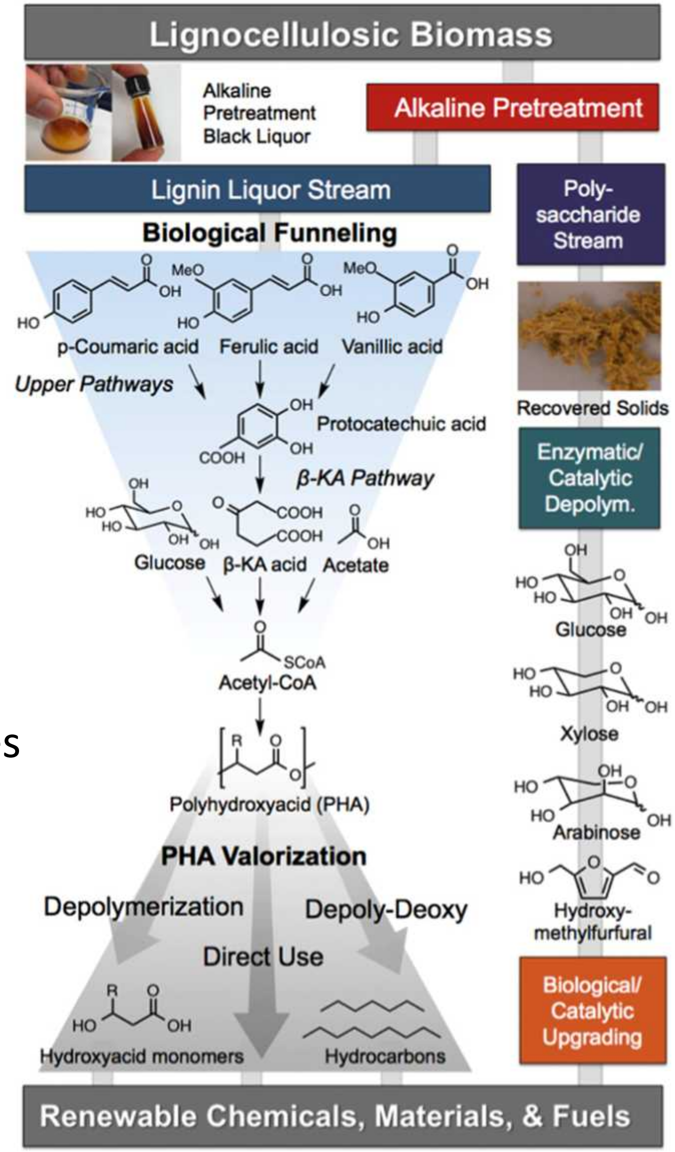


LIGNIN VALORIZATION

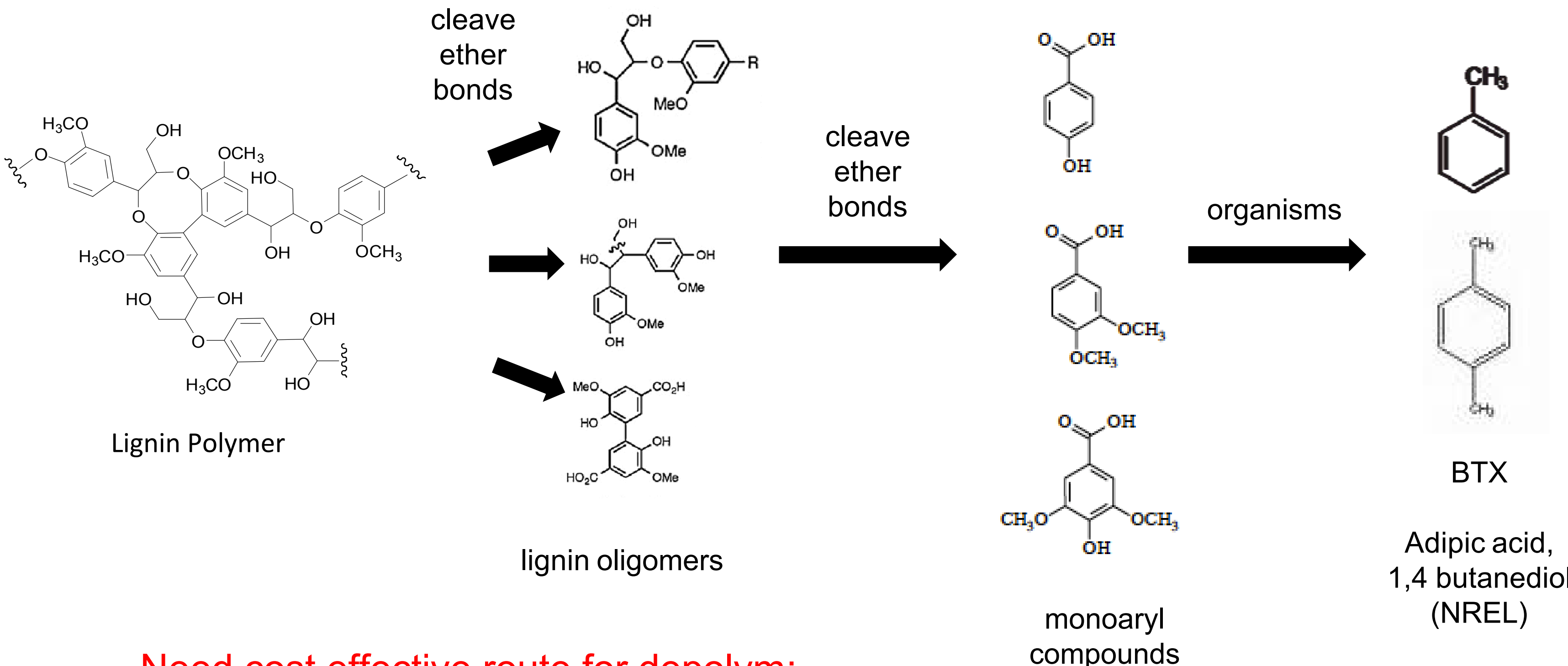
Biological funneling

G. Beckham et al
PNAS 2014

PHA - polyhydroxyalkanoates



One approach to lignin valorization



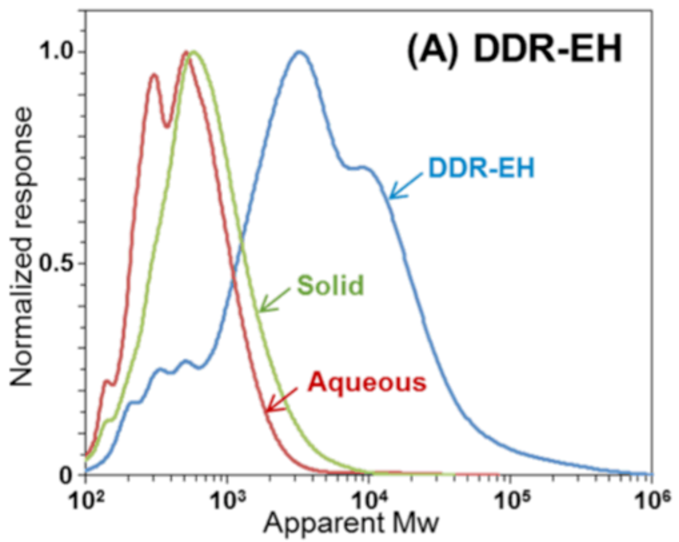
Need cost effective route for depolym:

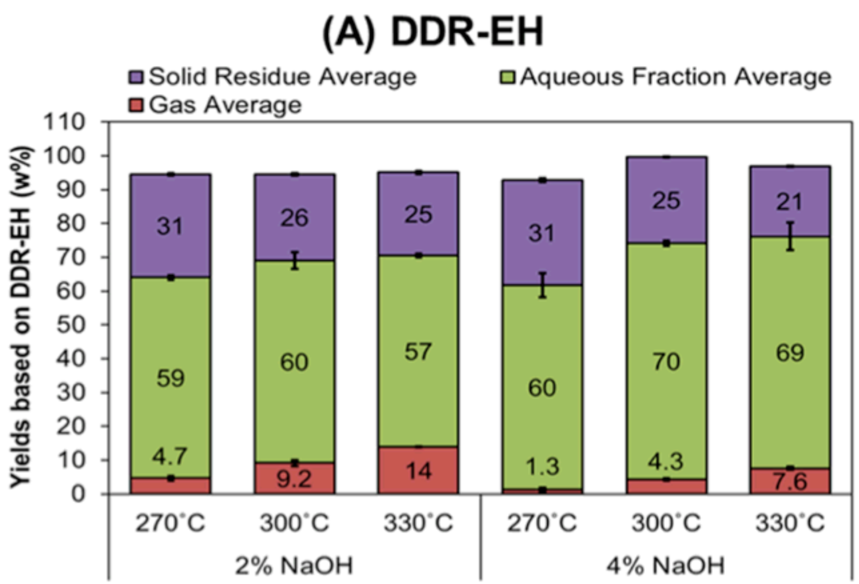
-hot alkaline (base-catalyzed depolym)
-high T, P catalysis
-enzymes/organisms

Breakdown products must not be toxic to organisms

Base-catalyzed Lignin depolymerization

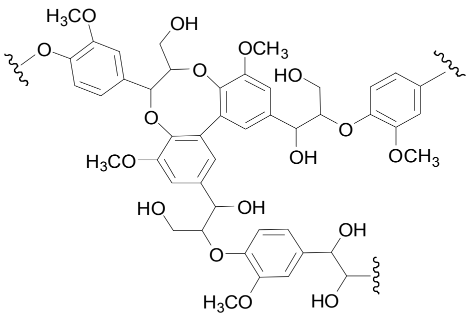
G. Beckham et al
ACS Sus. Chem 2016





Biological upgrading: fraction of carbon taken up is modest, toxicity is an issue, neutralization costs

alternative chemistry – ring opening



Lignin Polymer

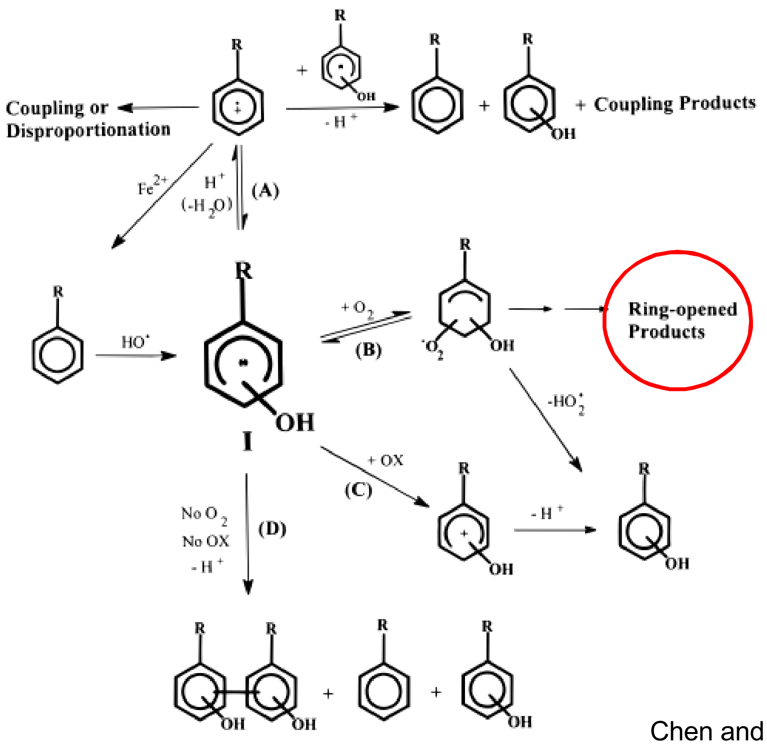
Polyacid
(dispersant)

High MW solubilized fragments rich in COOH

Fenton reaction

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + HO^{\bullet} + OH^{-}$$

Explored for water
purification -
removal of aromatics



Chen and Pignatello,
Environ Sci Technol 1997,
31, 2399-2406

FENTON CHEMISTRY

need to reduce Fe(III) to Fe(II)!

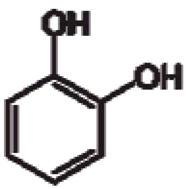
Fenton reaction

$$\mathrm{Fe(II)} + H_2O_2 \rightarrow \mathrm{Fe(III)} + HO^{\bullet} + OH^{-}$$
$$\mathrm{Fe(III)} + H_2O_2 \rightarrow \mathrm{Fe(II)} + HO_2^{\bullet}/O_2^{\bullet\,-} + H^{+}$$

slow, wastes H_2O_2

Fe(III) + chelator $\longrightarrow$ Fe(II)

Fe(III) + oxidized lignin $\longrightarrow$ Fe(II)



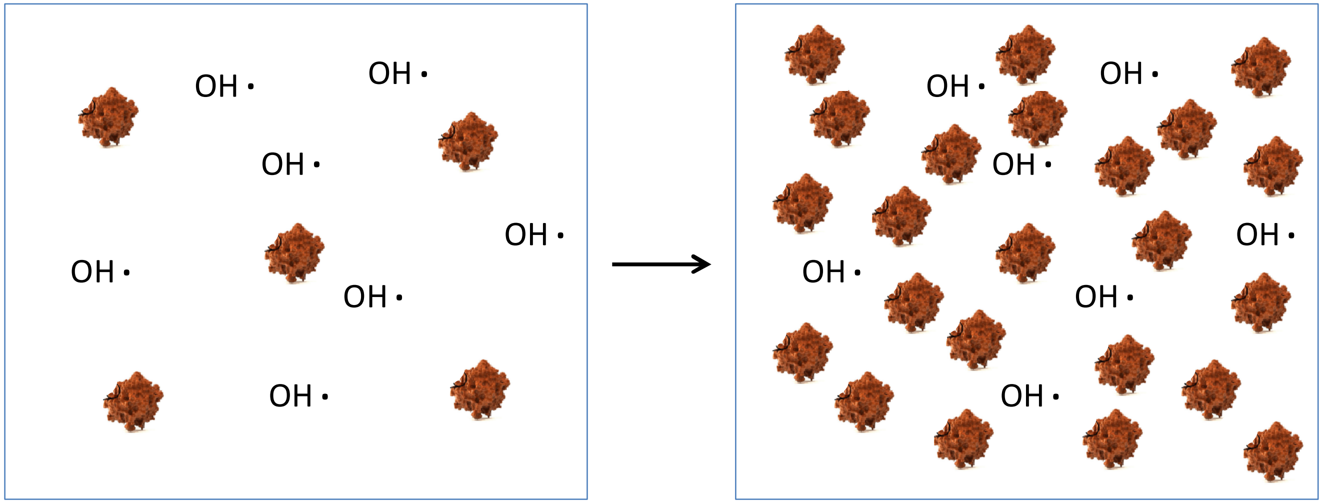
Fe chelator/reducer

chelator-mediated Fenton (CMF)

Technical hurdle – H_2O_2 usage

H_2O_2 is expensive: need to use H_2O_2 efficiently!

Homogeneous reaction



Hyroxyl radical – short half life

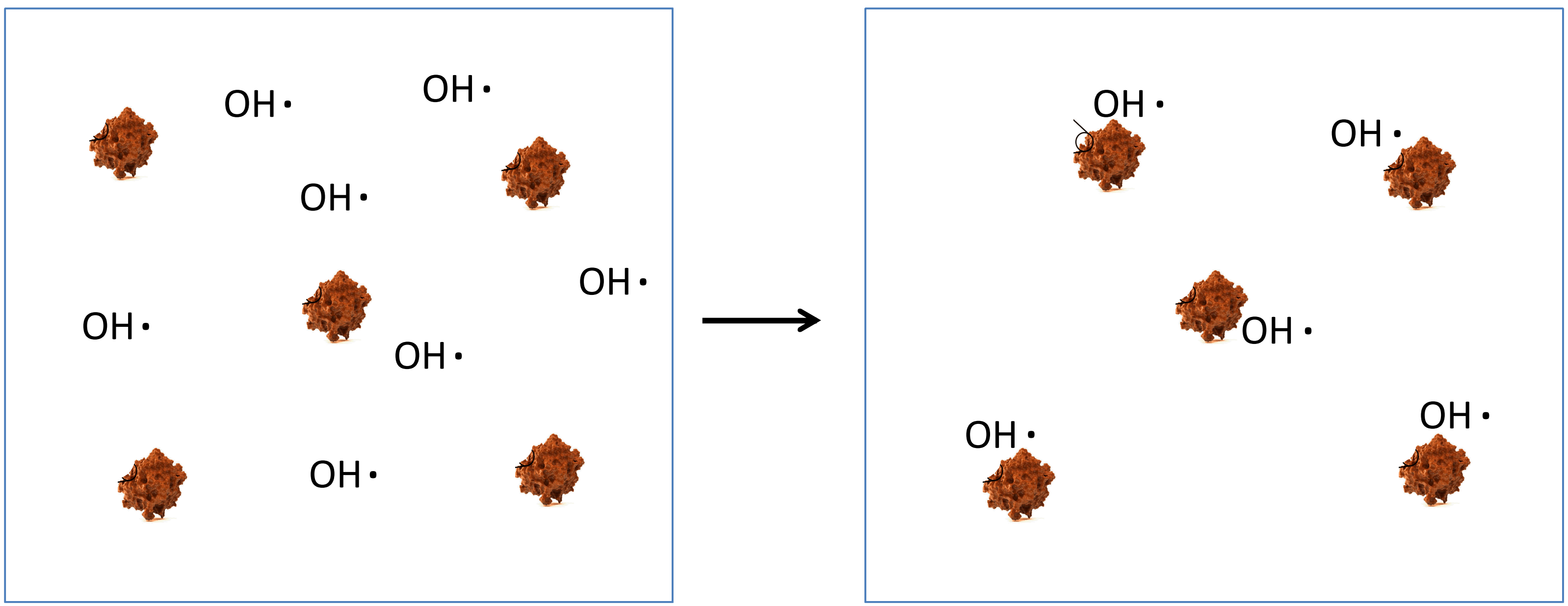
increase lignin conc.

Technical hurdle – H_2O_2 usage

Need to use H_2O_2 efficiently!

Homogeneous reaction

Heterogeneous reaction



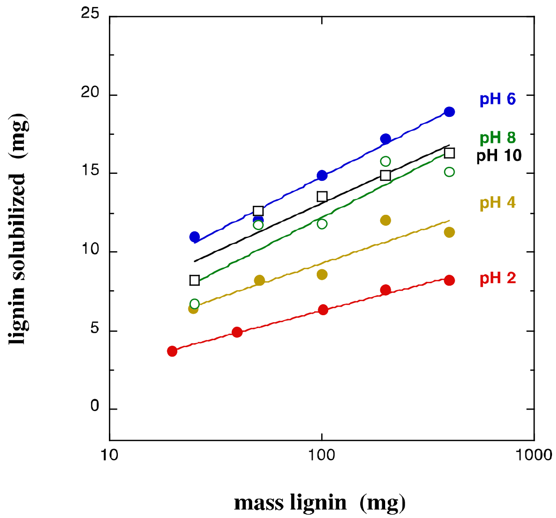
Hyroxyl radical – short half life

choose chelator that associates with lignin

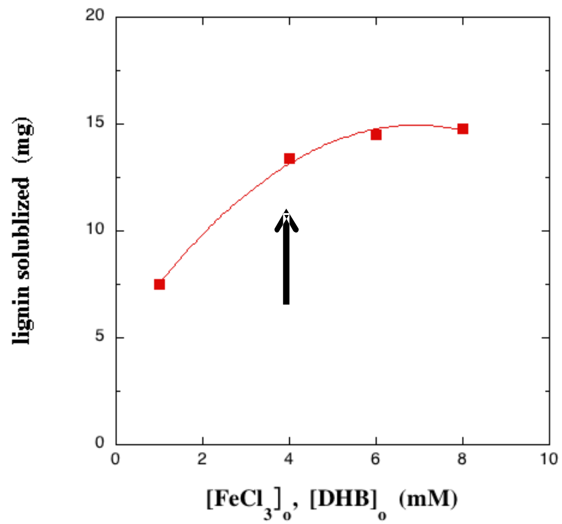
OPTIMIZATION OF CHELATOR-FENTON

Rxns: 8 mls total, organosolv lignin (Lignol Corp)

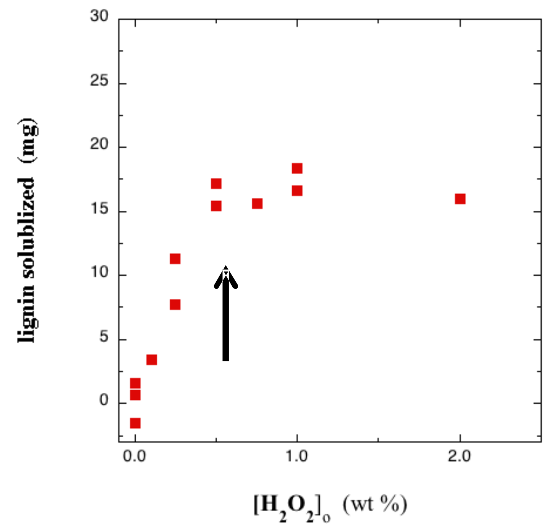
$[FeCl_3]_o = [DHB]_o = 4$ mM
0.5% H_2O_2



0.5% H_2O_2
pH 6, 200 mM lignin



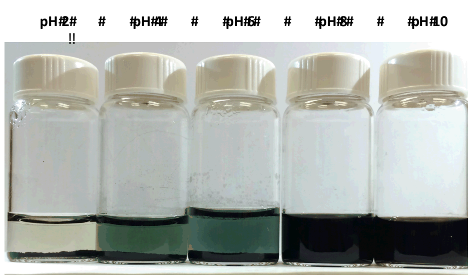
$[FeCl_3]_o = [DHB]_o = 4$ mM
pH 6, 200 mg lignin



optimum pH = 6

optimum $[FeCl_3] = [DHB] = 4$ mM

optimum $[H_2O_2] = 0.5\%$



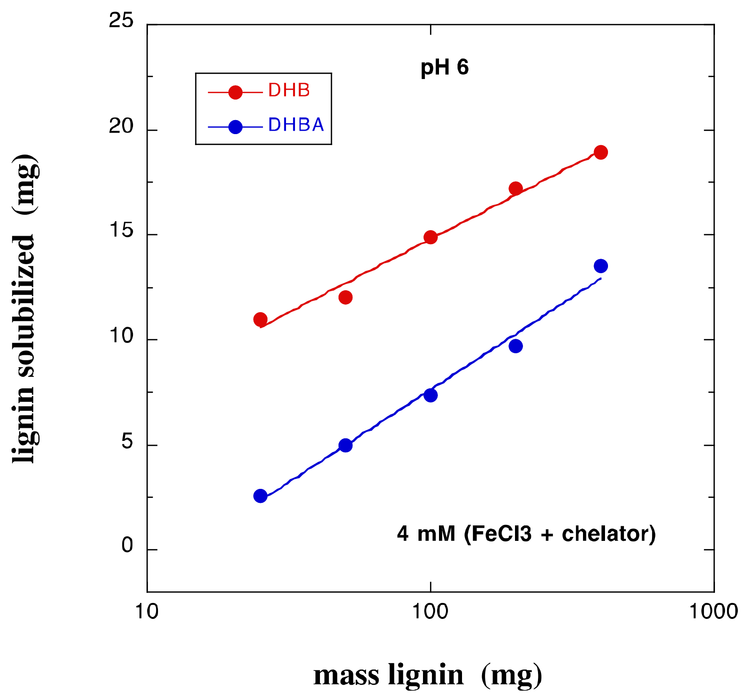
0.5% H_2O_2 = 150 mM

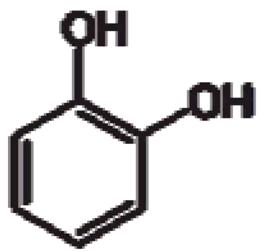
0.5% H_2O_2 in 8 mls = 40 mg

Optimization of chelator-Fenton

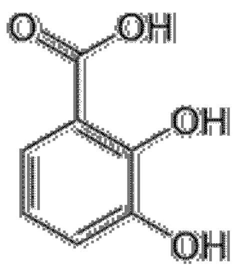
total vol = 8 ml

40 mg H2O2





DHB



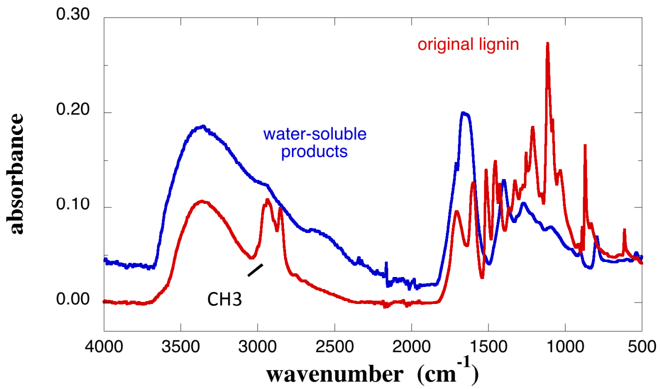
DHBA

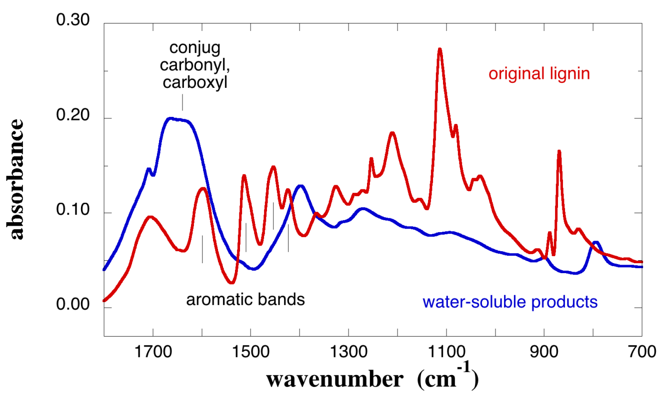
Table 1
Concentrations of Fe^{2+} and Cu^{1+} ions formed by the oxidation of phenol derivatives after 30 min reaction

No.	Phenol derivative	Fe^{2+} in μM	Cu^{1+} in μM
24	3,4-Dihydroxyphenylacetic acid	59 (1)	48.4 (0.1)
9	2,5-Dihydroxyterephtalic acid	54.6 (0.7)	50.3 (0.4)
6	Gallic acid	49 (1)	41.1 (0.5)
20	Chromotropic acid	48.7 (0.5)	47 (1)
10	3-Hydroxyanthranilic acid	44.8 (0.4)	44.0 (0.3)
→ 1	2,3-DHB acid	39 (1)	33.5 (0.3)
3	Gentisic acid	33.7 (0.1)	32.4 (0.6)
2	Protocatechuic acid	24.3 (0.2)	18.4 (0.1)
4	2,4-DHB acid	1.8 (0.2)	0
5	2,6-DHB acid	8.7 (0.3)	0
11	4-Hydroxybenzoic acid	0	0
14	4-Hydroxybenzaldehyde	0	0
17	4-Hydroxycinnamic acid	6.7 (0.1)	0
25	Vanillic alcohol	32.8 (0.5)	14.1 (0.1)
7	Vanillic acid	23.8 (0.1)	3.6 (0.2)
12	Vanillin	16.6 (0.5)	0
15	Ferulic acid	21.2 (0.7)	14.5 (0.2)
8	Syringic acid	31.0 (0.3)	21.9 (0.4)
13	Syringaldehyde	30 (2)	4.1 (0.3)
16	Sinapic acid	30.0 (0.9)	18.6 (0.1)
→ 18	Catechol	24.8 (0.5)	22.4 (0.1)
21	Purpurogallin	34 (2)	47 (1)
22	Chlorogenic acid	24.2 (0.8)	16.7 (0.1)
19	Hydroquinone	19.5 (0.1)	21 (1)

Characterization of water-soluble product

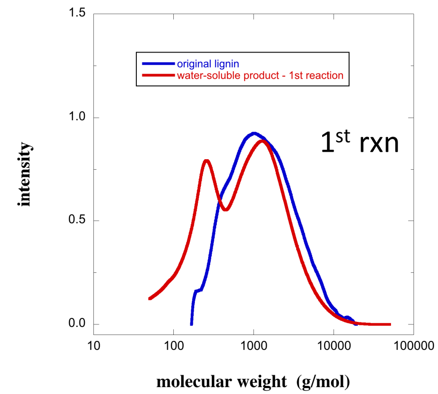
IR

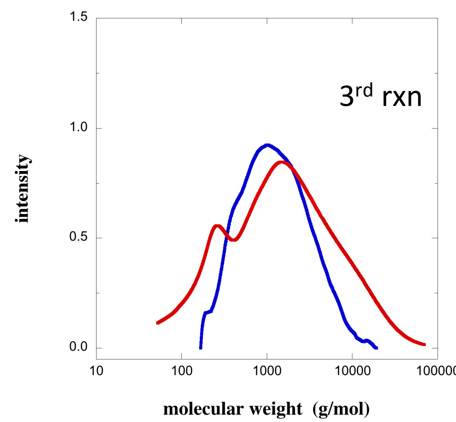




aromatic rings opened
methoxy groups gone

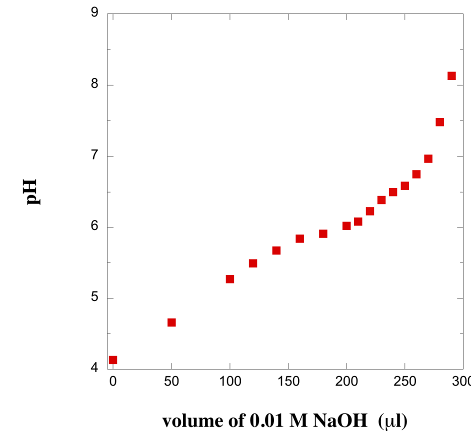
MW distribution





similar to original

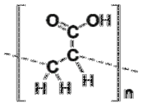
COOH titration



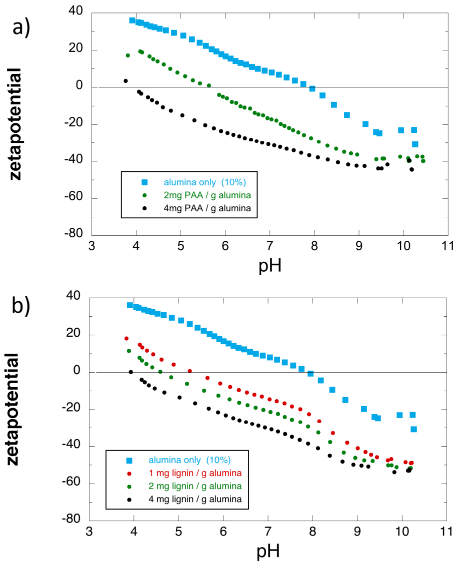
1 COOH per 180 g/mol

DISPERSANT PROPERTIES (WITH NELSON BELL)

poly(acrylic acid) - PAA – 2000 g/mol
commercial dispersant

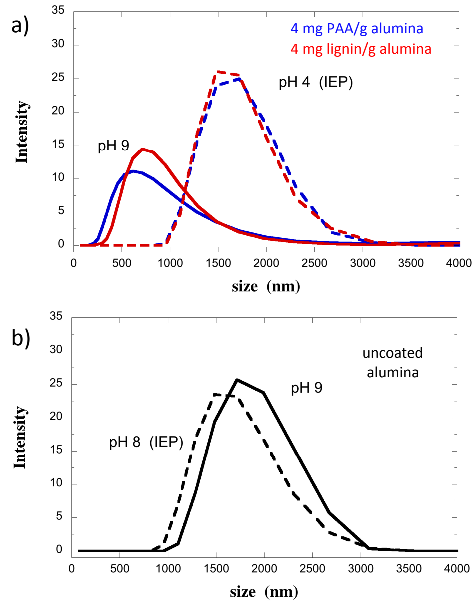


Zeta potential (alumina particles)

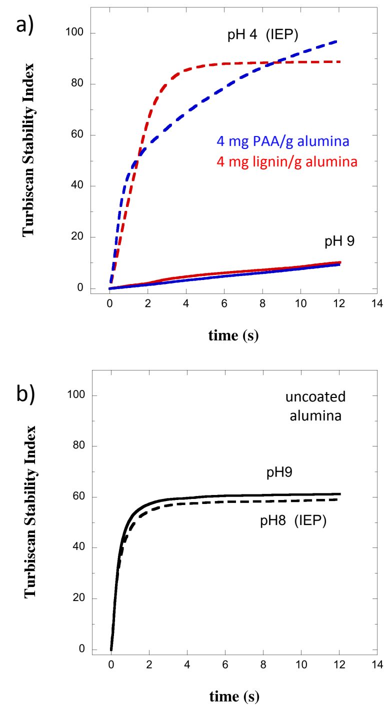


Zeta potential [mV]	Stability behavior of the colloid
from 0 to ±5,	Rapid coagulation or flocculation
from ±10 to ±30	Incipient instability
from ±30 to ±40	Moderate stability
from ±40 to ±60	Good stability
more than ±61	Excellent stability

alumina particle size distribution

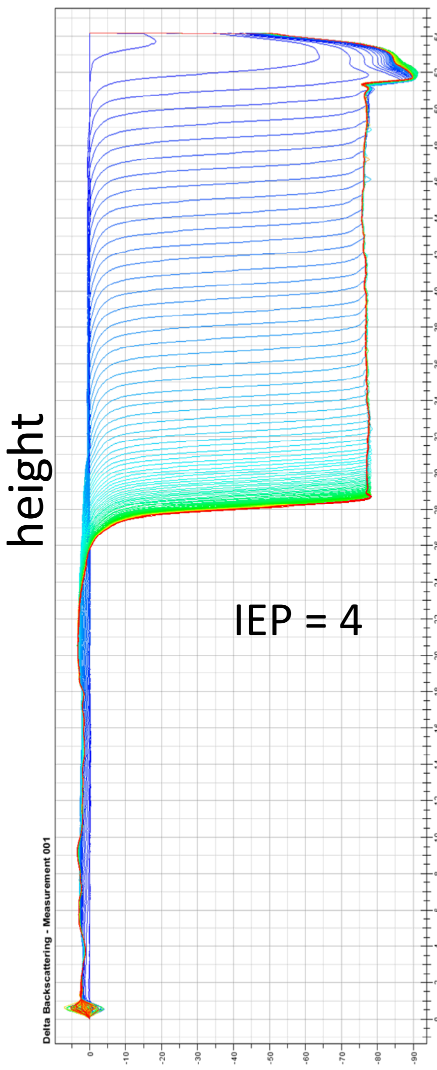


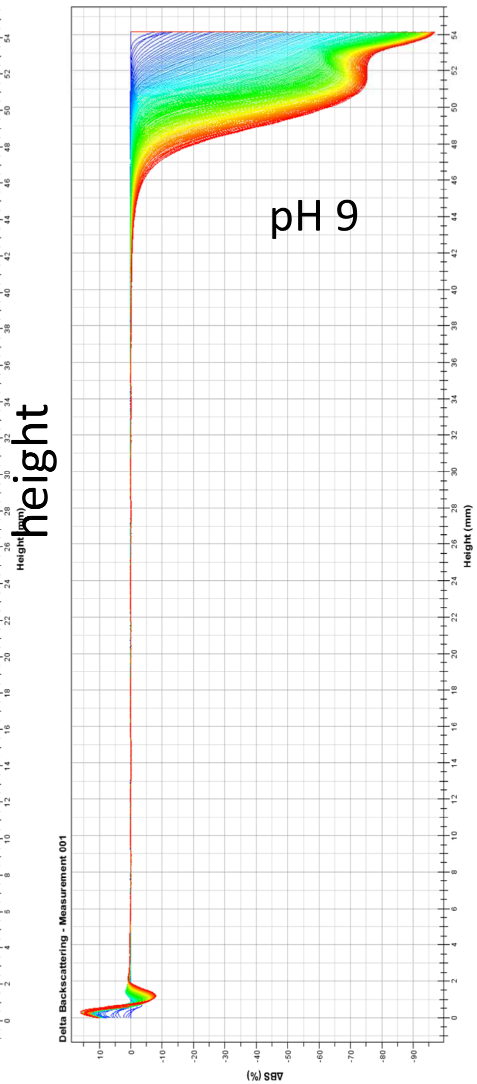
alumina particle size distribution



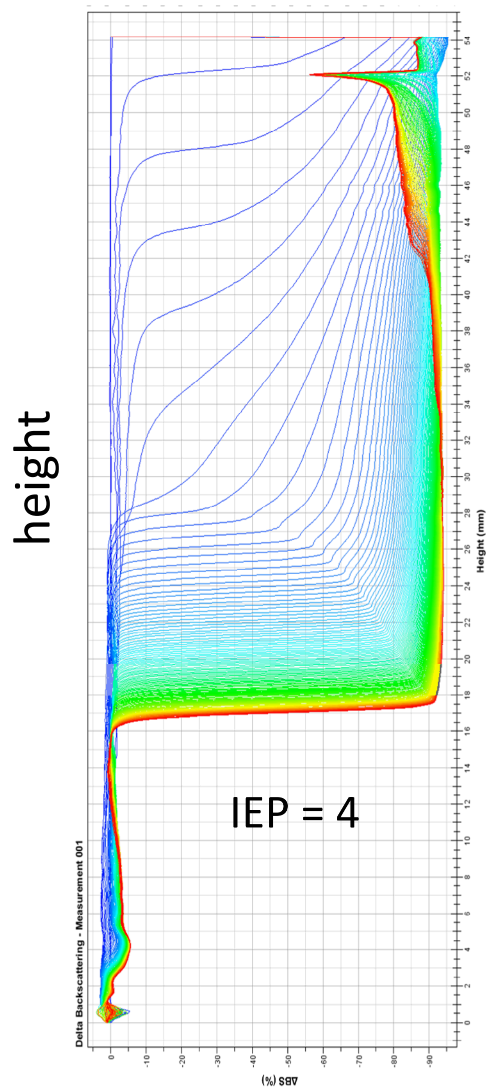
Turbiscan Stability measurements

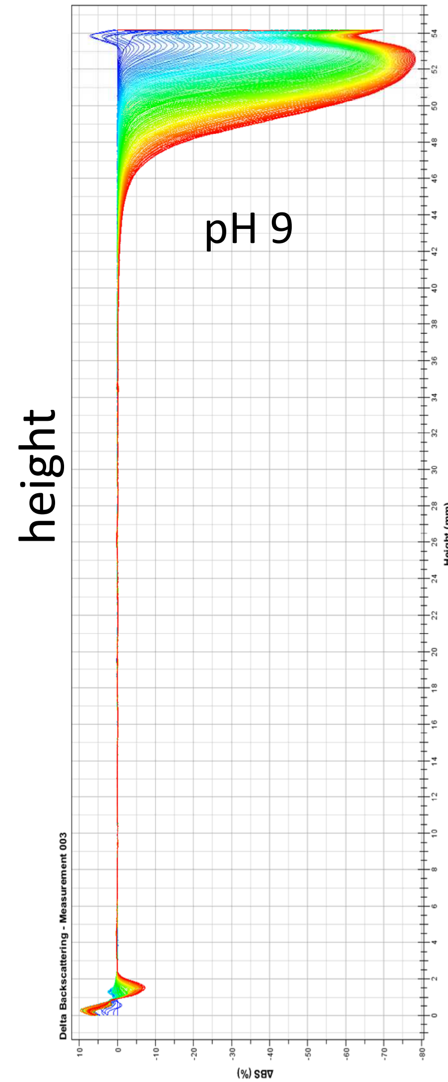
PAA Mw = 2000 g/mol





Lignin-derived material:
4 mM (FeCl3+DHB) + 0.5% H2O2





Economics?

(dyes, paints, concrete, pharmaceuticals, diapers, cosmetics, paper and paperboard, ceramics processing, to inhibit fouling in cooling water systems)

PAA 50% **POLYACRYLIC ACID** 50%

US $900-1300 / Metric Ton

5 Metric Tons (Min. Order)

$2200/MT PAA

our yield for 1 rxn:
1 g /g H_2O_2

H2O2 **Bulk Hydrogen peroxide** 50% for Mining,Paper,Textile,leather industry

US $330-470 / Metric Ton

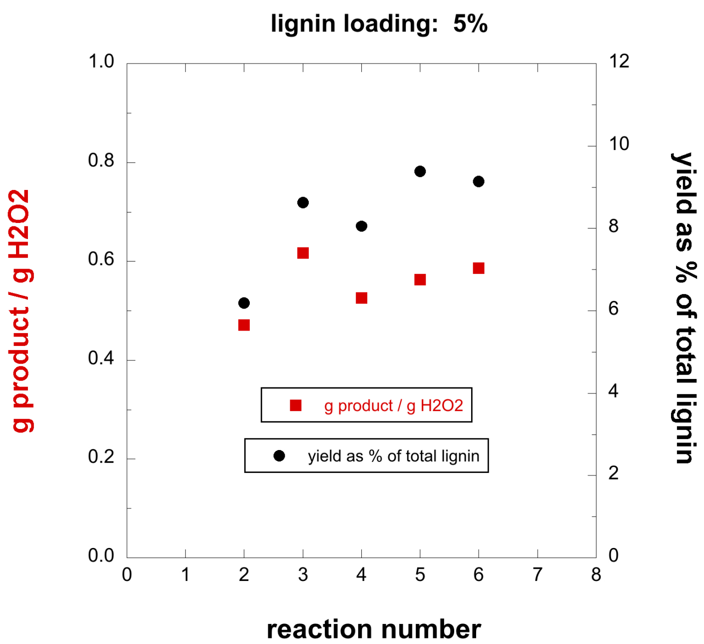
10 Metric Tons (Min. Order)

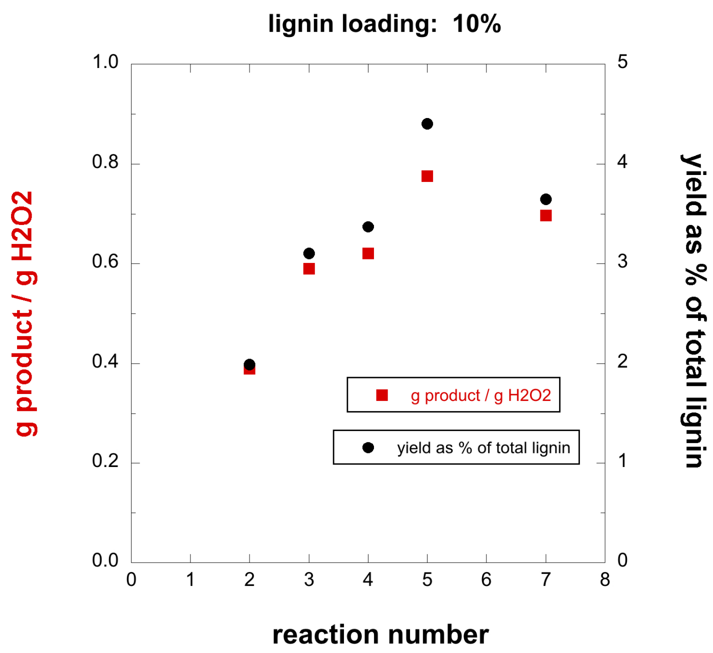
$800/MT H_2O_2

Ways to improve:

Yield increases for successive reactions
Could generate H_2O_2 in situ using enzymes

YIELD FOR SUCCESSIVE REACTIONS



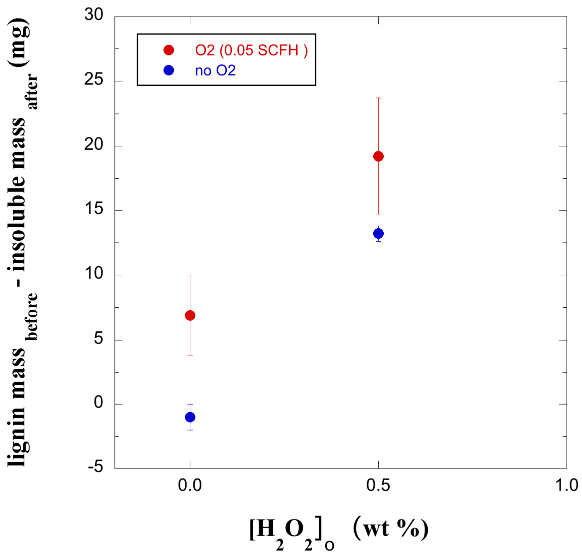


With increase in lignin loading:

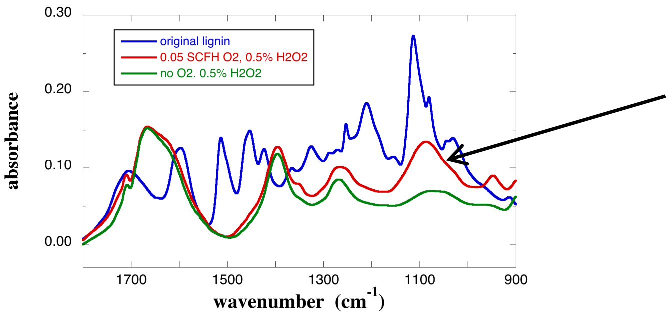
g product / g H_2O_2 increases

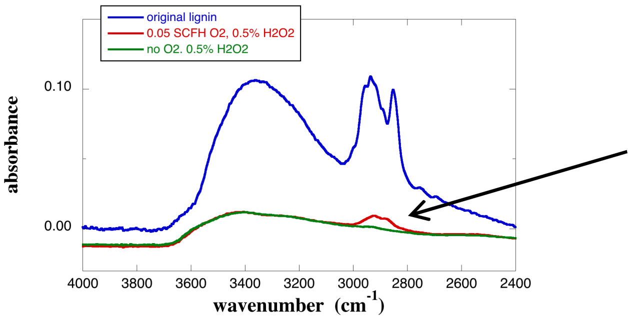
yield as % of total lignin decreases

Effect of O2 bubbling

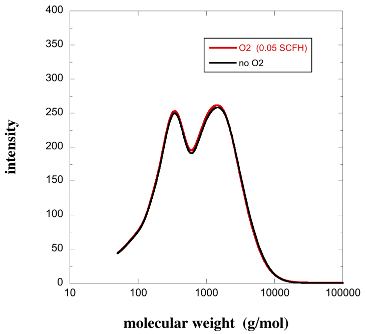


O_2 bubbling increases yield by 45%





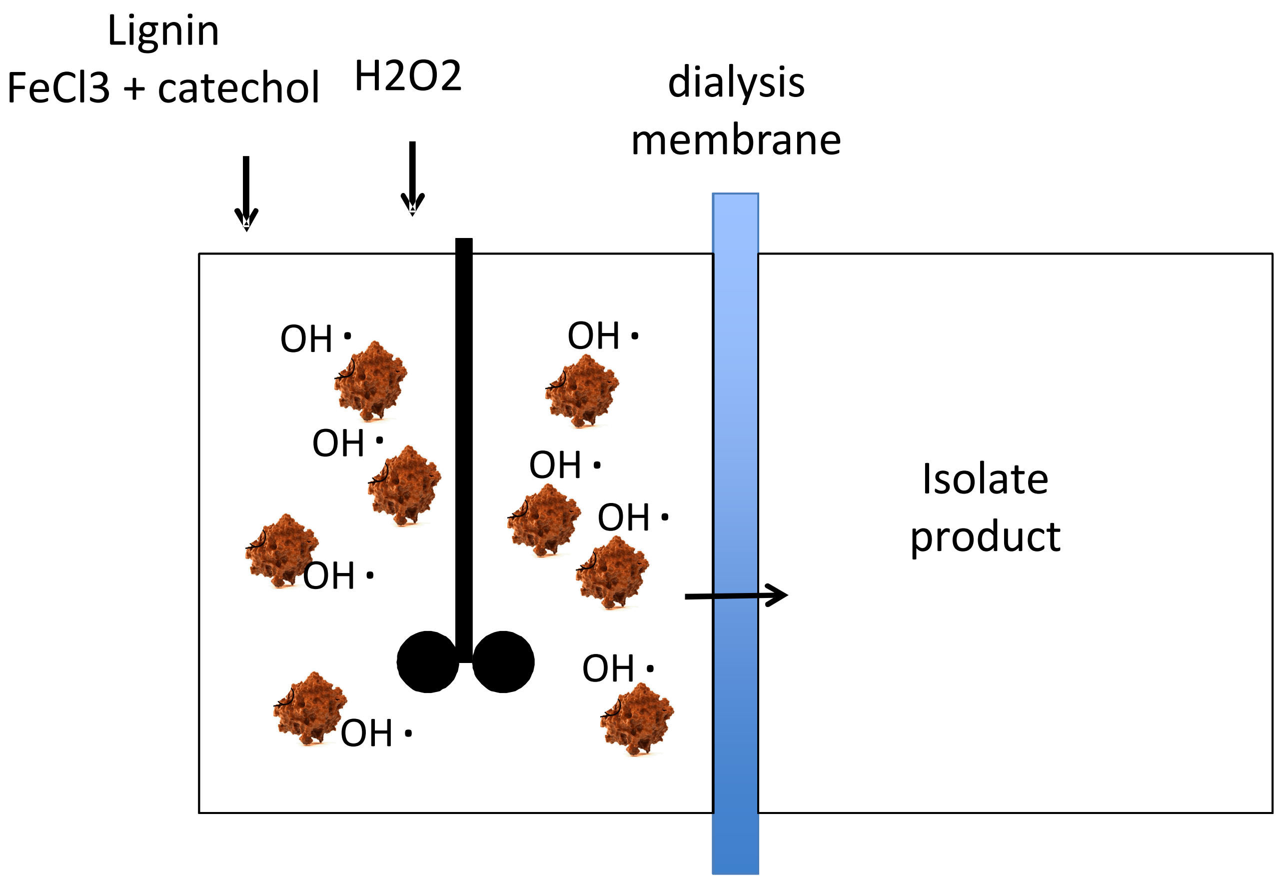
O_2 bubbling: extensive ring opening but some methoxy groups remain



O_2 bubbling: little effect on MW distribution

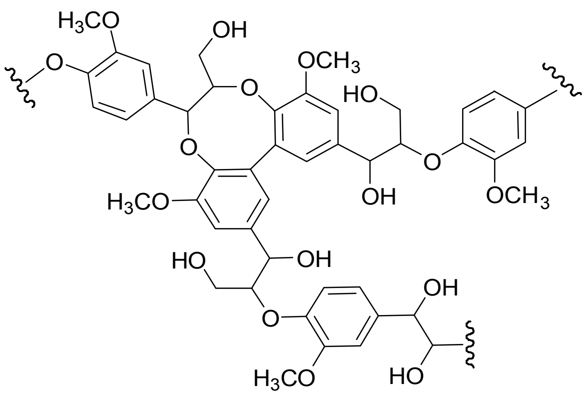
SUMMARY

Continuous process



heterogeneous catalyst?

GENERATE H2O2 IN SITU?

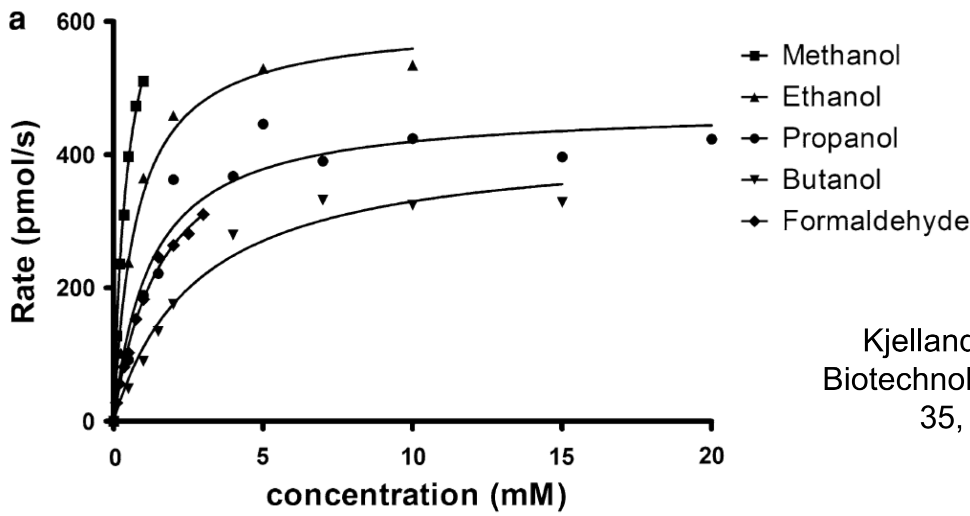


Hydroxyl radical adds to rings, generates methanol

Hammel et al, Enzym. Microb. Technol 2002, 30, 445.

Immobilized enzyme generates H2O2 from methanol

Fig. 1 **a** Rate of H_2O_2-generation as a function of concentration for "good" substrates using the single enzyme reactor in circulating mode. All concentrations are individually set for each alcohol. **b** Rate of H_2O_2-generation as a function of concentration for "poor" substrates using the single enzyme reactor in circulating mode. All concentrations are individually set for each alcohol



Kjellander et al, Biotechnol Lett 2013, 35, 585

OTHER PROBLEMS:

1. relatively small market:

    market for poly(acrylic acid): 5 megatons in 2014
    estimated amount of lignin: 300 megatons (1 billion ton biofuels economy)

2. color: brown

    whiten by removing unsaturated double bonds

3. Fe in product

    heterogenous catalyst, or remove Fe from product

4. high water usage

SUMMARY

Oxidation of lignin using H_2O_2 to produce water-soluble polyelectrolyte

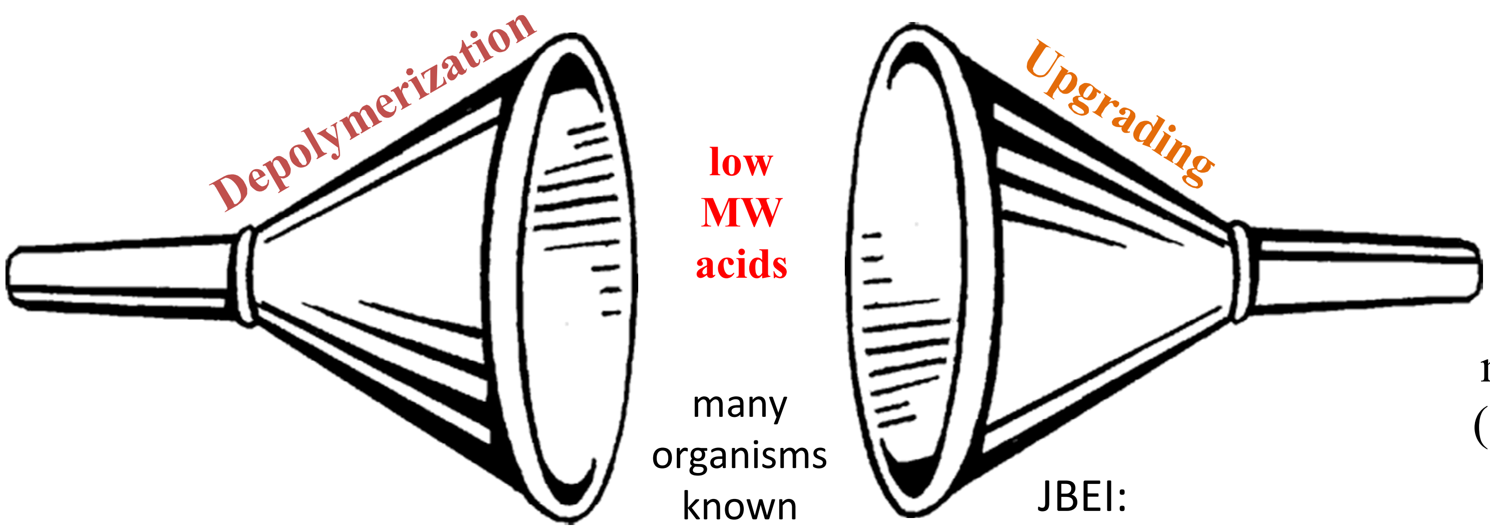
-0.5 to 0.8 g lignin solublized / g H_2O_2 consumed (max. so far)

- yields polyacid with similar MW as original lignin

-water-soluble product has surfactant properties like PAA

BIOLOGICAL FUNNELING

Lignin



low MW acids

many organisms known that consume LMW acids

JBEI:
John Gladden
Steve Singer

biomass (animal feed)

drop-in molecules (e.g. BTX)

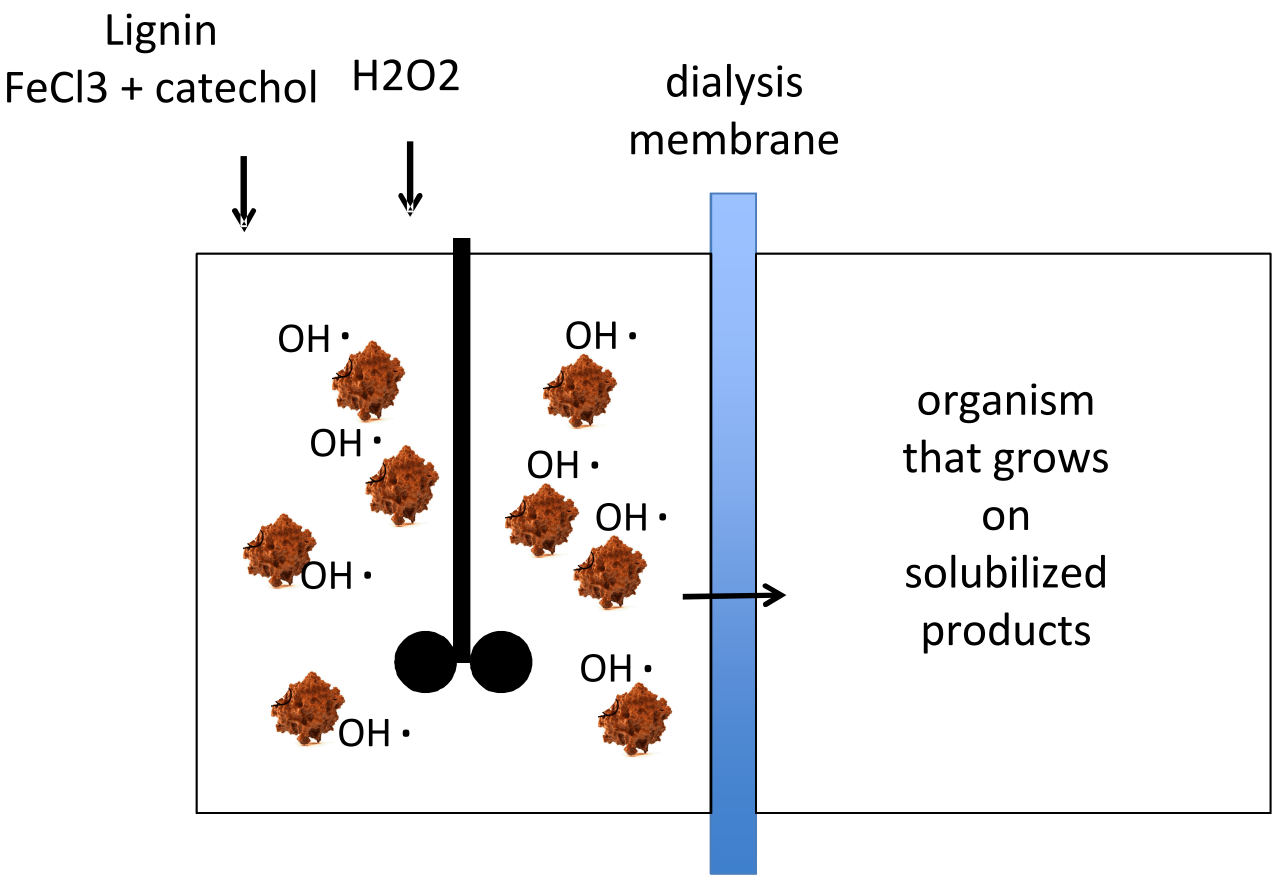
adipic acid etc

Base-catalyzed depolym – cleaves ether bonds (toxicity, low conversion)
Fenton oxidation – opens rings, generates acids

Combine BCD and Fenton, optimize for high % carbon converted by organisms

SUMMARY

Continuous process



heterogeneous catalyst?

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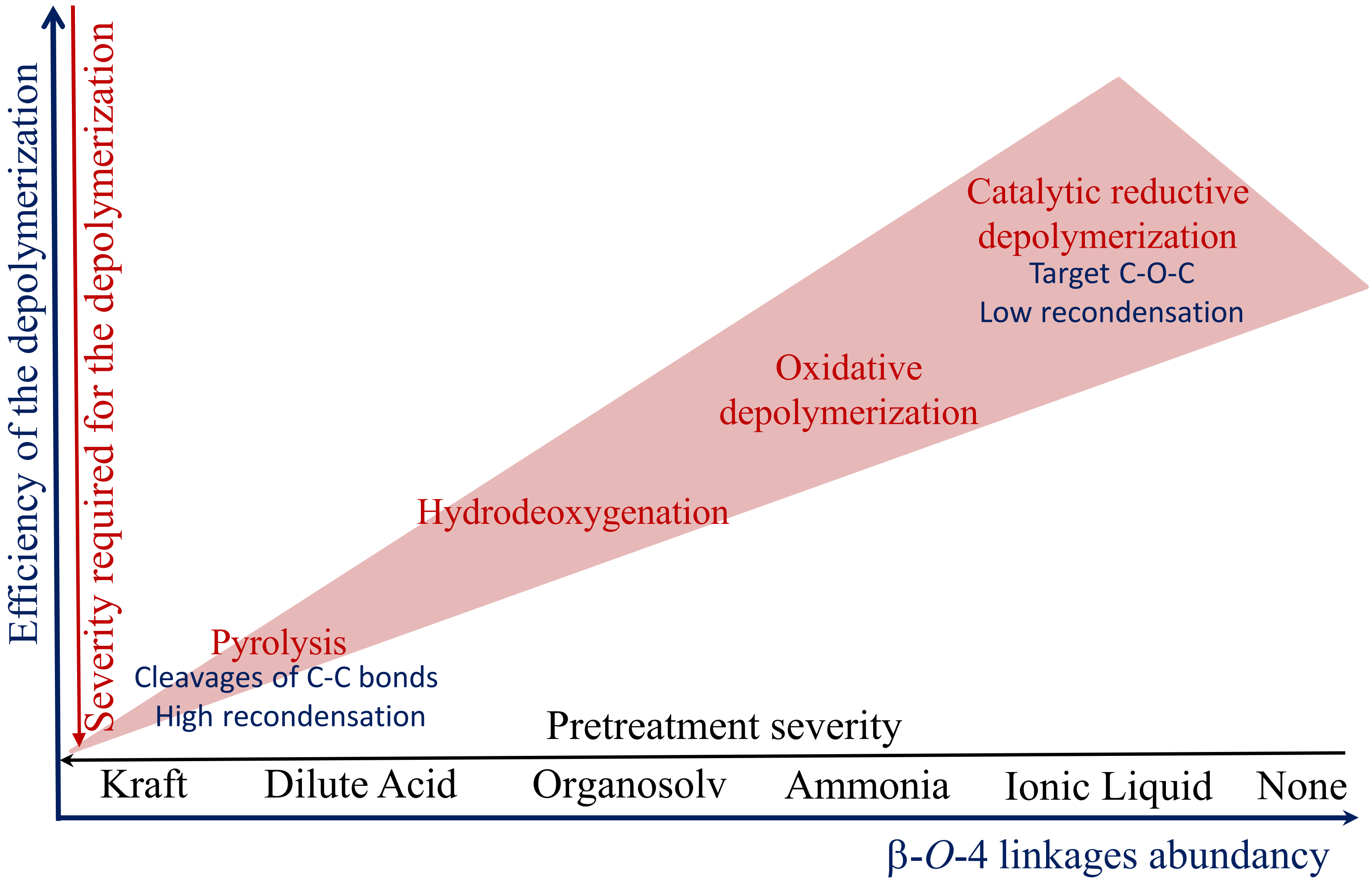
Lignin Depolymerization Approach
A function of biomass pretreatment



- ✓ Higher severity required for depolymerization of highly lignin (e.g. Kraft Lignin)
- ✓ Inversely, Catalytic reductive depolymerization of "native" lignin achieved up to 60% of monomers

Estimate of Theoretical yield

assume all rings opened for soluble product

1 OH radical can open 1 ring : 1 g H_2O_2 per 5.9 g lignin

aromatic ring = ½ mass of lignin monomer

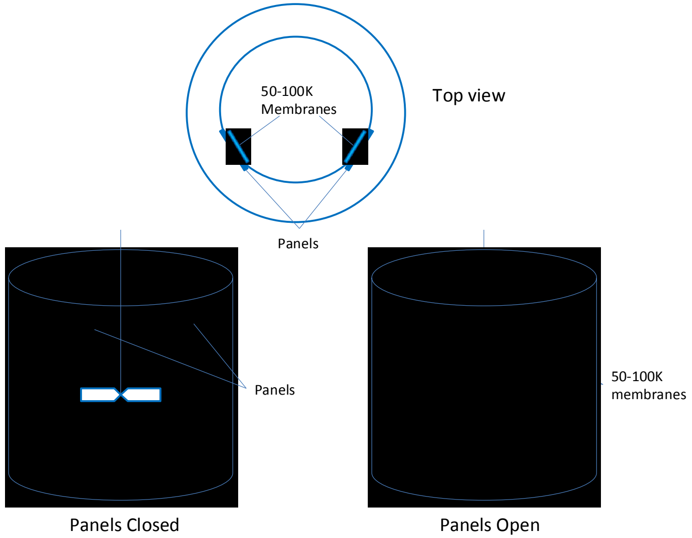
1 methoxy group per aromatic ring

If OH radical adds to aromatic ring at site of methoxy, likely product is MeOH

est theoretical max yield: $5.9 \times ½ \times 5/6 = 2.5$ g lignin/g

current best: 0.7 g lignin/g

Reactor design



RING OPENING CHEMISTRY

Changes in Solution Color During Phenol Oxidation by Fenton Reagent

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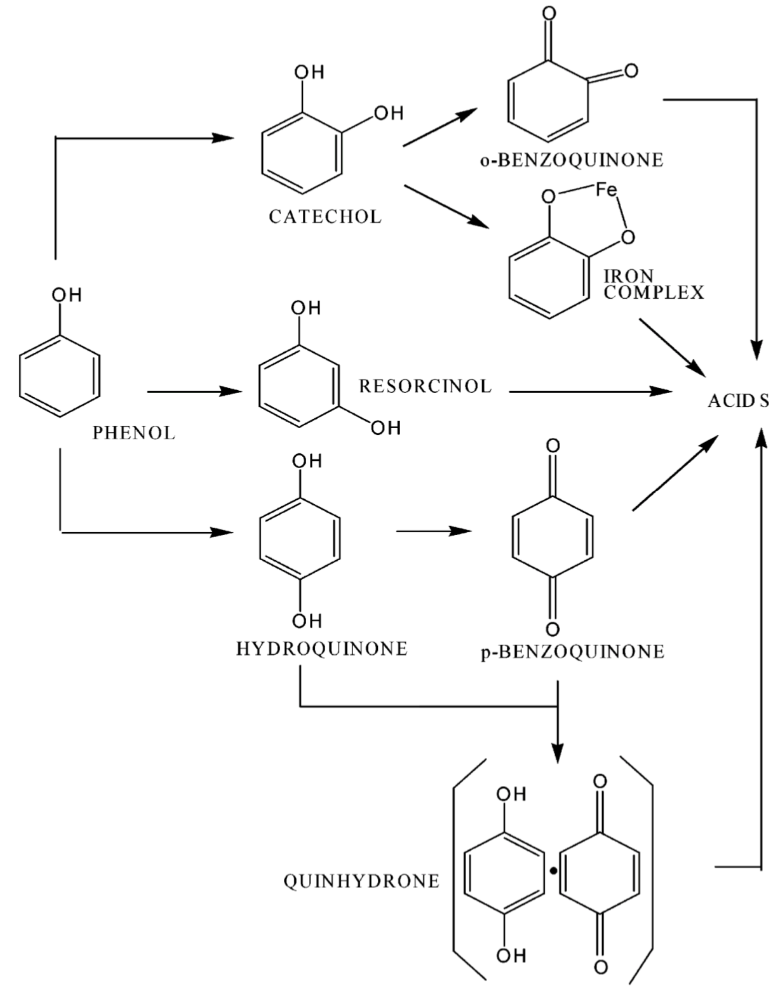

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