Catalytic Lignin Depolymerization in the BioCore Project

J.W. van Hal

J. Wildschut

A. van Zomeren

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ECN

Energy research Centre of the Netherlands

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Jaap W. van Hal, Jelle Wildschut and Andre van Zomeren

BIO-COMMODITY REFINING

A 4-YEAR EU PROJECT

24 partners - 13 countries - 5 SMEs 4 MNI

Cost : 20 274 484 €
EU contribution : 13 920 238 €

Coordination : INRA M. O'Donohue)

EUROPE WORKING TOGETHER FOR TOMORROW'S BIOECONOMY

INRA

VTT

ECN
Energy research Centre of the Netherlands

cimv
Biomass technologies

Chimar Hellas S.A.

ARKEMA

ifeu

KATHOLIEKE UNIVERSITEIT LEUVEN

SYRAL
Formulae of the future

Tarkett
THE ULTIMATE FLOORING EXPERIENCE

synpo

WAGENINGEN UR
For quality of life

CHALMERS

koksnes ķīmijas institūts
institute of wood chemistry

INRA Transfert
Filiale de l'INRA

teri

SZENT ISTVÁN EGYETEM GÖDÖLLŐ
Tudománnyal a vidék felemelkedéséért!

capax
environmental services

WE CREATE SUSTAINABLE GROWTH

DSM

nova Institut
für Ökologie und Innovation

Solagro

Imperial College London

biocore

SEVENTH FRAMEWORK PROGRAMME

OPTIMAL BIOMASS CRACKING

- CIMV Organosolv
  - Uses a formic/acetic peracid system
  - Produces three useable fractions
    - Obeys the « whole biomass principle »
    - Produces valuable lignins and partially depolymerized hemicellulose
  - Pilot operation underway since 2006

biocore

Varied biomass

Fractionation

Intermediates

Chemistry Biotechnology

Hemicellulose

Cellulose

Lignin

Final products

2nd generation fuels

Ethanol

Thermoplastics

PVC, polyolefins, polyurethanes, polyesters

Resins/Adhesives

Food additives

Detergents

Wood panels

Application sectors

Energy

Materials

Packaging

Building

Adhesives and paints

Petten: energy research capital of Europe

Petten: energy research capital of Europe

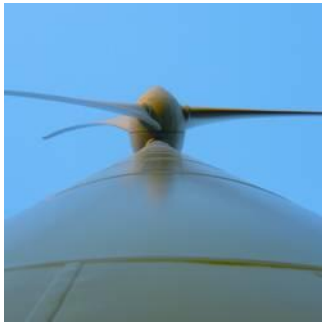
Core competence

Cooperation and worldwide networks

R&D units

Solar energy

Biomass



Wind energy

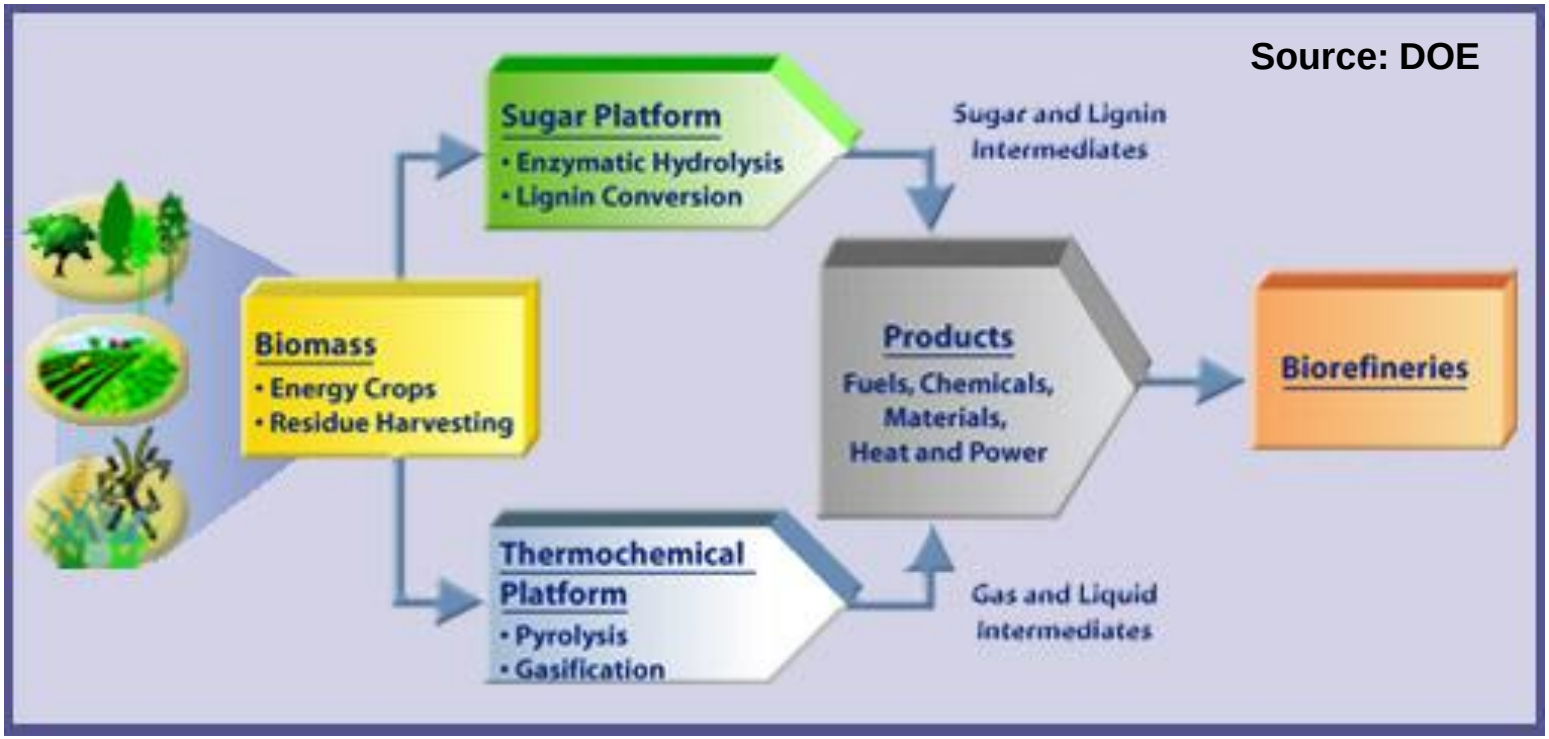
Efficiency & Infrastructure

Policy Studies

Biomass, Coal and Environmental research

- Heat and Power
  - Co-firing, B2O torrefaction, CHP, …
- Syn-gas and SNG
  - Milena gasification, Olga tar removal, ..
- Carbon Capture Technologies
  - CO_2 capture, H_2 production,..
- RISMIL
  - Leaching, NO_x emissions,…..

Chemicals from biomass by biorefining



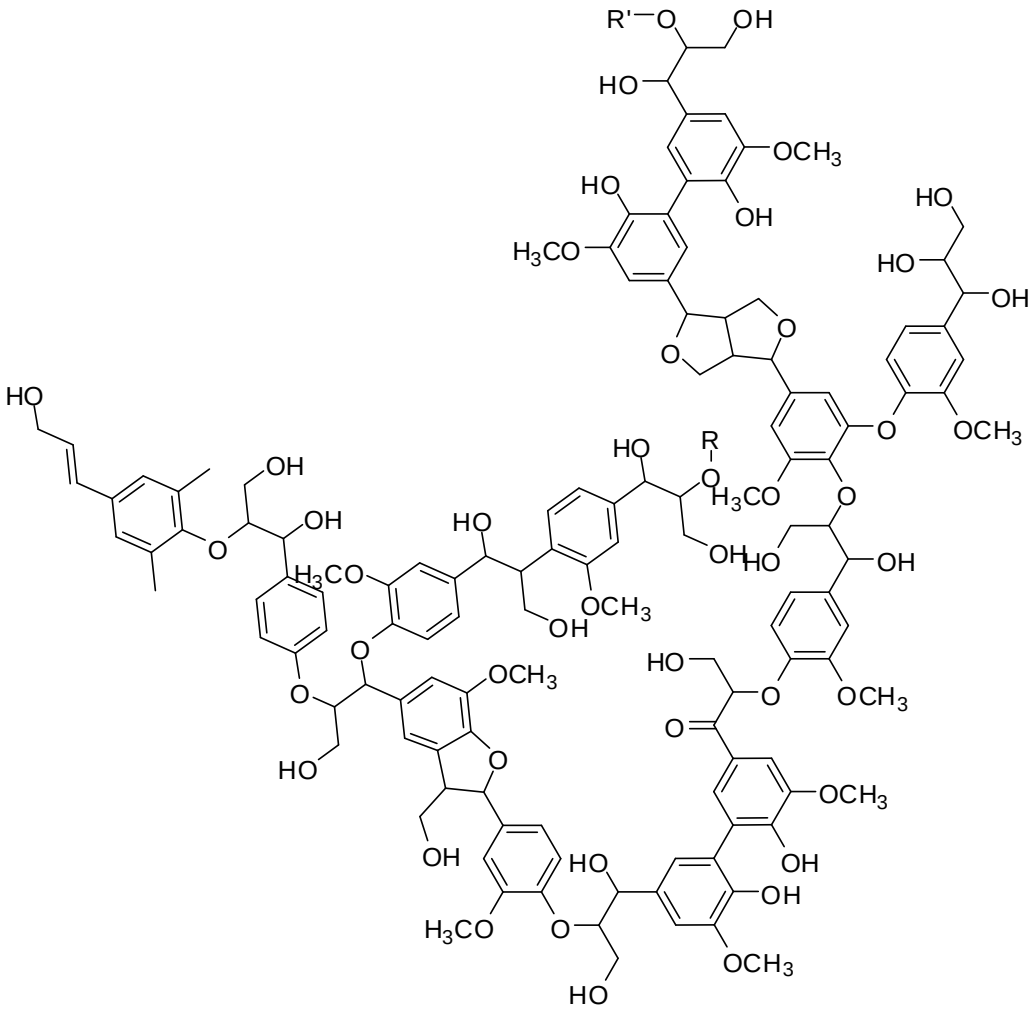
Aim: Adapt MCC process to lignin

- Selective liquid phase oxidation of lignin
- Similar to oxidation of p-xylene to teraphtalic acid (BP/Amaco Midcentury Process, MCC)
- Solvents of choice:
  - Acetic acid/formic acid (mixtures)
  - CIMV Pulping Liquid
  - Compare with acetic acid
  - Compare lignins

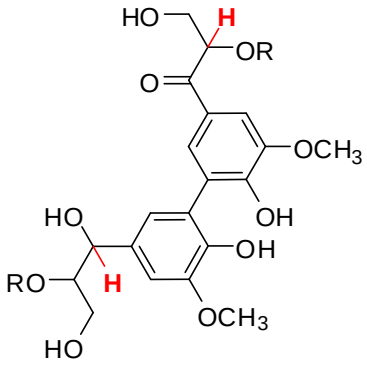
Lignin Oxidation in Acetic Acid

- Batch, No Continuous Air Feed
- Products
  - Vanillin
  - Vanillic acid
  - Syringaldehyde
  - Syringic acid
  - Furfural
  - Etc.
- Ref: Partenheimer, *Adv. Synth. Cat.*, **2009**, 351(3), 456-466

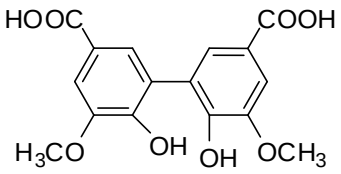
The Structure of Lignin



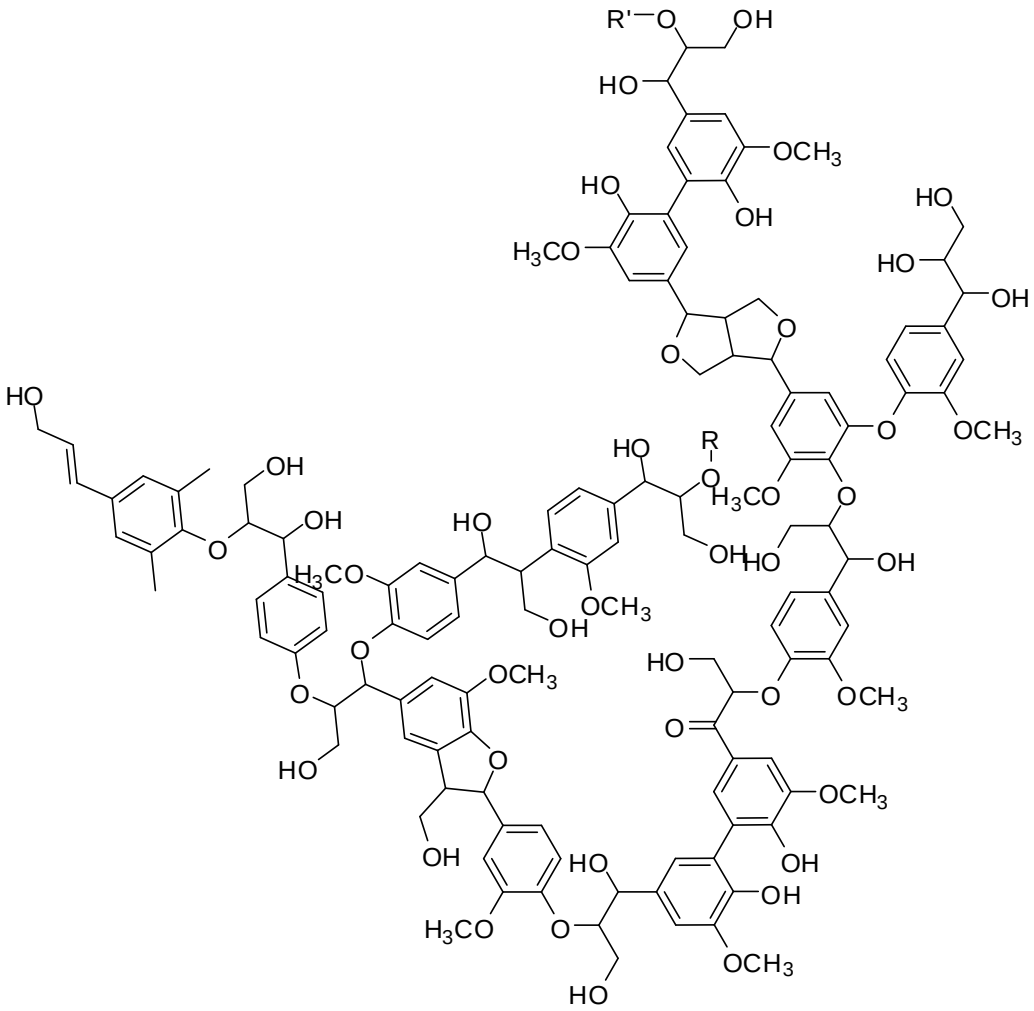
The Structure of Lignin



The Structure of Lignin



The Structure of Lignin



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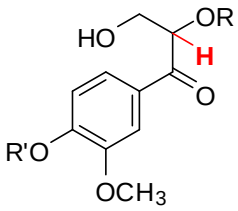

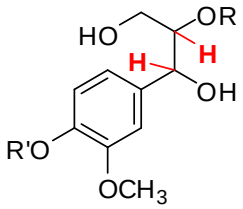

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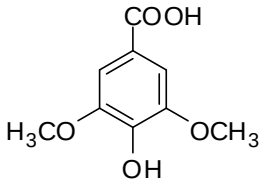

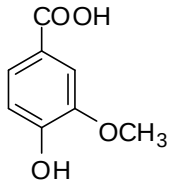

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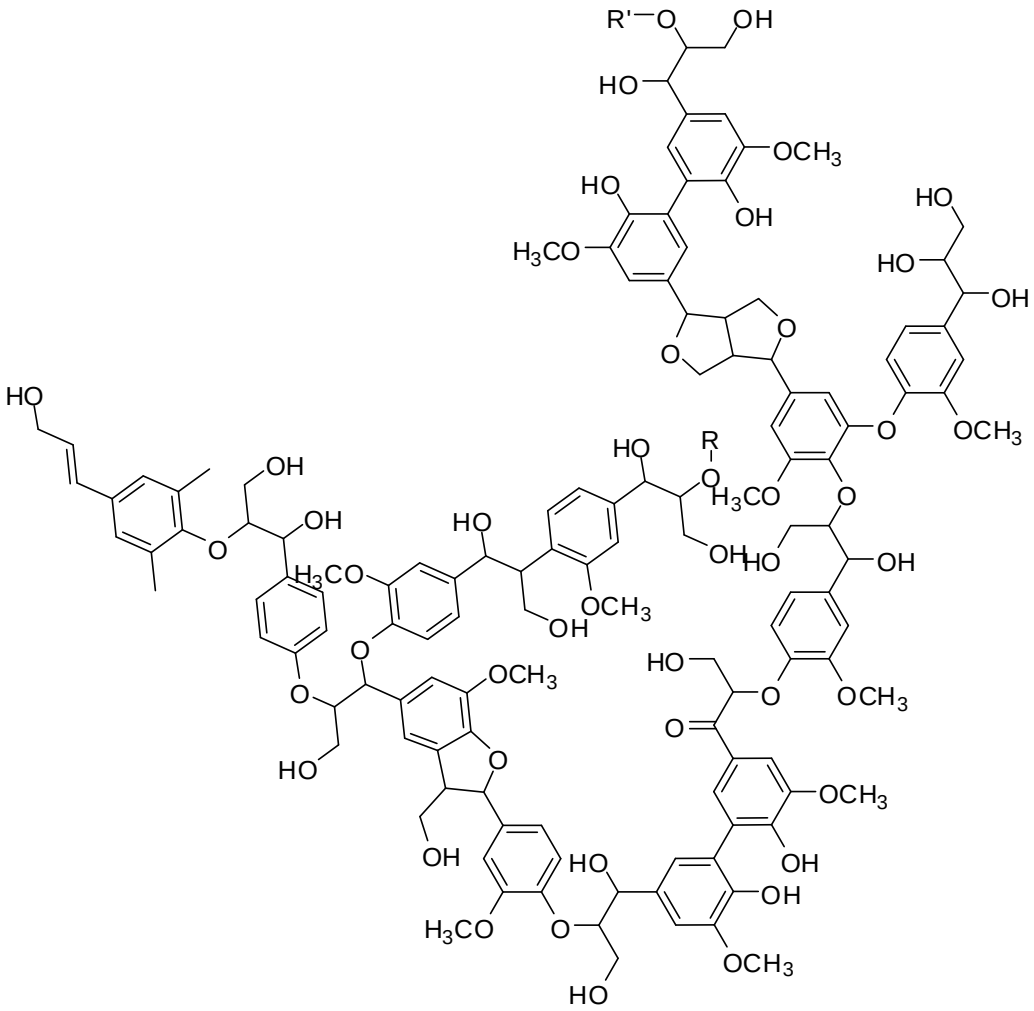

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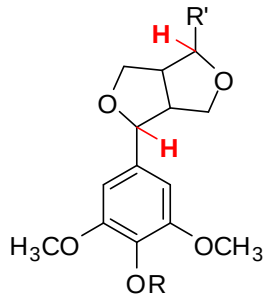

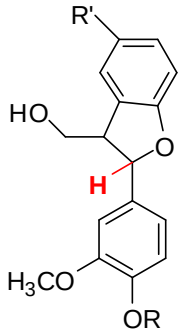

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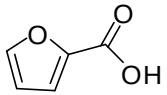
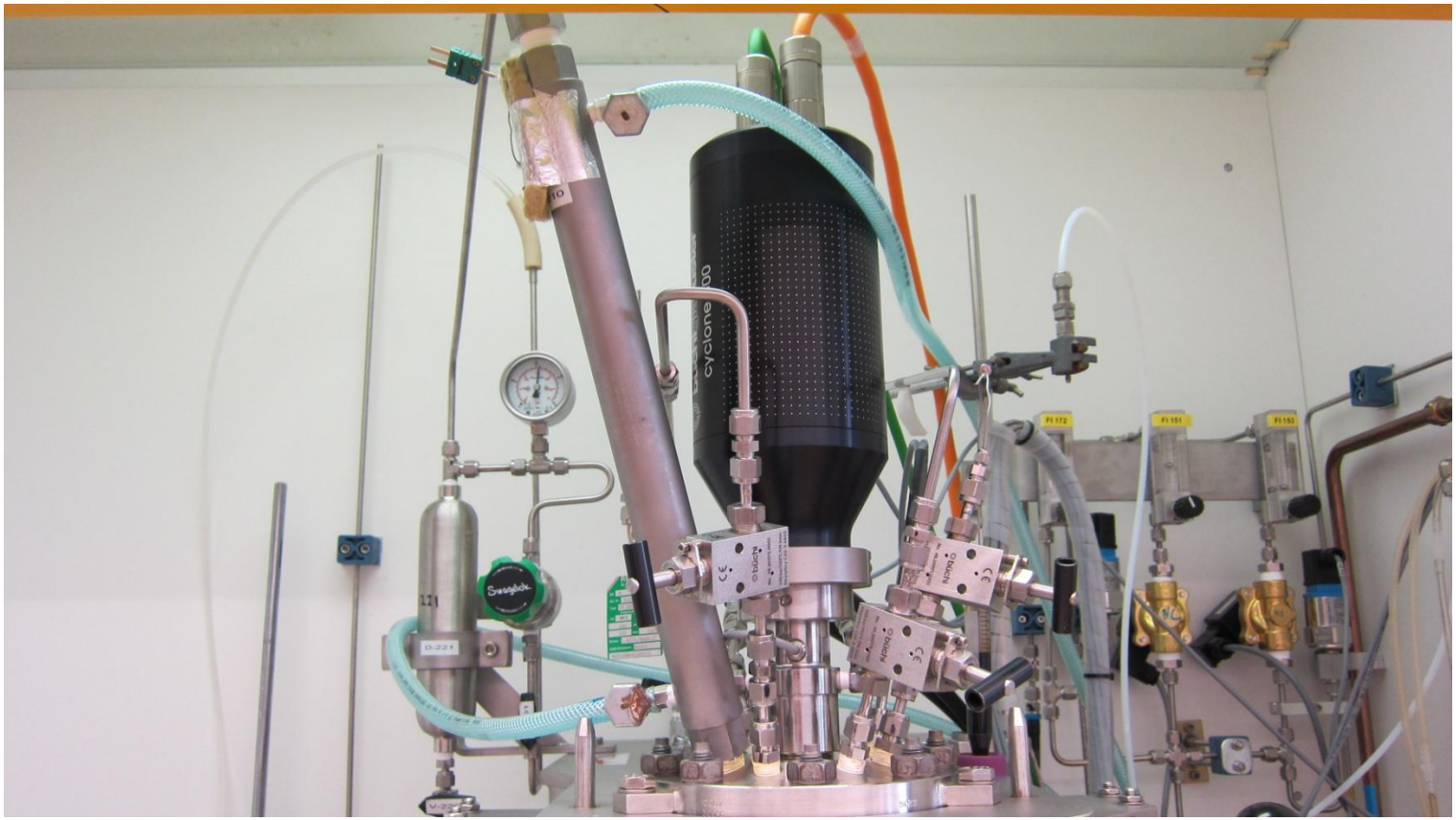


Fed Batch setup



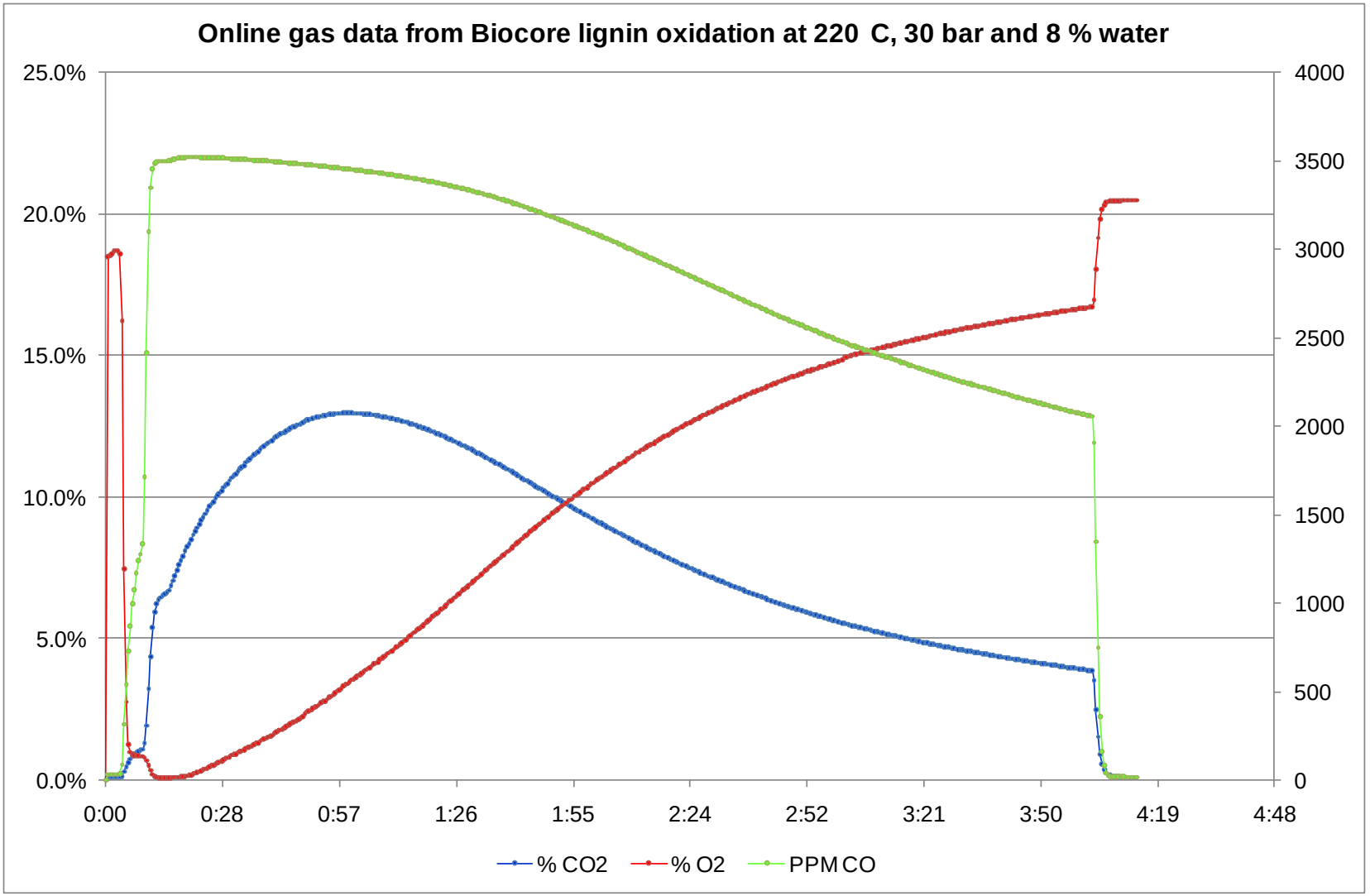
Fed Batch Setup

Experimental matrix

- Effect of Lignin
  - Allcell, CIMV, ECN
- Effect of solvent
  - Formic acid, water
- Effect of temperature
- Effect of flow
- Effect of stir speed
- Effect of catalyst
- Effect of reaction time

Analysis

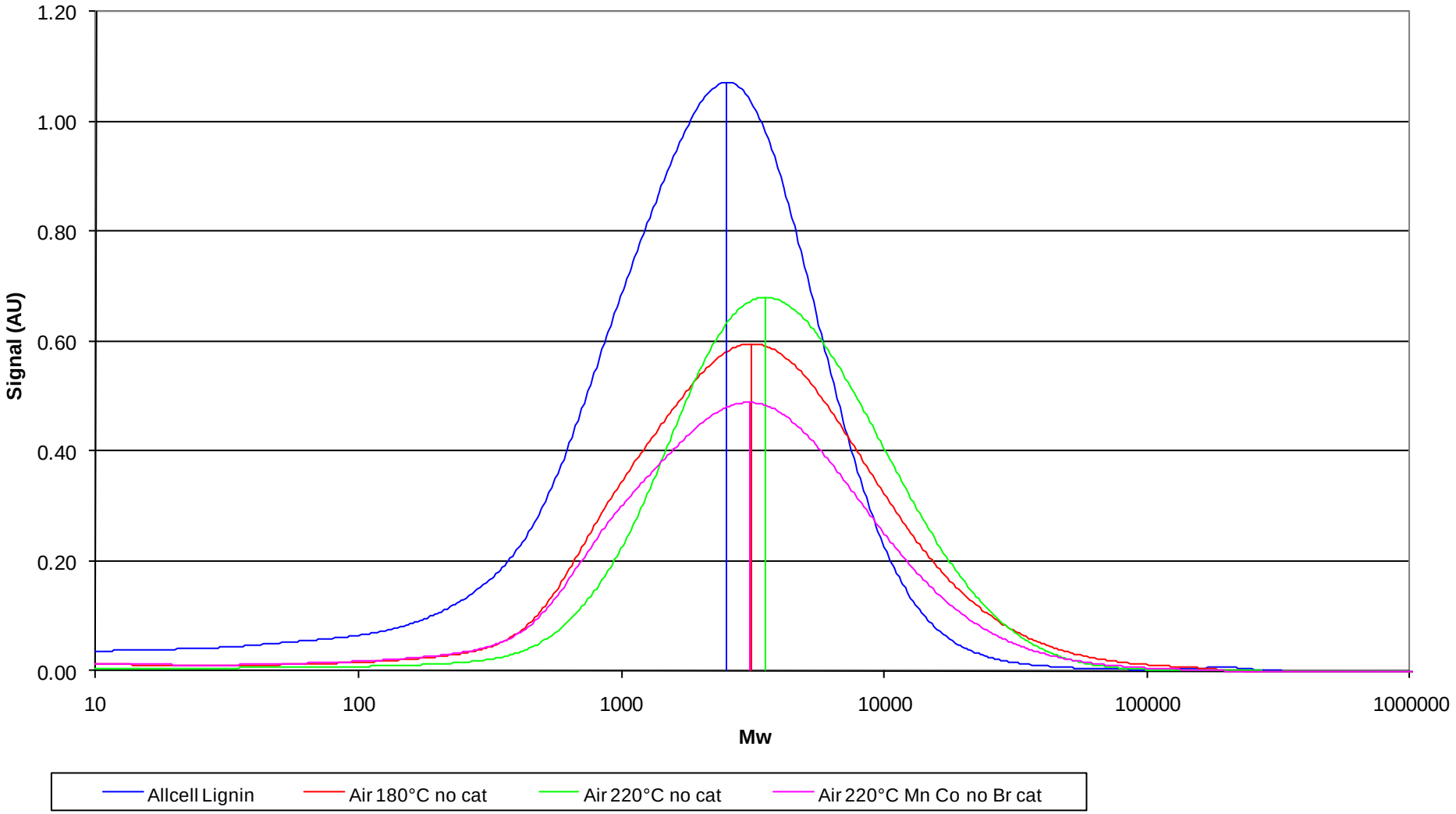
- Gas
  - O_2, CO_2, CO, online (analyzer)
- Solids:
  - SEC
- Liquid fraction
  - GC-MS, SEC (of the solids)


Online gas data from Biocore lignin oxidation at 220 C, 30 bar and 8 % water
25.0%
20.0%
15.0%
10.0%
5.0%
0.0%
4000
3500
3000
2500
2000
1500
1000
500
0
0:00
0:28
0:57
1:26
1:55
2:24
2:52
3:21
3:50
4:19
4:48
% CO2
% O2
PPM CO

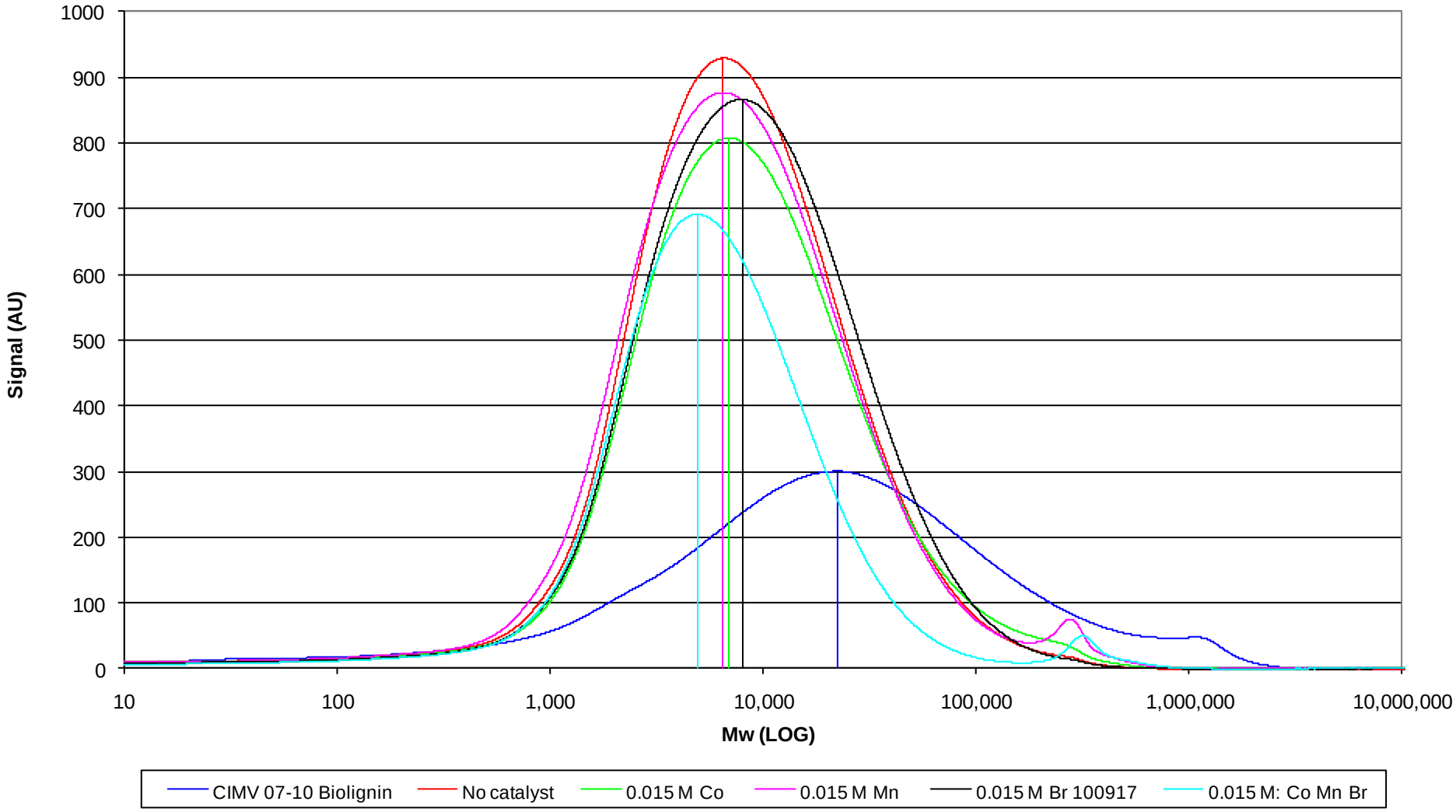
Monomeric phenols from oxidation of Biolignin in acetic acid

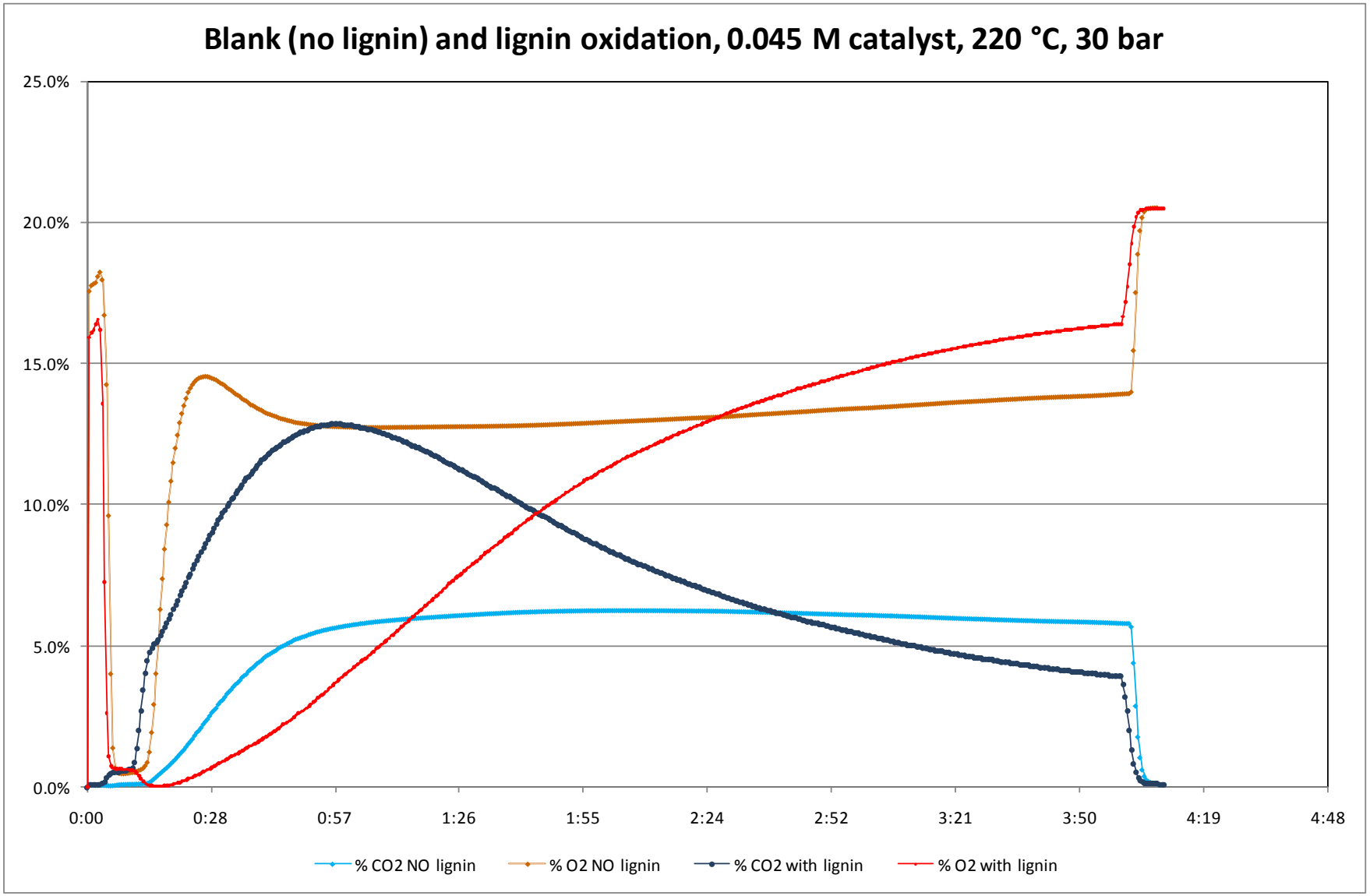
T (°C)	Time (min.)	Gas	Catalyst system	Code	Vanillin	Syring-aldehyde	4-hydroxy-benzaldehyde
220	120	N_2	None	100909	74	50	20
220	120	air	None	100910	56	30	13
220	120	air	0.015M Co/Mn IL	100928	27	21	0.0
180	120	air	0.015M Co/Mn IL	101001	382	301	89
150	120	air	0.015M Co/Mn IL	100930	433	255	94
180	120	air	6.9 mM Co, 6.9mM Mn, 0.69 mM Zr, 13.8 mM IL	101004	365	222	91

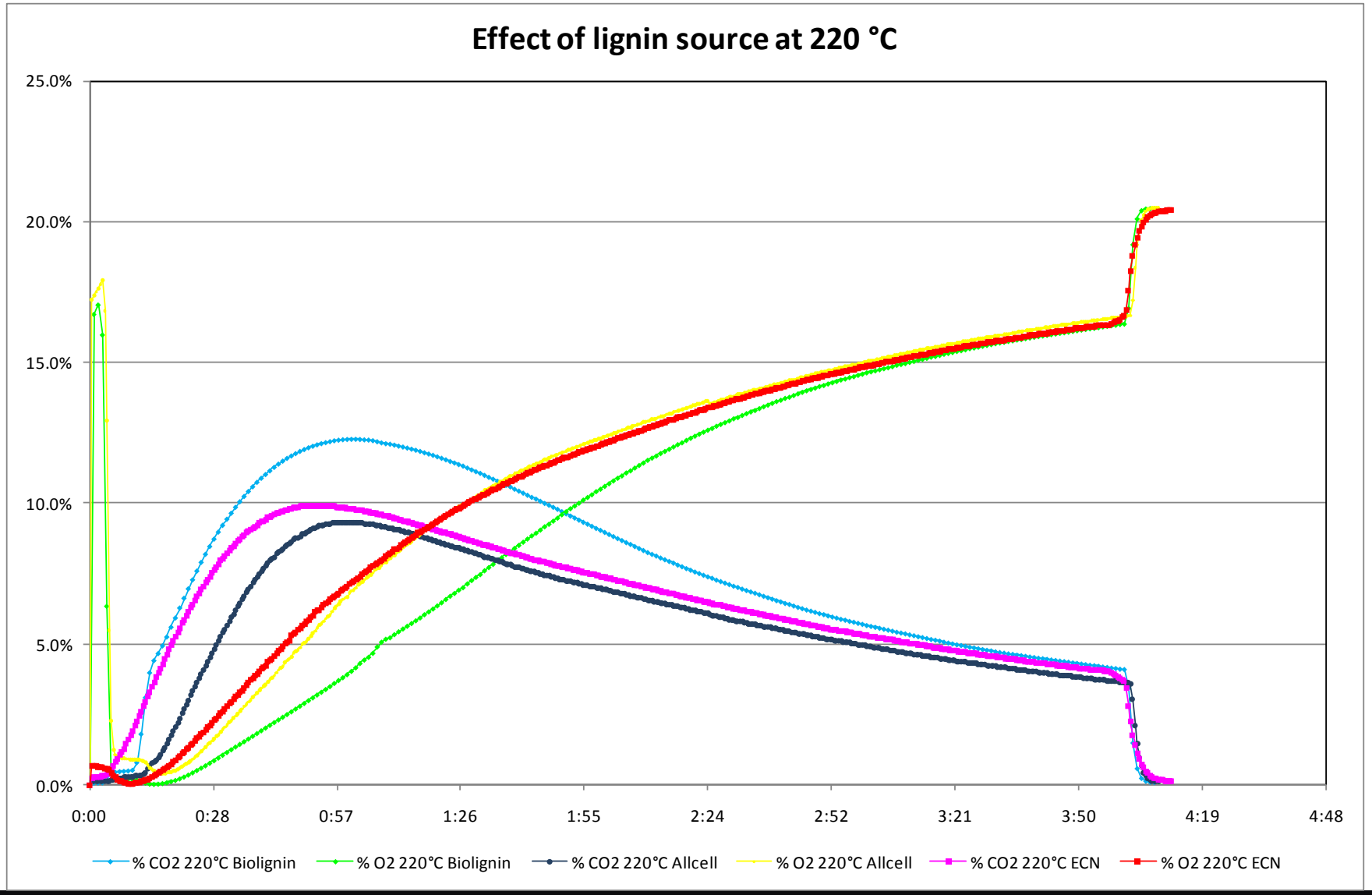
Results from the allcell lignin oxidation in 10% formic acid/ acetic acid



Comparison of no catalyst, single component and triple component catalyst at 220 °C, 30 bar, 120'




Blank (no lignin) and lignin oxidation, 0.045 M catalyst, 220 °C, 30 bar
25.0%
20.0%
15.0%
10.0%
5.0%
0.0%
0:00
0:28
0:57
1:26
1:55
2:24
2:52
3:21
3:50
4:19
4:48
% CO2 NO lignin
% O2 NO lignin
% CO2 with lignin
% O2 with lignin


Effect of lignin source at 220 °C
25.0%
20.0%
15.0%
10.0%
5.0%
0.0%
0:00
0:28
0:57
1:26
1:55
2:24
2:52
3:21
3:50
4:19
4:48
% CO2 220°C Biolignin
% O2 220°C Biolignin
% CO2 220°C Allcell
% O2 220°C Allcell
% CO2 220°C ECN
% O2 220°C ECN

Trends

- Need three/four component catalyst
  - $Co(OAc)_2$, $Mn(OAc)_2$, "Br^-", optional $Zr(OAc)_4$
- Higher reaction temperatures lead to more depolymerization
- Longer reaction times lead to more depolymerization
- More catalyst leads to more depolymerization
- Reaction is effective even with lignin slurry
- Significant acetic acid burn
- Monomeric phenols only at low temperatures

Further information

Jaap W. van Hal
The Energy Research Center of the Netherlands (ECN)
Biomass, coal and environmental research
Transportation fuels and chemical
P.O. Box 1, 1755 ZG Petten
+31-(0)224-564297
vanhal@ecn.nl
www.ecn.nl
http://www.biocore-europe.org/