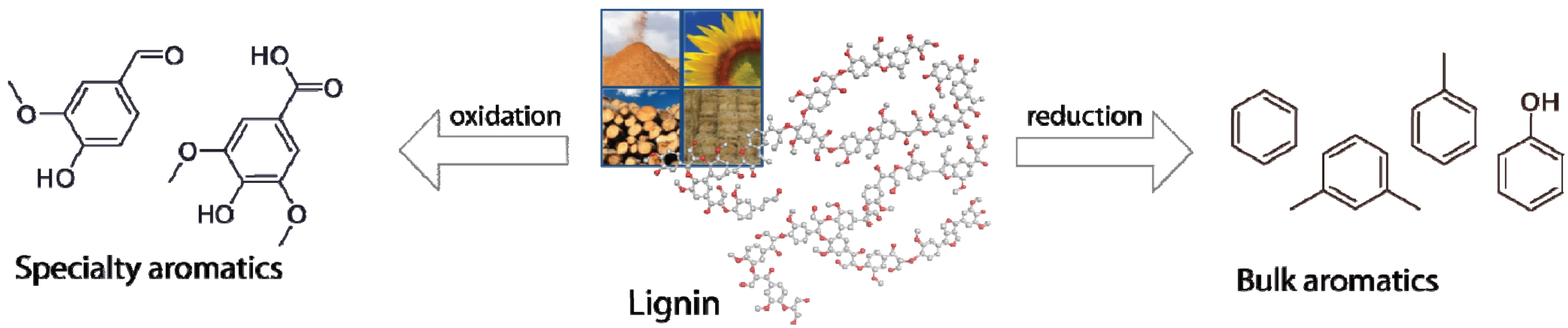
Catalytic Conversion of Lignin and its Derivatives for the Production of Renewable Chemicals



Heterogeneous & Homogeneous Catalysis
In Situ Spectroscopic Methods

Pieter. C. A. Bruijnincx, Joseph Zakzeski, Anna L. Jongerius, and Bert M. Weckhuysen

Universiteit Utrecht

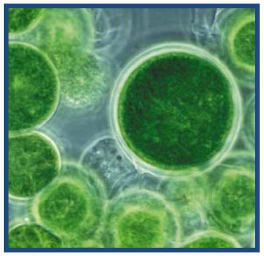
Catalytic Biomass Conversion

- Catalyst/process development

- Mainly focused on bulk chemicals production

- Application of in-situ spectroscopic approach to biomass conversion



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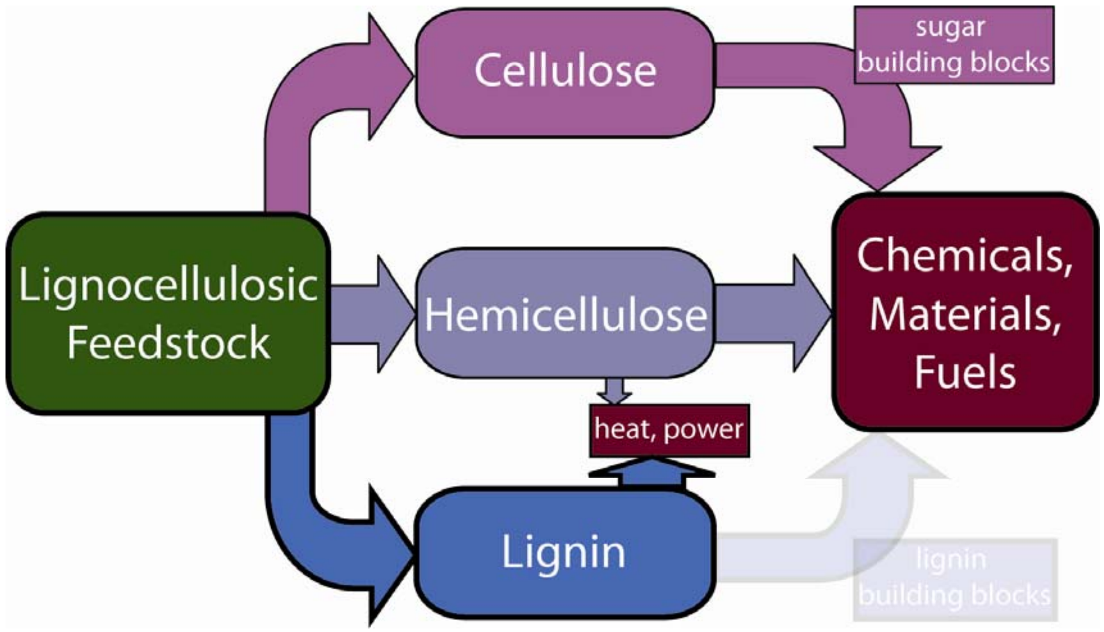
Weckhuysen Group
www.anorg.chem.uu.nl

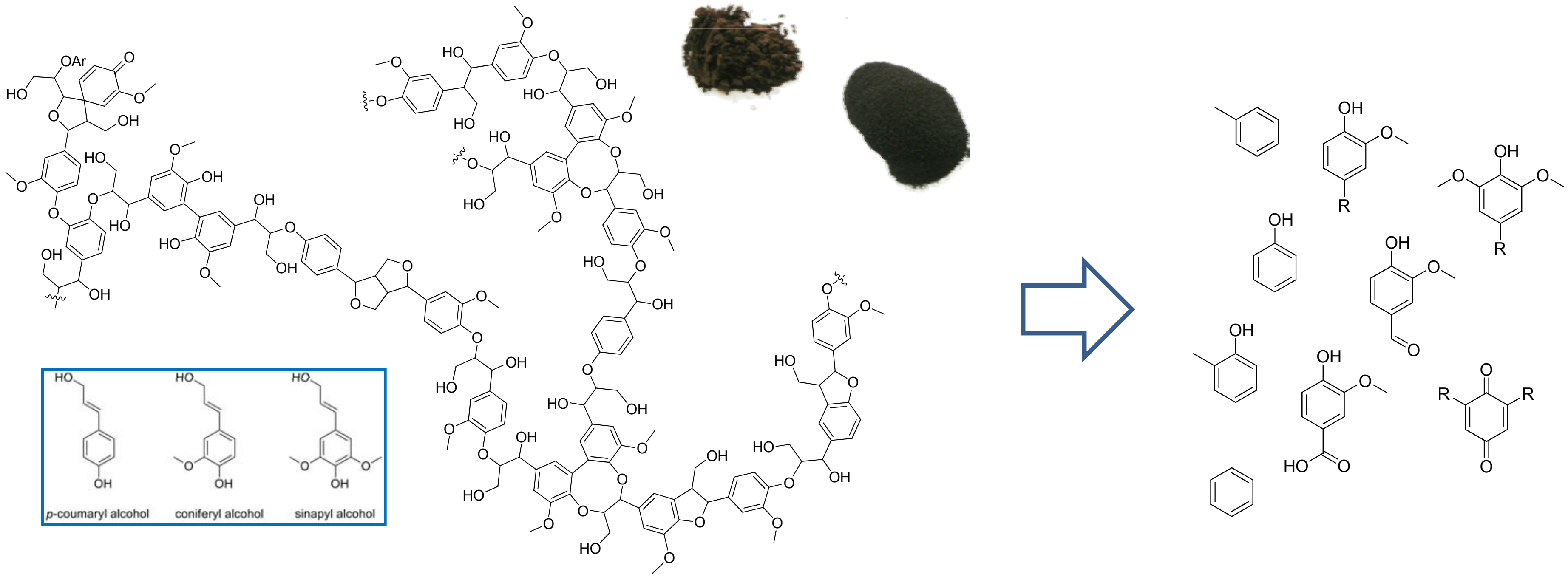


- future biorefinery operations need to produce **high value biobased chemicals** in addition to **lower value biofuels** to be economically competitive

- waste nothing: **all fractions of lignocellulosic biomass** should be valorized

- **catalytic biomass conversion**: lignin receives relatively little attention

Zakzeski, Bruijnincx, Jongerius, Weckhuysen, *Chem. Rev.* **2010**, 110, 3552



Complex, highly aromatic biopolymer:

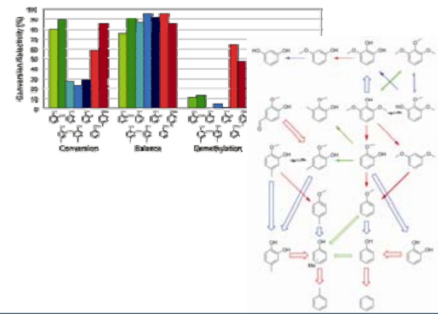
- Structure depends on plant species and pretreatment method
- Many different kinds of functional groups and linkages

- catalytic depolymerization/conversion technology needed

Catalytic Lignin Valorization: Towards Renewable Aromatics

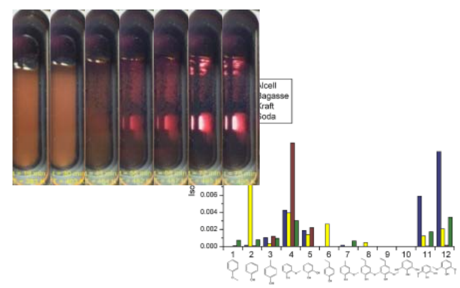
- **Two-step reductive hydrodeoxygenation of lignin**

(J. Catal. 2011, doi:10.1016/j.jcat.2011.10.006)



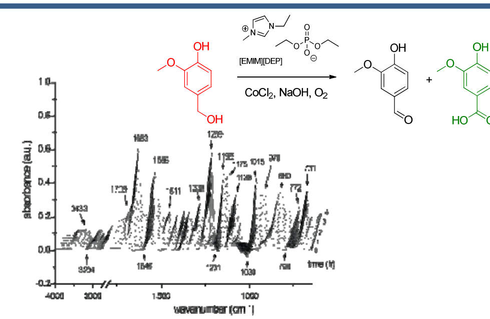
- **Aqueous/Liquid phase reforming of lignin**

(ChemSusChem 2011, 4, 369)



- **Valorisation of lignin by selective oxidation**

(Green Chem. 2010, 12, 1225; Appl. Catal. A 2011, 394, 79)



Two-Step Reductive Hydrodeoxygenation of Lignin

- **Two-step reductive hydrodeoxygenation of lignin**

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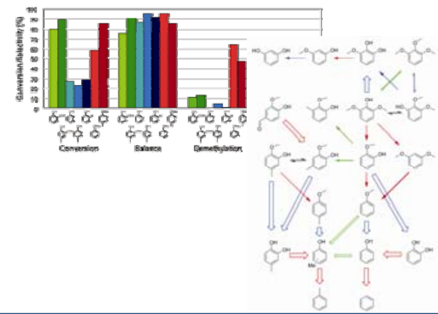
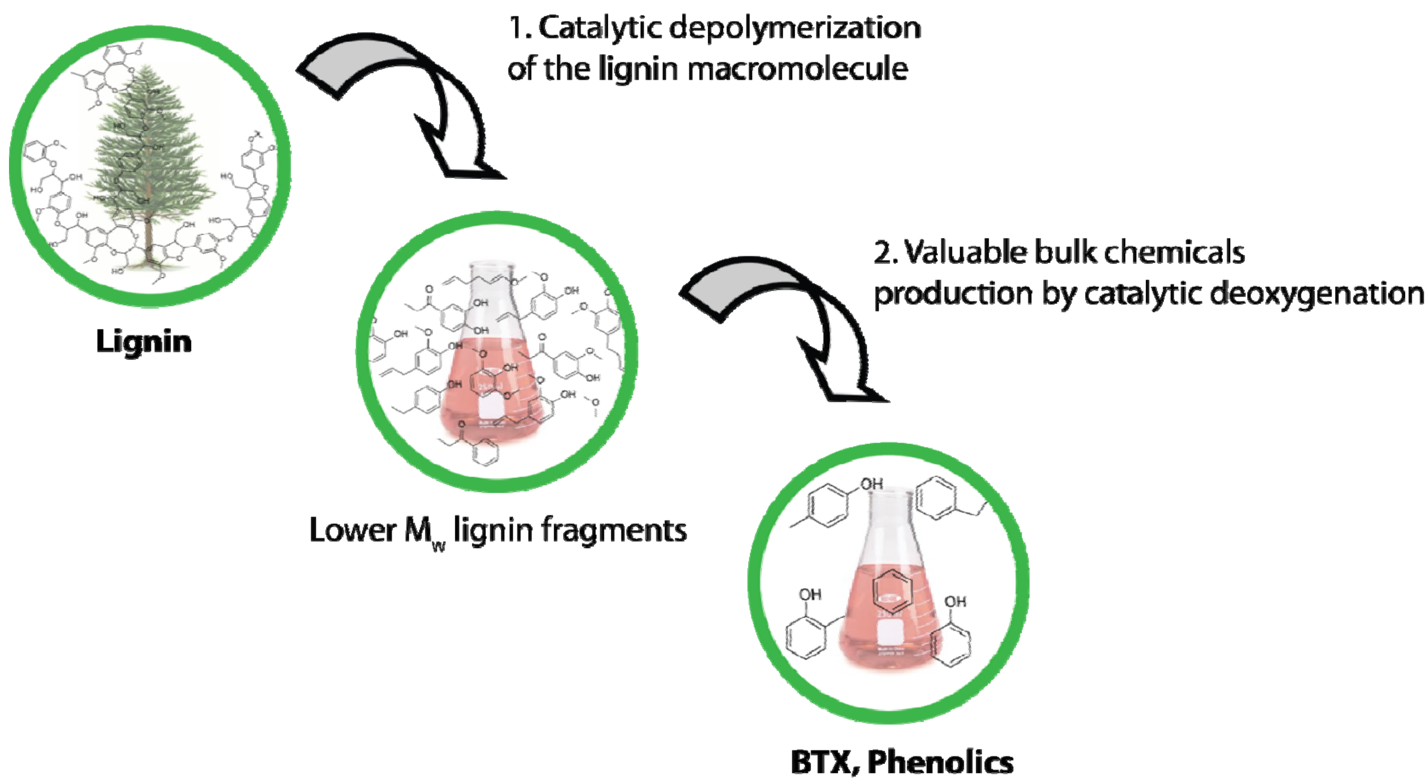


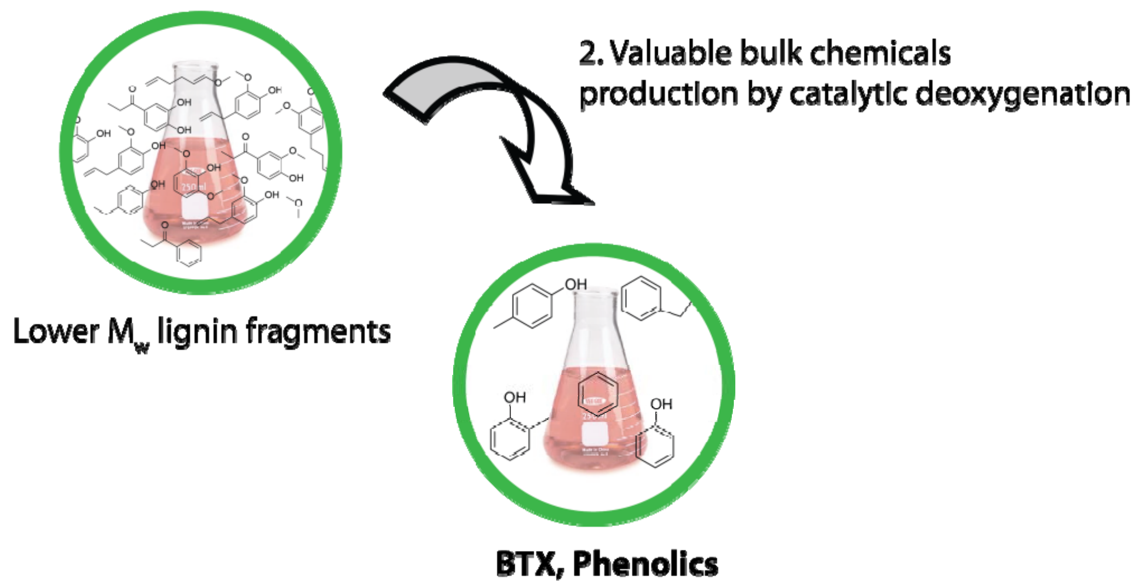


CatchBio

Two-Step Reductive Hydrodeoxygenation of Lignin

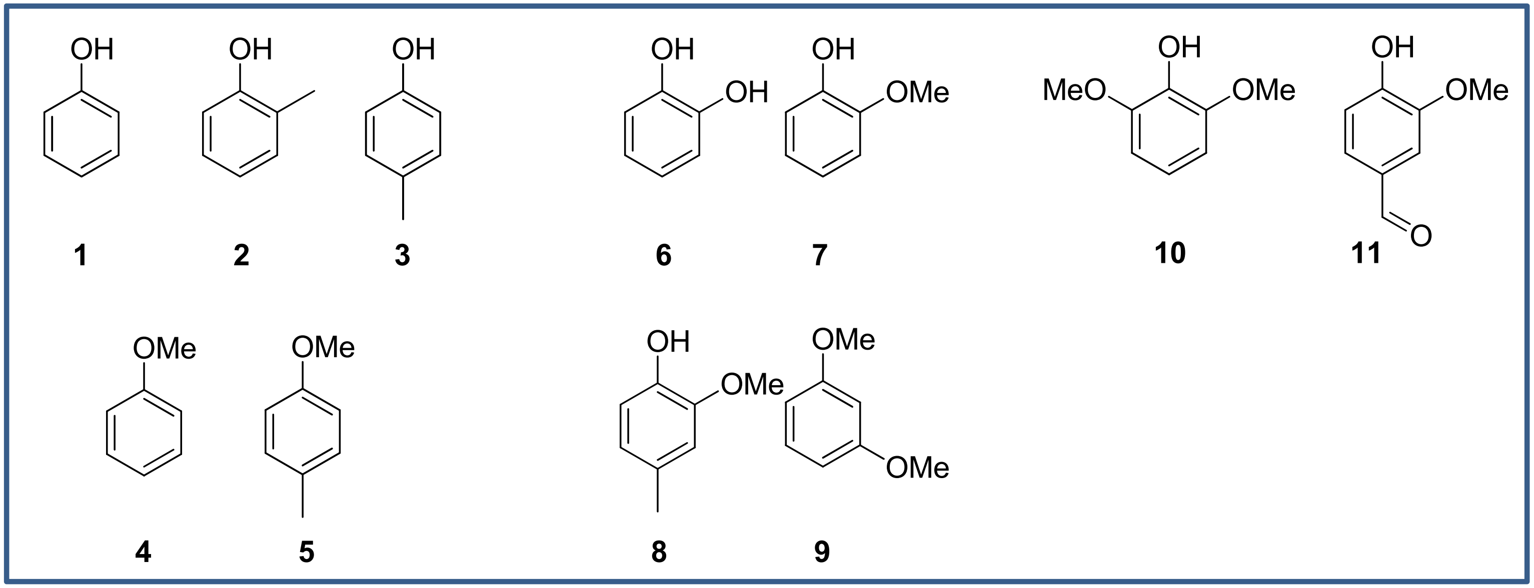
- the production of bulk chemicals from lignin requires a **reduction of the oxygen content** in the final step

- **hydrodeoxygenation** by **sulfided CoMo catalysts** has been explored for the conversion of lignin-derived feed and for upgrading of bio-oils



Lignin HDO: Model compound Studies

- **A systematic study** on the hydrodeoxygenation of **a library of aromatic oxygenates** by sulfided CoMo catalysts:

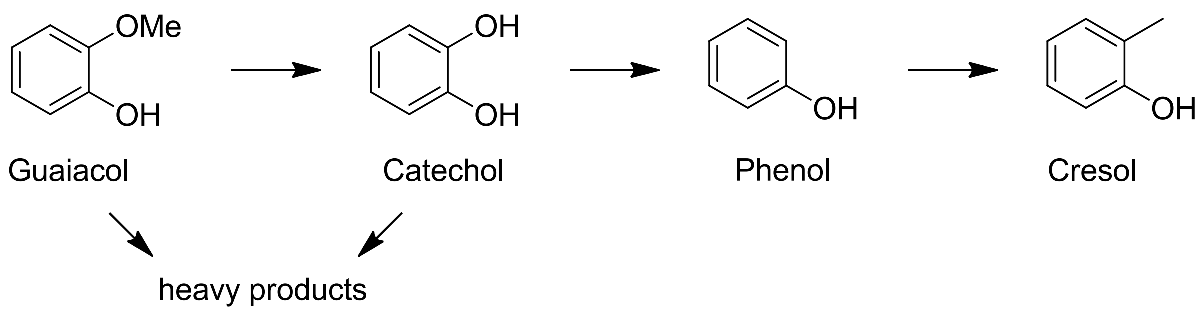


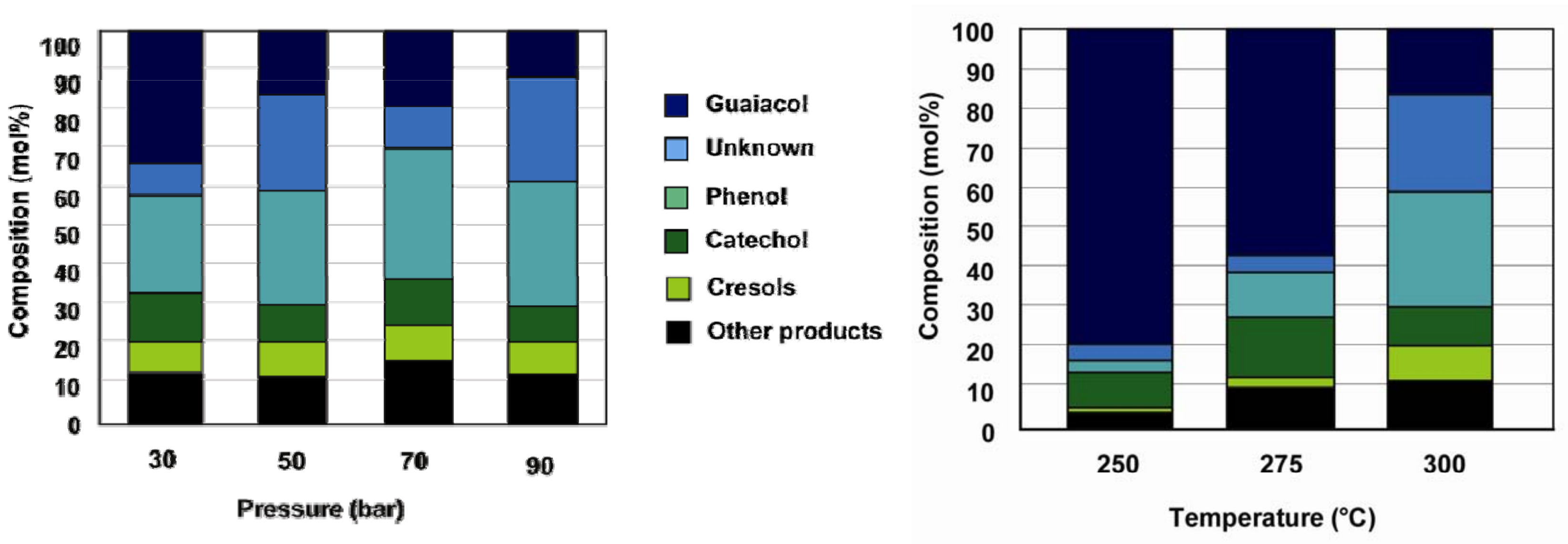
Typical experimental conditions:

- 100 mL batch autoclave
- Catalyst: presulfided, activated $CoMo/Al_2O_3$ from Albemarle Catalysts
- Reaction conditions: 300 °C, 50 bar H_2, 4h, dodecane solvent

Lignin HDO: Model compound Studies

- **Guaiacol** as a typical example:

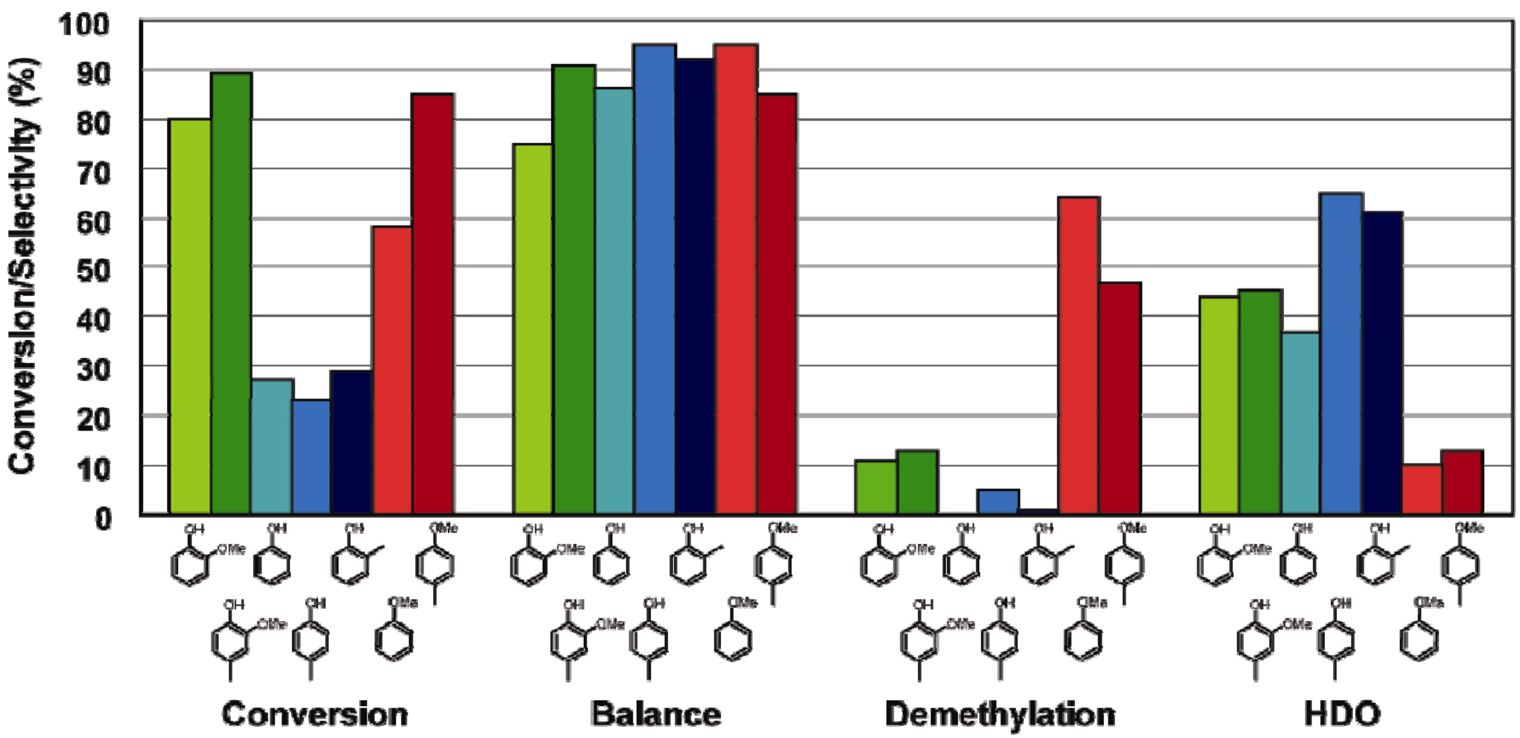




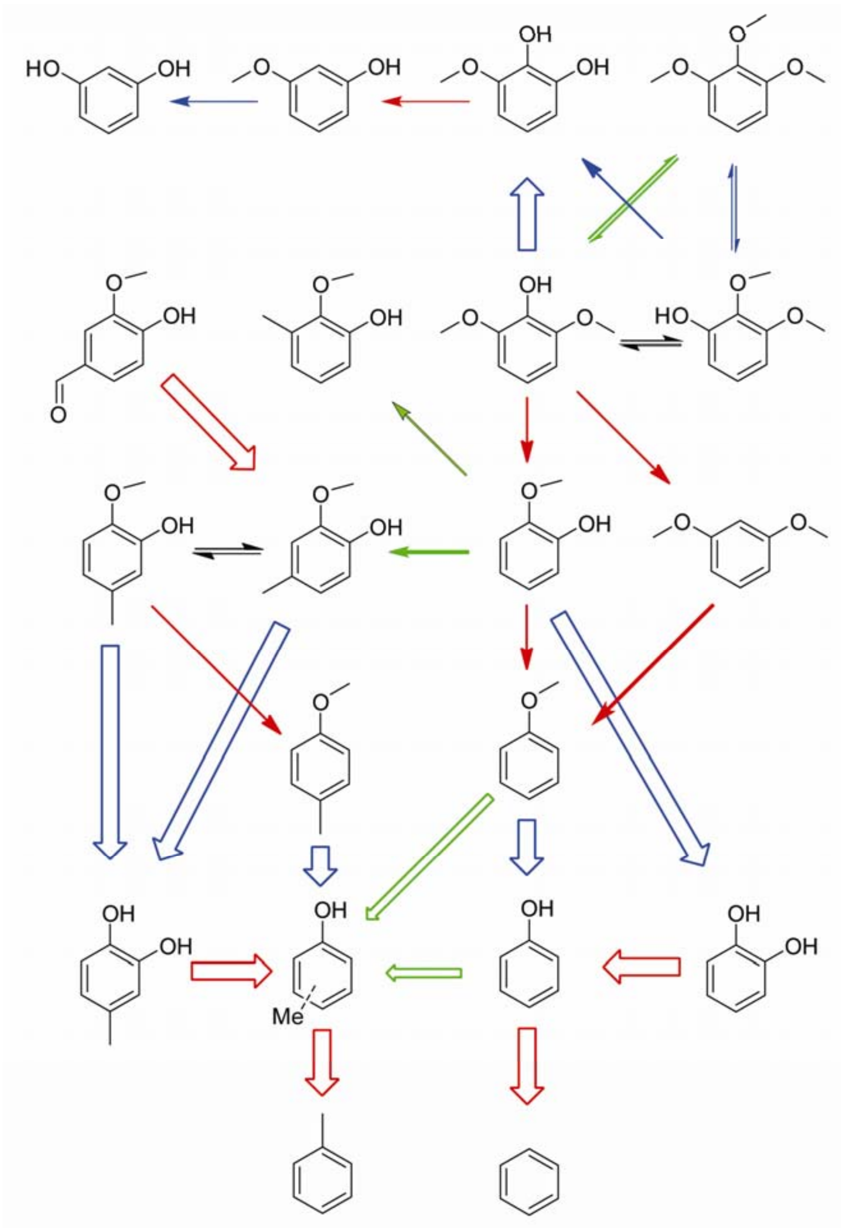
Jongerius, Jastrzebski, Bruijnincx, Weckhuysen, *J. Catal.*, 2011, doi:10.1016/j.jcat.2011.10.006

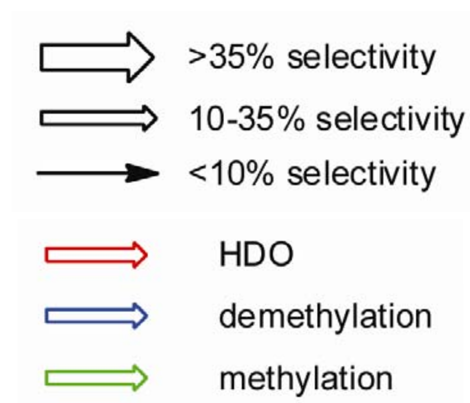
Lignin HDO: Model compound Studies

- Typical conversion around 80%, less for mono-oxygenated compounds
- Mass balance between 75% and 95%, heavy products not quantified
- Selectivity towards demethylation and HDO changes with the substrate

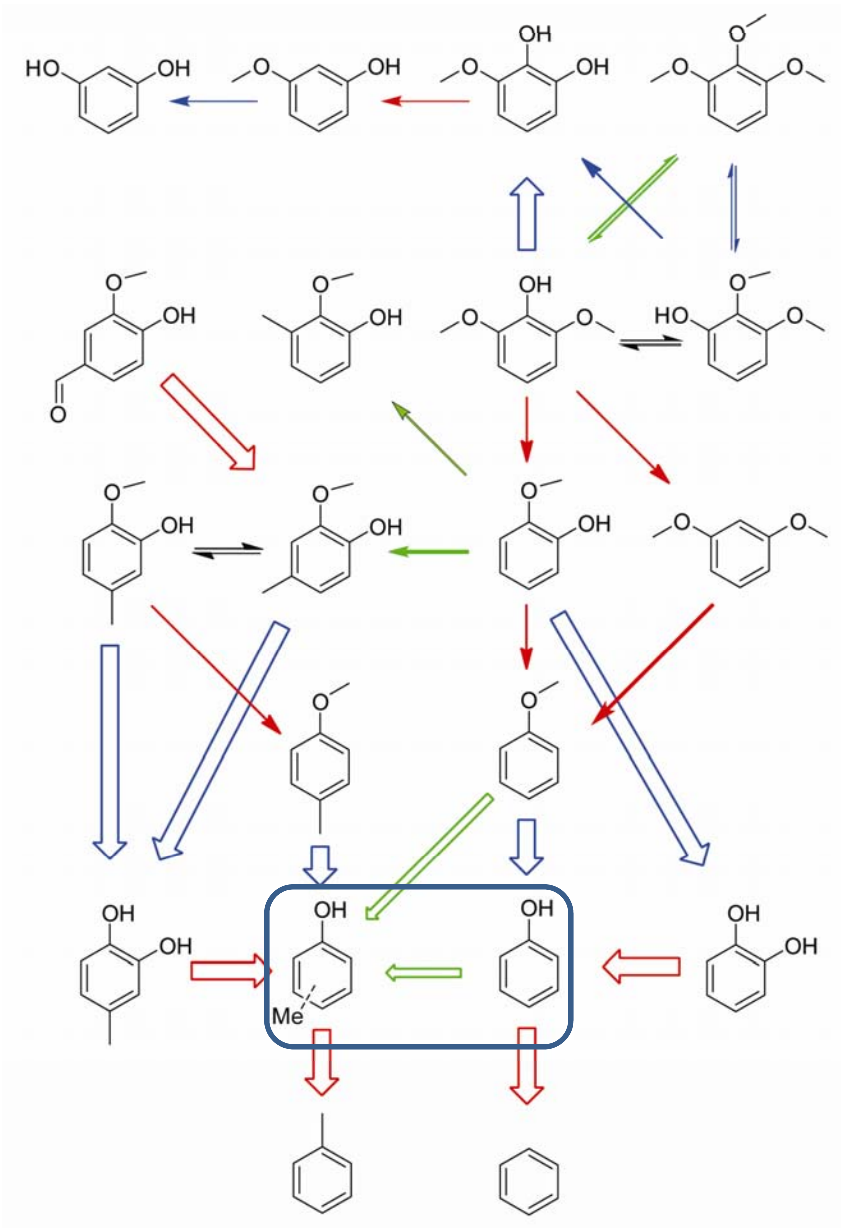


Lignin HDO: Model compound Studies





Lignin HDO: Model compound Studies

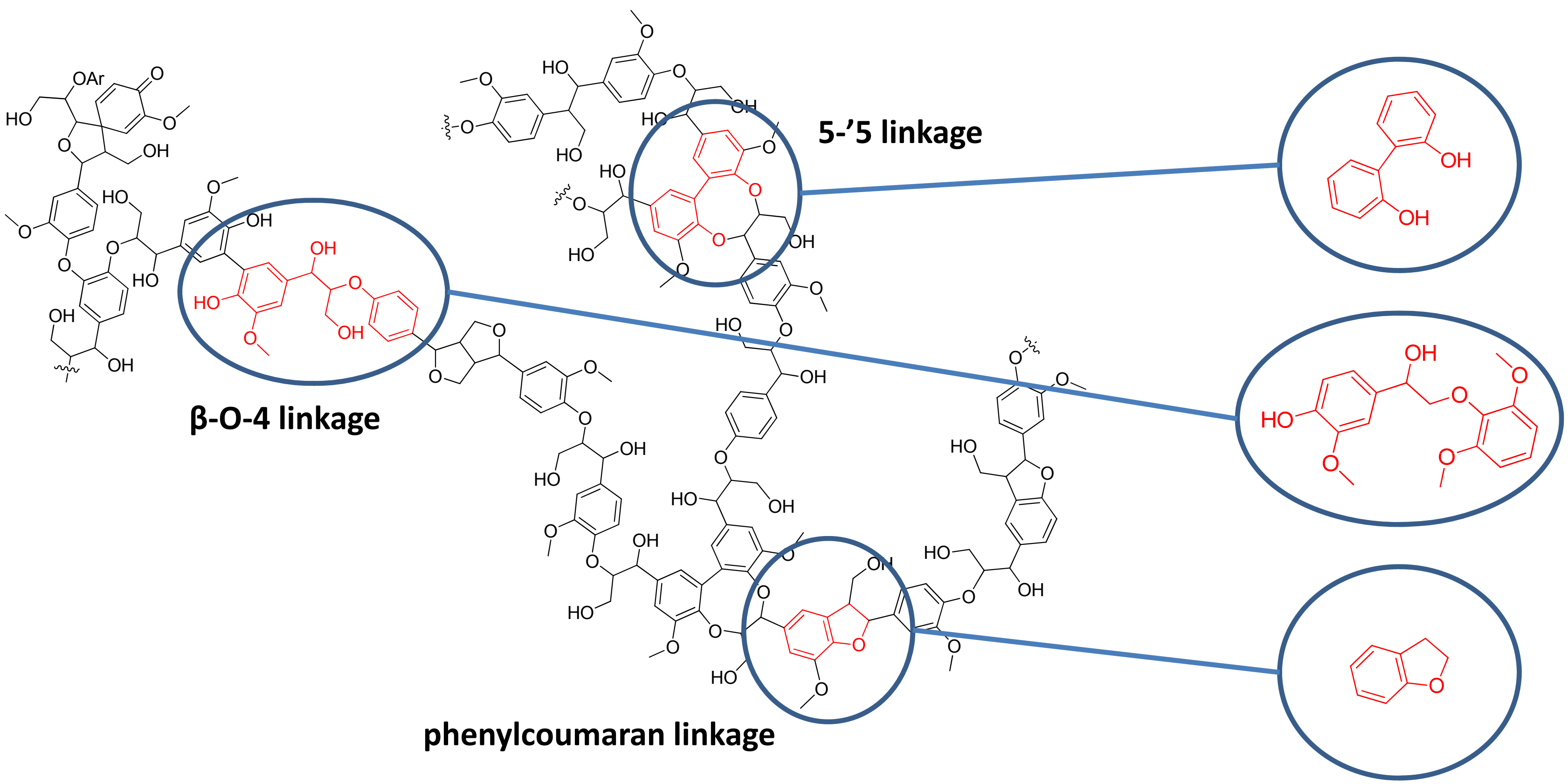


An extended reaction network:

- low hydrogenation activity
- fast HDO on the first hydroxy-group
- mono-oxygenated aromatics most stable
- **phenol and cresols** are the main reaction products

Lignin HDO: Model compound Studies

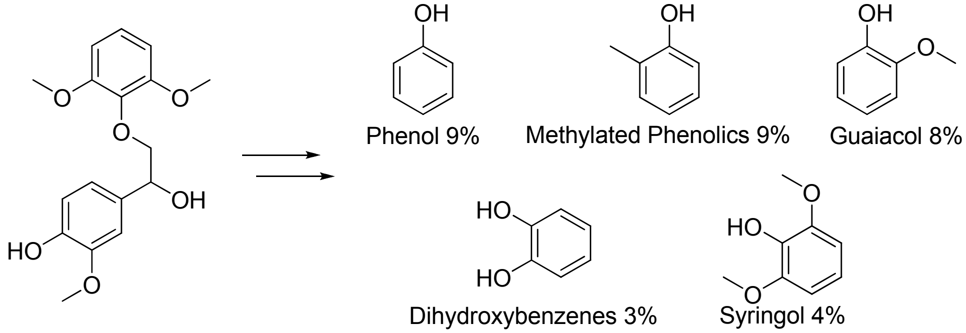
- The product of first conversion step likely still contains **larger lignin fragments**
- Reactivity of **typical linkages** studied under the same HDO conditions



Lignin HDO: Model compound Studies

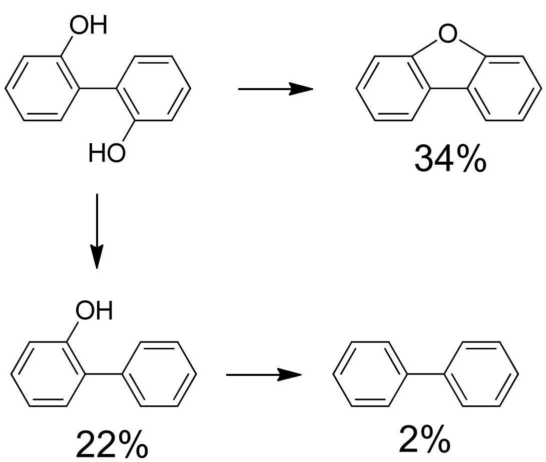
β-O-4 (conv. 100%)

- Breaking of ether bond observed
- No substituted ethylbenzenes observed by GC



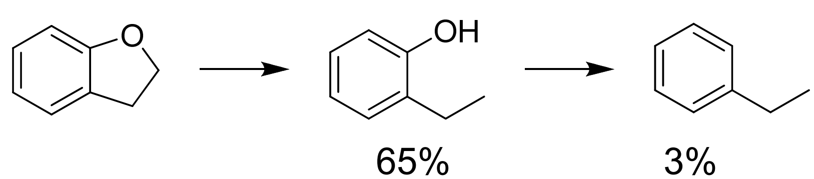
5-5' (conv. 55%)

- Aryl-aryl linkage remains intact



Phenyl coumaran (conv. 18%)

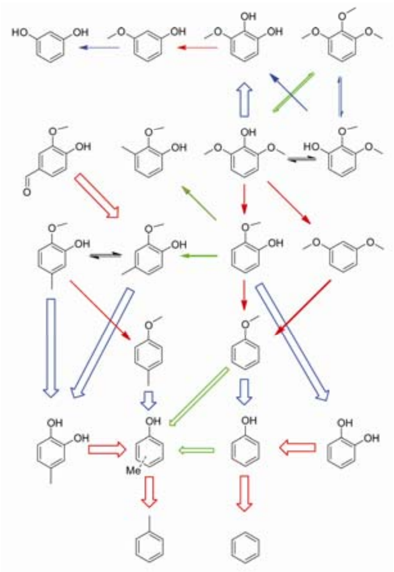
- Selective cleavage of alkyl-ether bond

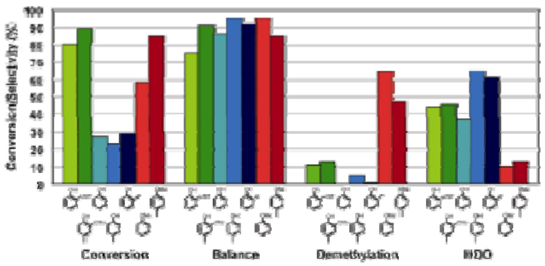


Lignin HDO: Model compound Studies

In the CoMo-catalyzed HDO of lignin derived model compounds:

- Fast demethylation precedes the deoxygenation step, little hydrogenation observed
- Phenol and cresols are the main reaction products
- Lignin β-O-4 ether linkages are broken under HDO conditions, 5-5’ stay intact

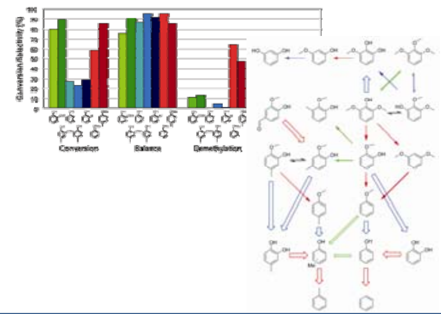




Catalytic Lignin Valorization: Towards Renewable Aromatics

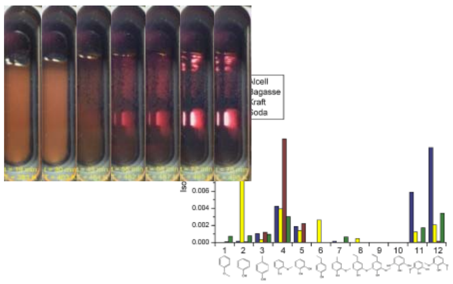
- **Two-step reductive hydrodeoxygenation of lignin**

(J. Catal. 2011, doi:10.1016/j.jcat.2011.10.006)



- **Aqueous/Liquid phase reforming of lignin**

(ChemSusChem 2011, 4, 369)



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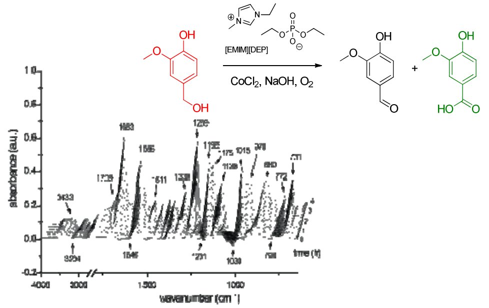

Catalytic Lignin Valorization: Towards Renewable Aromatics

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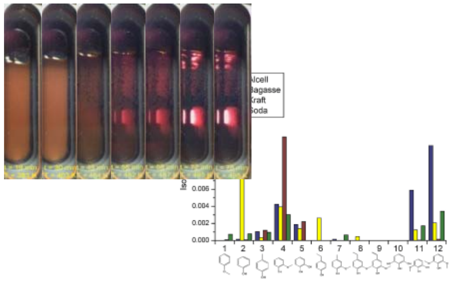
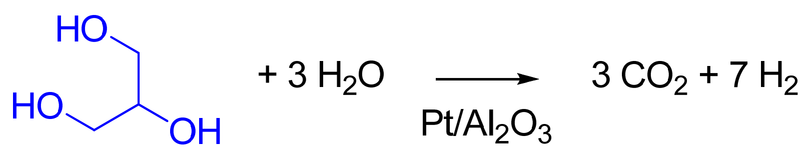


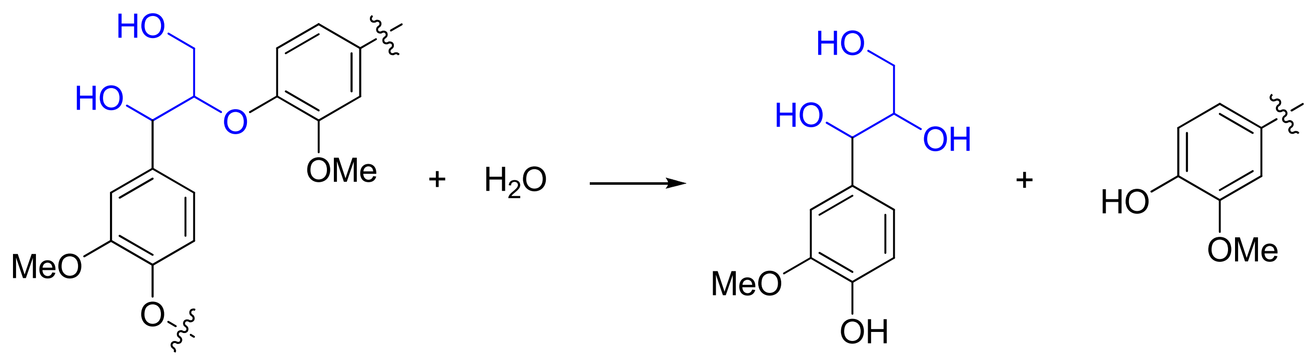
Lignin Solubilization and Aqueous Phase Reforming

- Aqueous-phase reforming of glycerol (Dumesic):

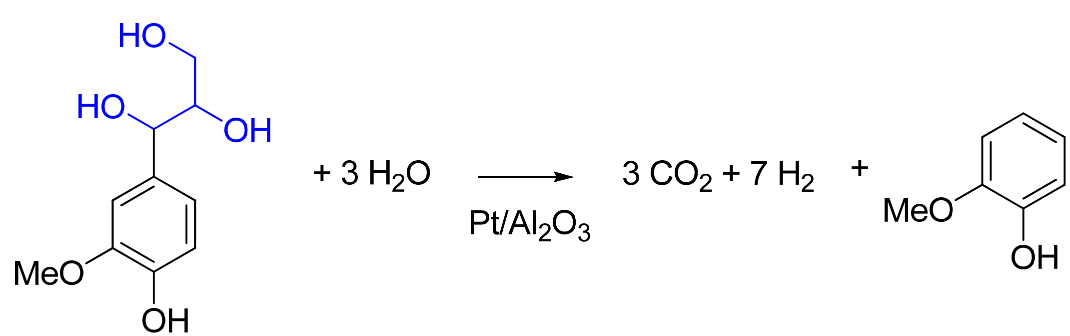


- Aqueous-phase reforming of lignin:

1) Hydrolysis

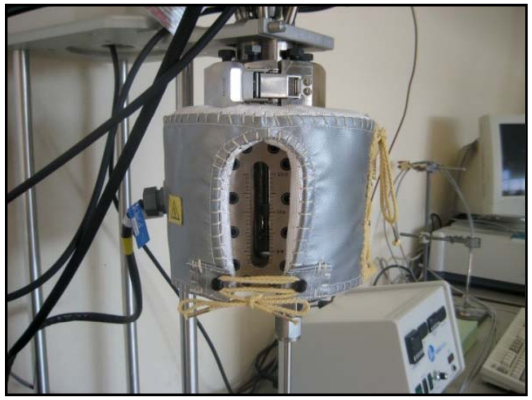


2) APR



Zakzeski et al. ChemSusChem, 2011, 4, 369-378

Lignin Solubilization and Aqueous Phase Reforming



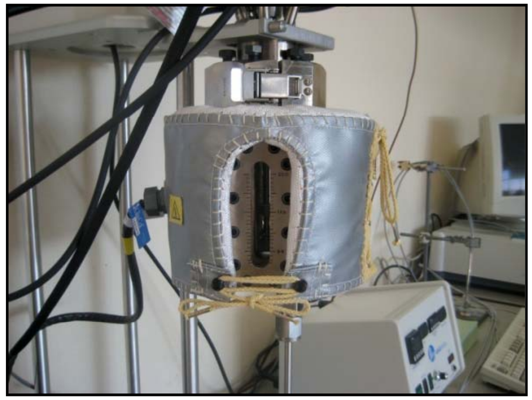
200 mL H_2O
2 g lignin compound

0.2 g Pt/Al_2O_3
29 bar; 90 min
T_{max} = 225 ^oC

• solubilization of various lignins tested under typical APR conditions

• alcell, kraft, soda and sugarcane bagasse lignins tested

Lignin Solubilization and Aqueous Phase Reforming



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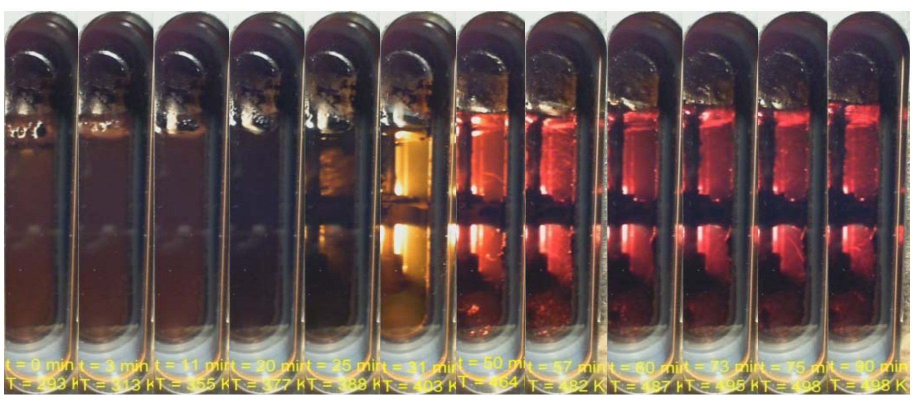
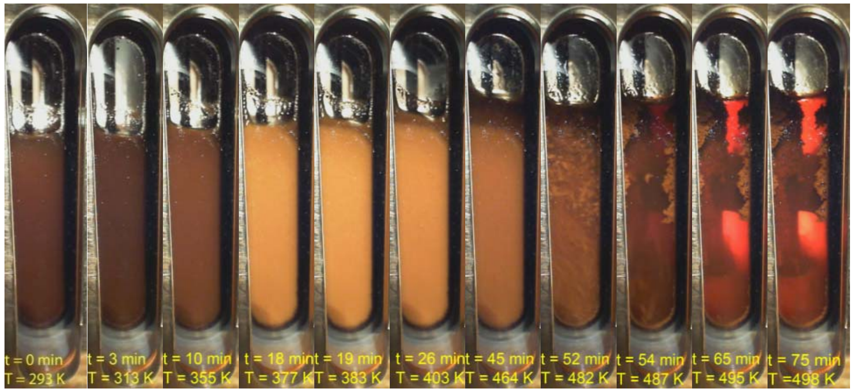


Alcell Lignin

T_d = 130 °C
7% solids recovered

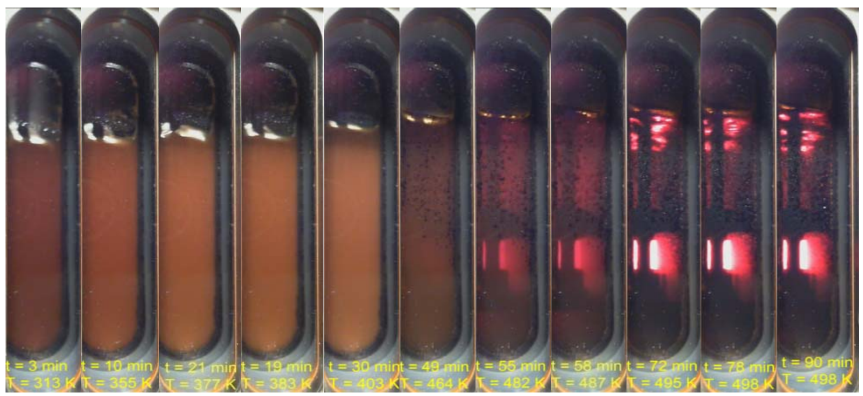
Lignin Solubilization and Aqueous Phase Reforming

Kraft lignin



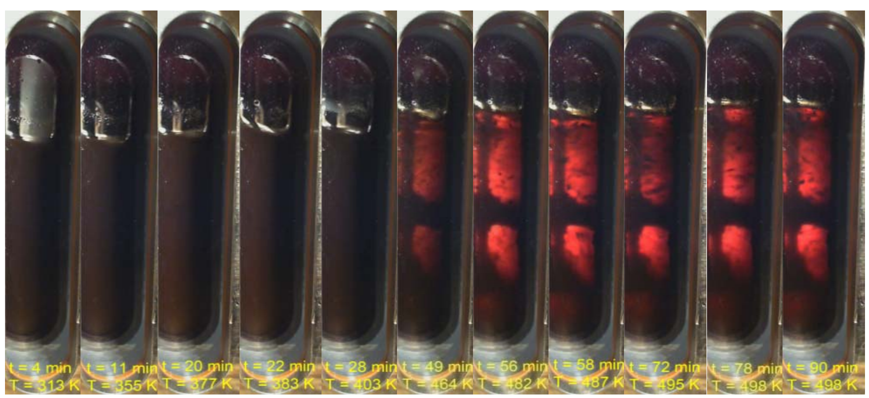
T_d = 222 °C
62% solids recovered

Soda lignin



T_d = 209 °C
17% solids recovered

Sugarcane bagasse



T_d = 209 °C
49% solids recovered

Lignin Solubilization and Aqueous Phase Reforming

• Combination of Pt/Al_2O_3, H_2SO_4, H_2O gives best results

• Conversion of up to 14 wt%; composition of GC-detectable monomers lignin-dependent

Table 2. Solids and liquids obtained from the aqueous phase reforming of lignin samples. Reaction conditions: 10.98 g H_2O, 0.58 g H_2SO_4, 0.1245 g 1% Pt/Al_2O_3, P = 29 bar He, T = 498 K, t = 1.5 h.

Entry	Lignin	Avg. start mss [g]	Recovered solids[a] [g]	Total isolated Products [g]	GC-detected isolated products [g]	Conv.
1[b]	kraft	1.384	1.302	0.026	0.012	1.9
2[c]	kraft	1.383	1.157	0.069	0.026	4.9
3	kraft	1.386	1.219	0.136	0.020	9.8
4	alcell	1.384	1.099	0.203	0.038	14.6
5	sugar-cane	1.387	0.935	0.174	0.028	12.6
6	soda	1.387	0.963	0.159	0.025	11.4

[a] After subtraction of catalyst weight. [b] No H_2SO_4. [c] No Pt/Al_2O_3.

Lignin Solubilization and Aqueous Phase Reforming

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- Conversion of up to 14 wt%; composition of GC-detectable monomers lignin-dependent

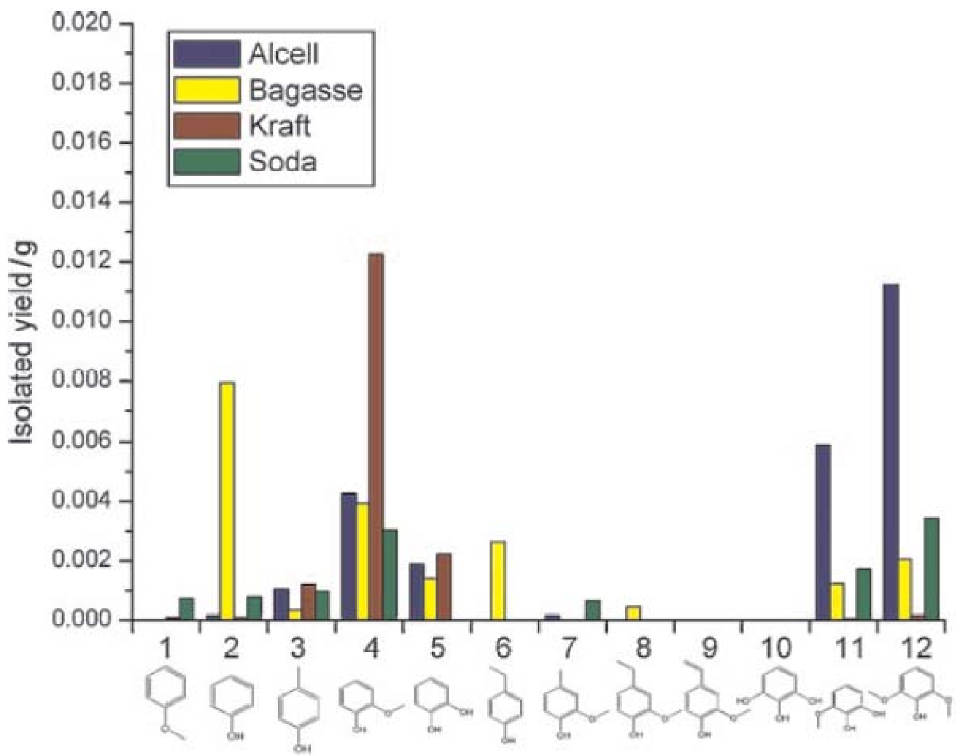


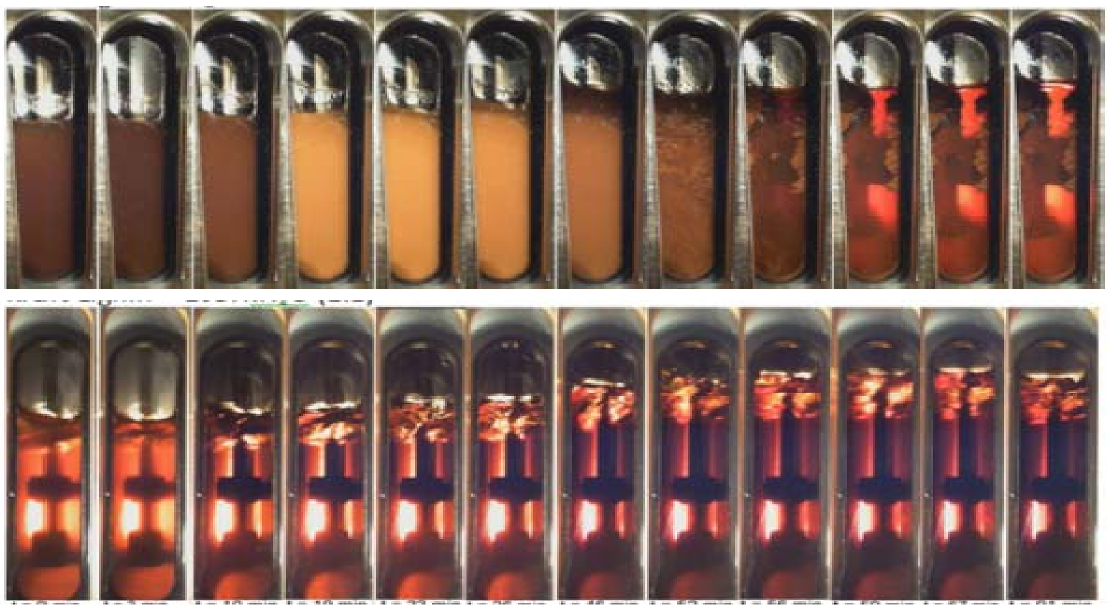
Table 3. Autoclave gas composition following the aqueous phase reforming of the lignin samples. Reaction conditions: 10.98 g H_2O, 0.58 g H_2SO_4, 0.1245 g 1% Pt/Al_2O_3, P=29 bar He, T=498 K, t=1.5 h.

Entry	Lignin	H_2 [%]	CO_2 [%]	CH_4 [%]	C_2H_6 [%]	C_3H_8 [%]
1[a]	kraft	0.03	0.00	1.05	0.55	0.03
2[b]	kraft	0.47	0.00	1.10	4.36	0.00
3	kraft	4.28	0.95	2.55	3.38	0.02
4	alcell	8.83	1.52	3.06	5.52	0.06
5	sugarcane bagasse	5.03	1.14	1.98	4.26	0.03
6	soda	5.51	2.35	3.74	1.12	0.07

[a] No H_2SO_4. [b] No Pt/Al_2O_3.

Lignin Solubilization and Catalytic Conversion

- use of **ethanol/water mixture** for solubilization:



H_2O

$EtOH/H_2O$

293 K

498 K

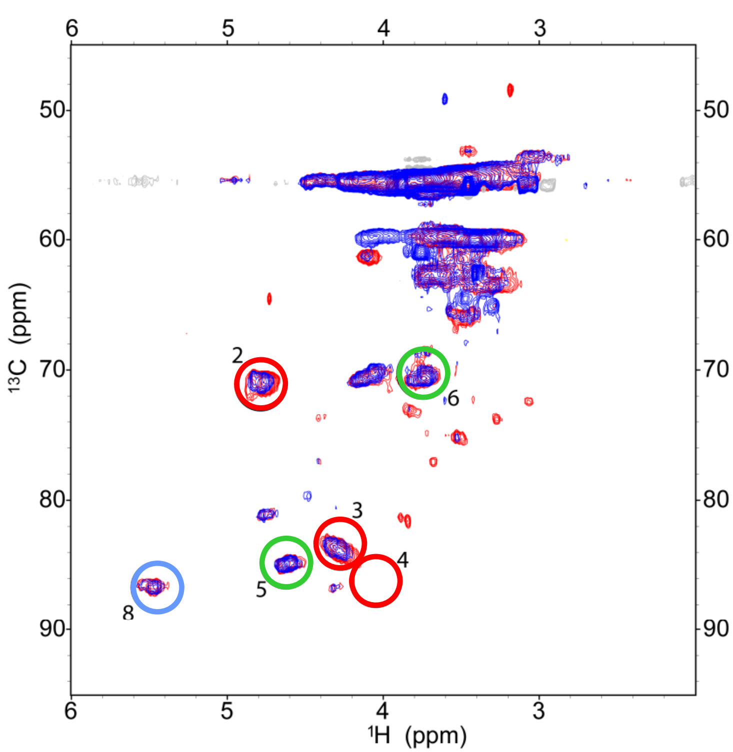
- Kraft lignin is **nearly 100% soluble** with no agglomeration of solids
- Reduction in Mw (by GPC) from 5300 to 3800 Da

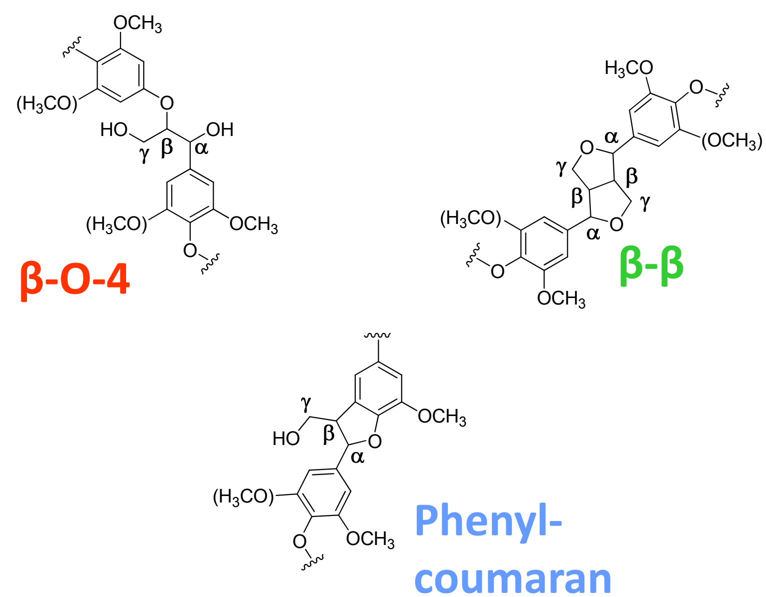
Zakzeski, Jongerius, Bruijnincx, Weckhuysen, submitted

Lignin Solubilization and Catalytic Conversion

- use of **ethanol/water mixture** for solubilization:

- quantitative data on structural changes from **2D HSQC NMR**:

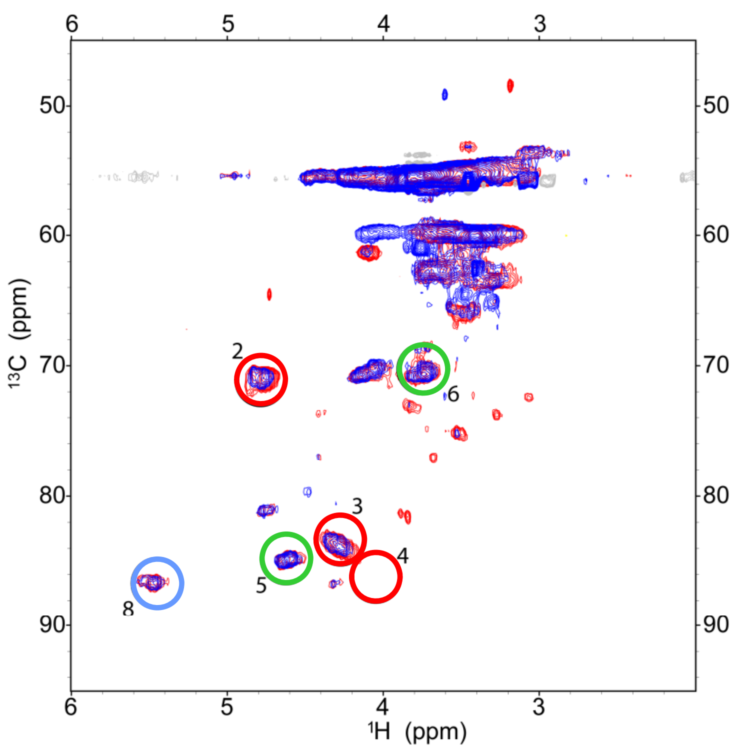




--- Kraft Lignin
--- Solubilized Lignin

Lignin Solubilization and Catalytic Conversion

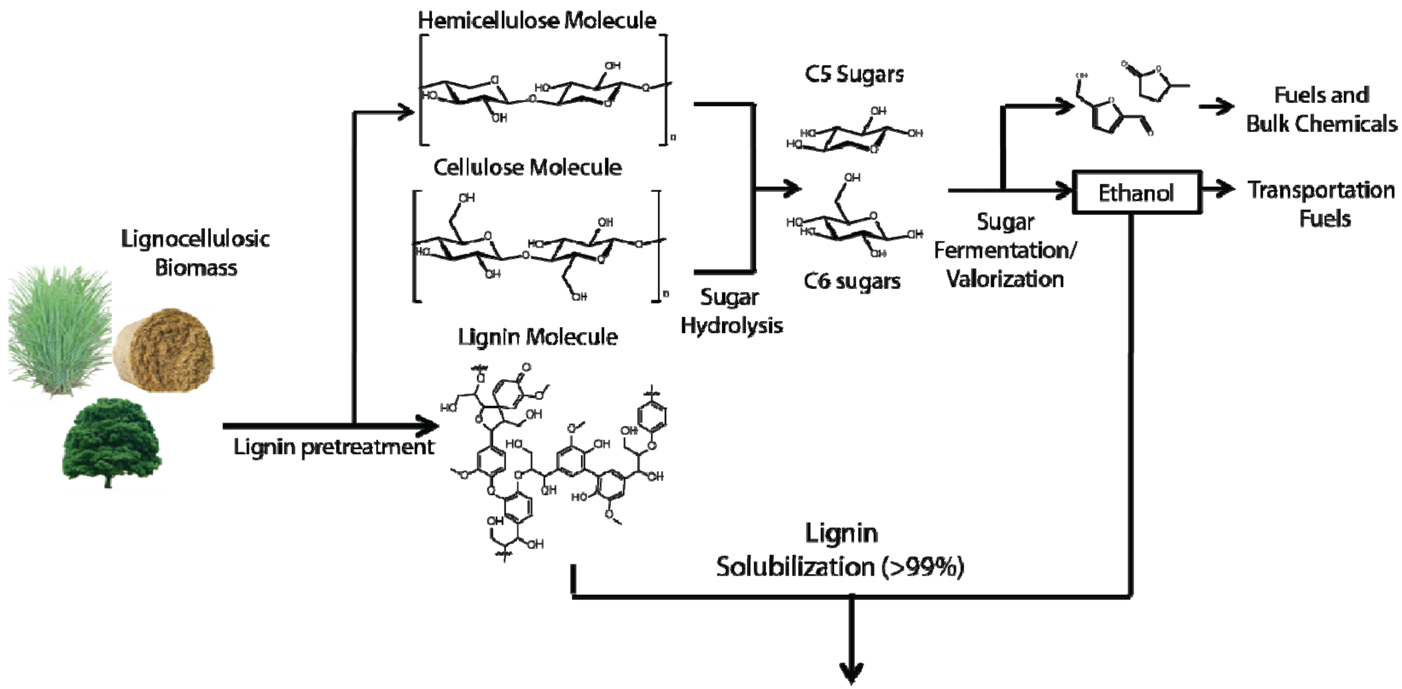
- use of **ethanol/water mixture** for solubilization:
- quantitative data on structural changes from **2D HSQC NMR**:



	Linkage	^{1}H signal	Decrease (%)
2	β-O-4	α	53
3	β-O-4	β (guaiacyl)	49
4	β-O-4	β (syringyl)	51
5	β-β	α	22
6	β-β	γ	19
8	phenyl coumaran	α	24

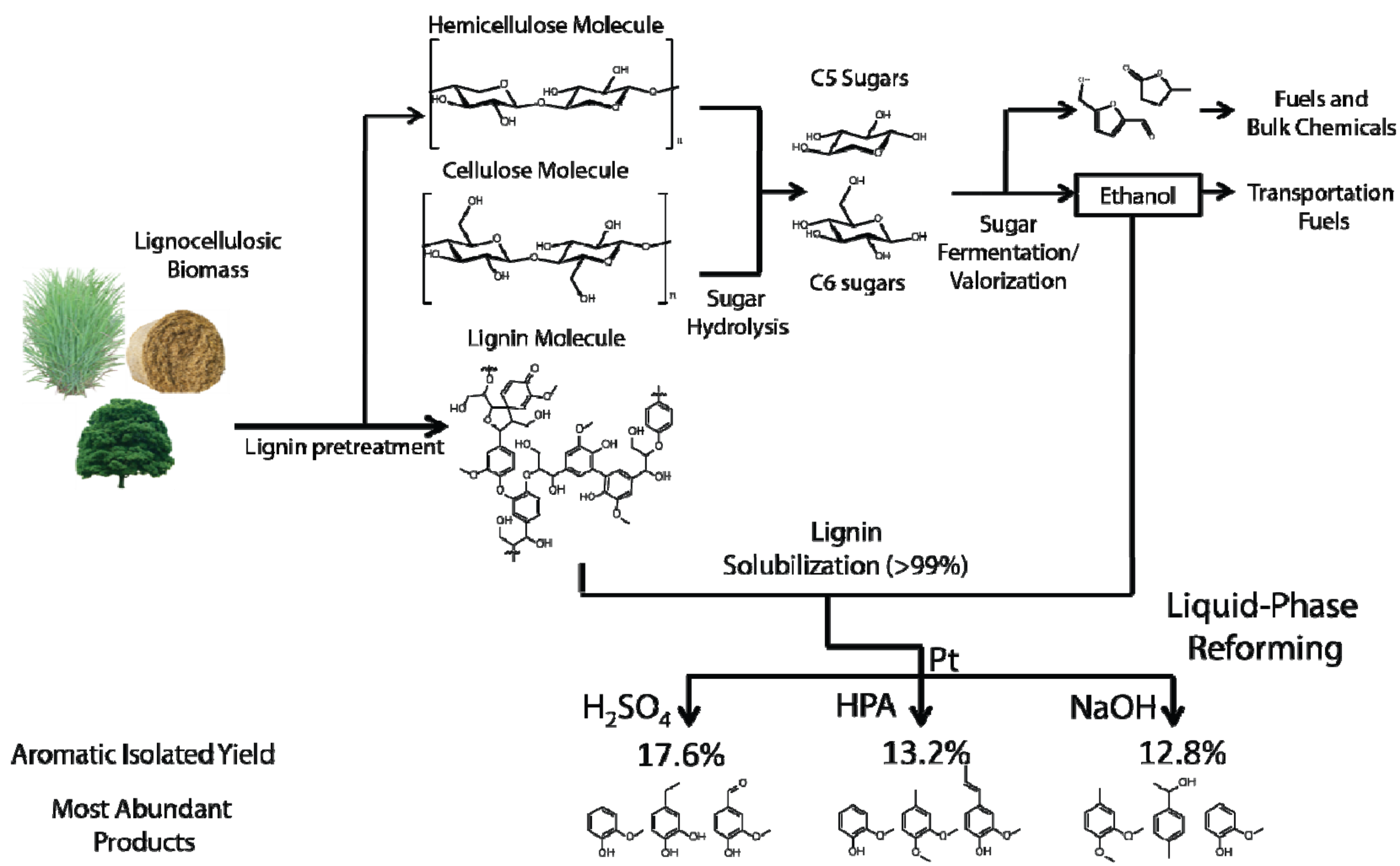
Zakzeski, Jongerius, Bruijnincx, Weckhuysen, submitted

Lignin Solubilization and Catalytic Conversion

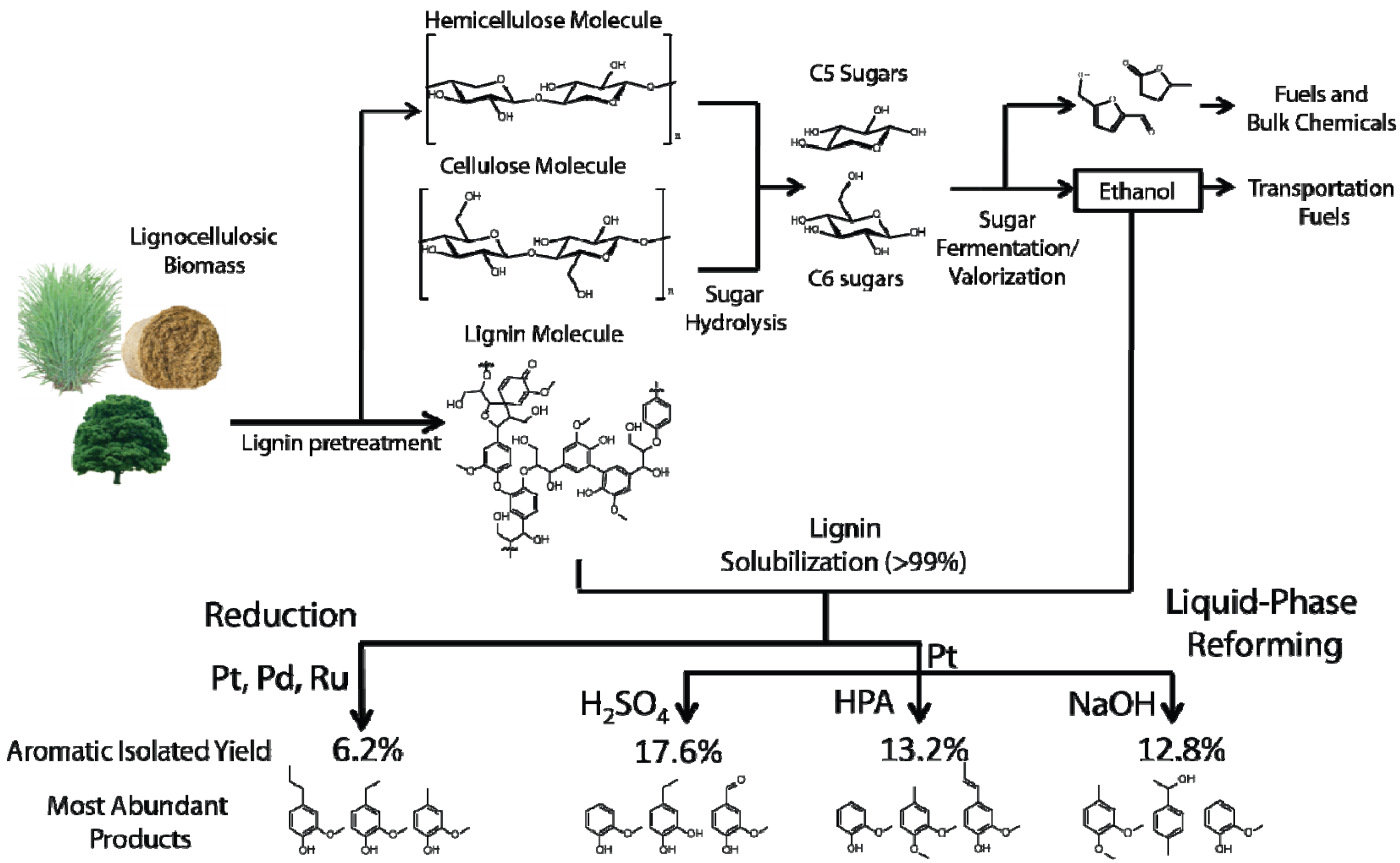


- solubilization opens up possibilities for catalytic depolymerization
- various catalysts and conditions tested
- influence of additives on monomer yield

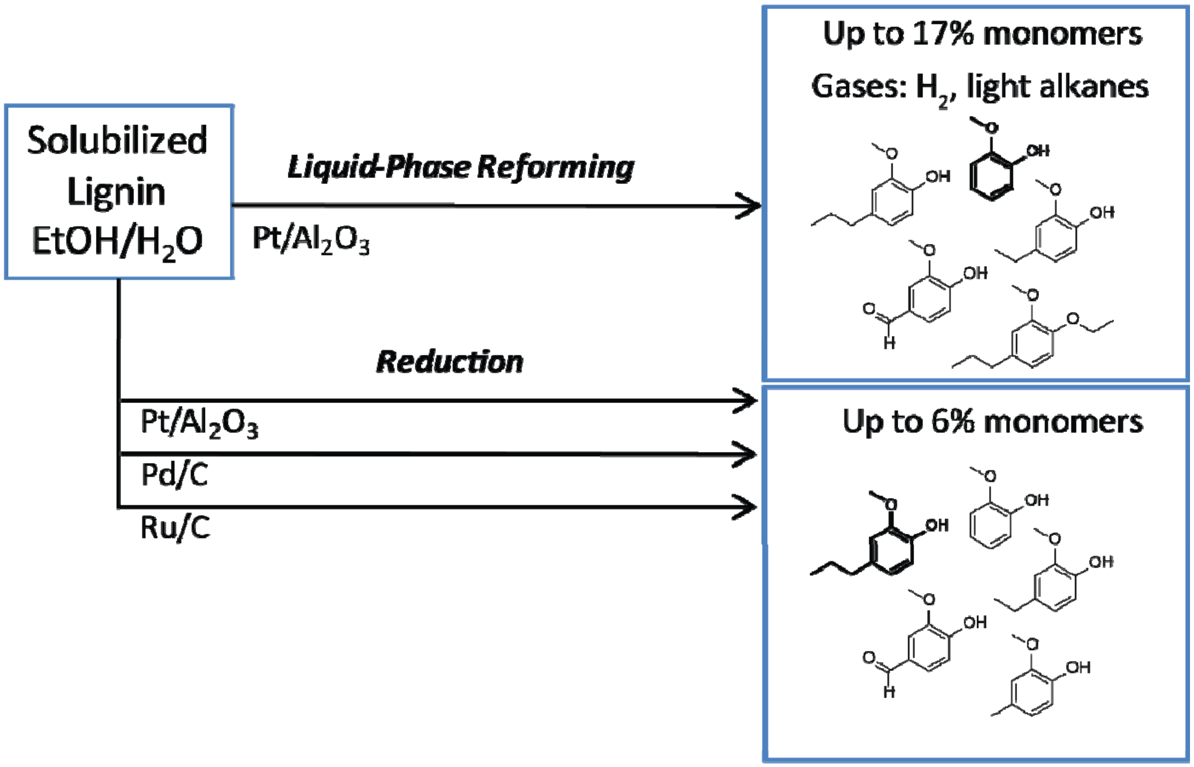
Lignin Solubilization and Catalytic Conversion



Lignin Solubilization and Catalytic Conversion



Lignin Solubilization and Catalytic Conversion



Typical conditions:

498K, 90 min, 59 bar He
1/1 v/v $EtOH/H_2O$

473K, 4h, 30 bar H_2
1/1 v/v $EtOH/H_2O$

- Product yield and composition depends on the **process/catalyst combination**
- **(Alkylated) monoaromatics** are the main components of the volatile fraction
- Heavier fraction needs further analysis; monomer yields need to be improved

Zakzeski, Jongerius, Bruijnincx, Weckhuysen, submitted

Acknowledgements



Universiteit Utrecht

Anna L. Jongerius

Robin Jastrzebski

Dr. Joseph Zakzeski

Agnieszka Debczak

Prof. dr. ir. Bert Weckhuysen

NSF

NWO

CatchBio

COST ACTION CM0903

ALBEMARLE

Leen Gerritsen (CoMo and NiMo catalysts)
Gerbrand Mesu (Lignin and pinewood sawdust)

Agrotechnology & Food Sciences Group, Wageningen UR

Richard Gosselink (Organosolv lignin)
Jacinta van der Putten (GPC measurements)

ECN Energieonderzoek Centrum Nederland

Wouter Huijgen (Soda lignin)
Jaap van Hal (Kraft Lignin)

Dow

Matthijs Ruitenbeek (Sugarcane bagasse)

BASF The Chemical Company

Annemarie Beers (Ionic liquids)