HTL of Lignin and impact of sulfur salts

BL2F Midterm workshop, 22.03.2022

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BL2F

Transforming Black Liquor to Biofuel

This project has received funding from the European Union Grant Number 884111

Outline

HTL of Lignin and impact of sulfur salts

- Background information
  - Hydrothermal Liquefaction (HTL)
  - Depolymerization of Lignin
- Preliminary experimental results
  - HTL of Black Liquor in general
  - Influence of Sulfide (S^{2-})
- Summary
- Outlook

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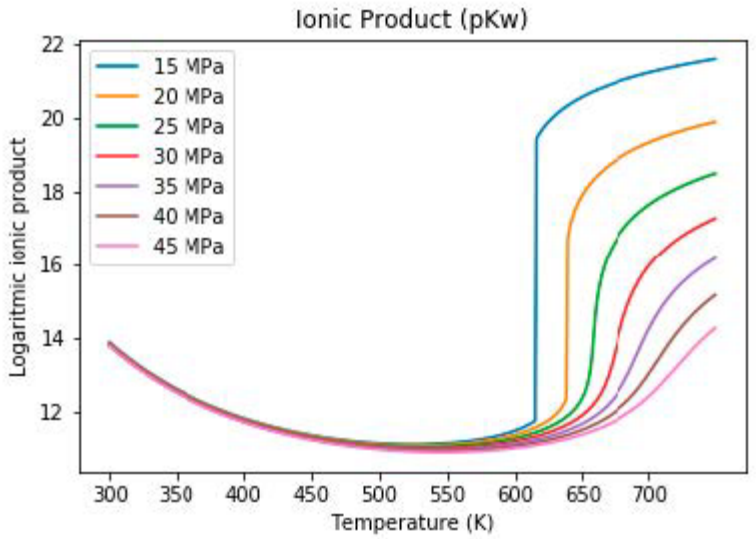
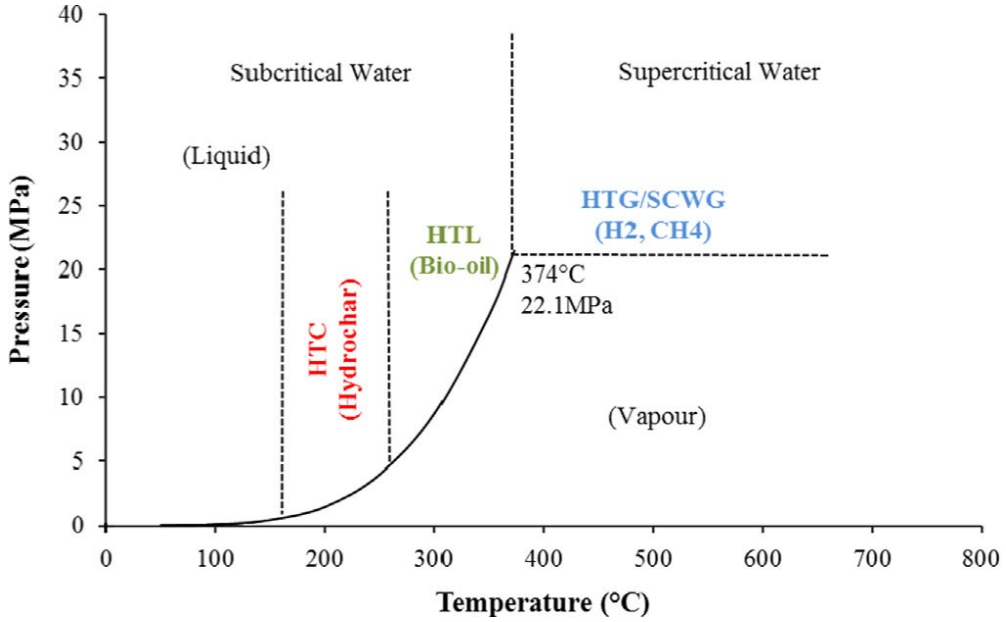
Hydrothermal Liquefaction (HTL)

- HTL is especially suitable when feedstock is wet
- Process conditions close to the critical point of water
- Drastic changes in water properties, i.e. ionic product, heat capacity, density etc.



Lappalainen et al. : Sub- and Supercritical Water Liquefaction of Kraft Lignin and Black Liquor Derived Lignin, 2020



Kambo et al. : A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications, 2015

- HTL of extracted lignin is already done
- Direct use of BL makes extraction of lignin and re-dissolving before HTL obsolete

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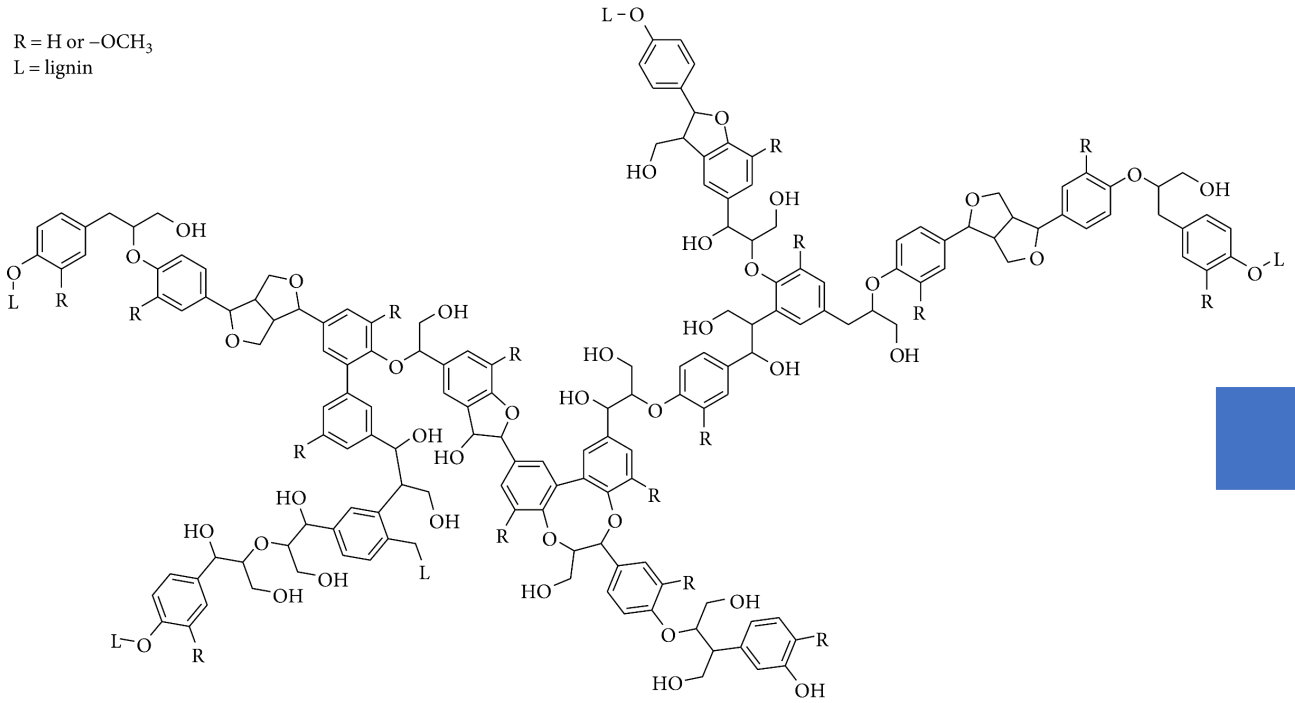
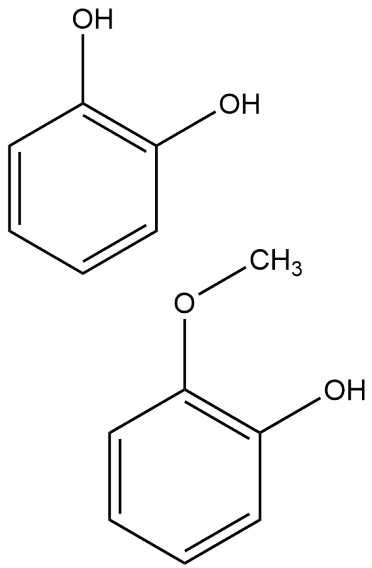
Depolymerization of Lignin



Hydrothermal Liquefaction (HTL)



Lu et al. 2017: Structural characterization of Lignin and its degradation products with spectroscopic methods

Lignin:

- Only natural macromolecule with such a high aromatic content
- Built up from three different phenylpropanoid monomers

Products:

- Biocrude, gas solids
- Aromatic compounds e.g. Catechol, Guaiacol, …

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Experimental Setup (Batch)

Batch experiments:

- micro autoclaves (V = 25 mL)
- Material: Stainless steel 1.4571
- Sand bath is used for heating (approx. 10 min heating time to reach T_R)
- Investigated temperature range: T_R = 250 – 400 °C
- Pressure: around 250 bar (via fill level)

Feedstock composition:

- Ca. 15 wt. % dry matter
- Ca. 9 wt. % organic matter

	C / wt. %	H / wt. %	N / wt. %	S / wt. %	O / wt. %	Na / wt. %	K / wt. %
dry matter	34	3,4	<0,1	4,7	38,8	17,7	1,3
lignin	60,3	5,7	<0,1	2,6	31	0,4	<1

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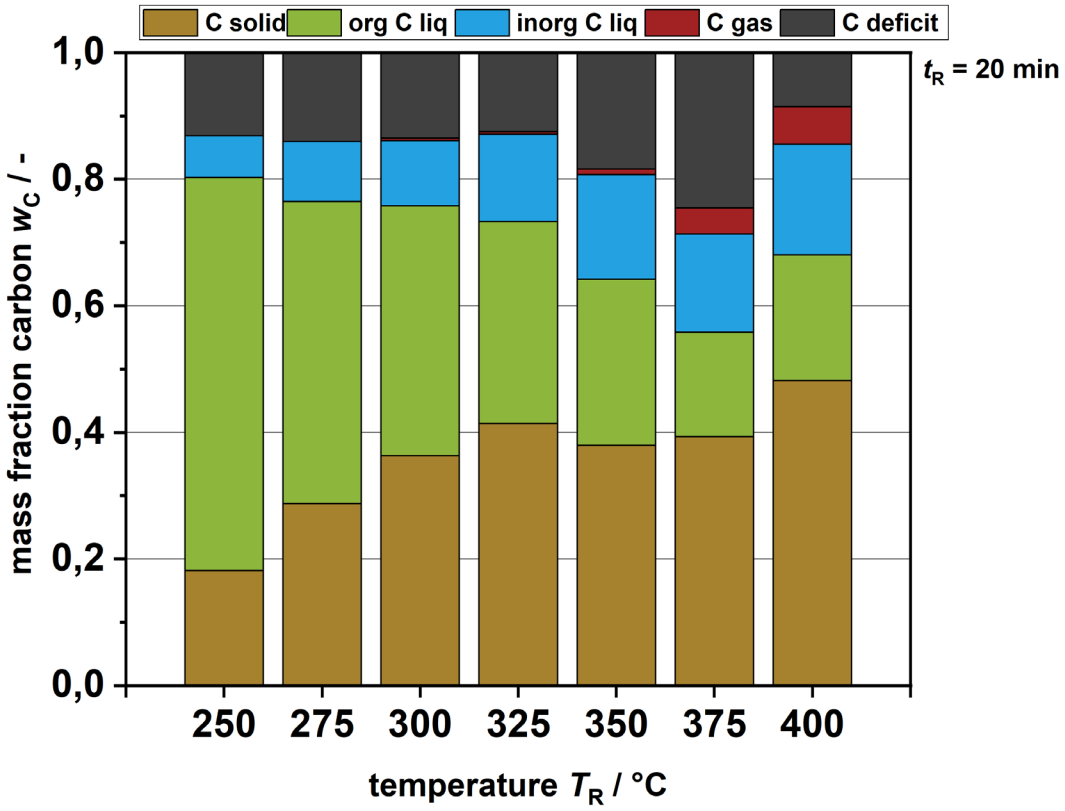
Carbon mass balance

- Between 75 – 90 wt. % of carbon collected
- Most of carbon in solid residue
- Organic content in liquid is reduced with higher temperature
- Gaseous content is increasing with higher temperature (mostly CO_2, only few hydrocarbons)
- Increase in inorganic carbon maybe due to dissolved CO_2



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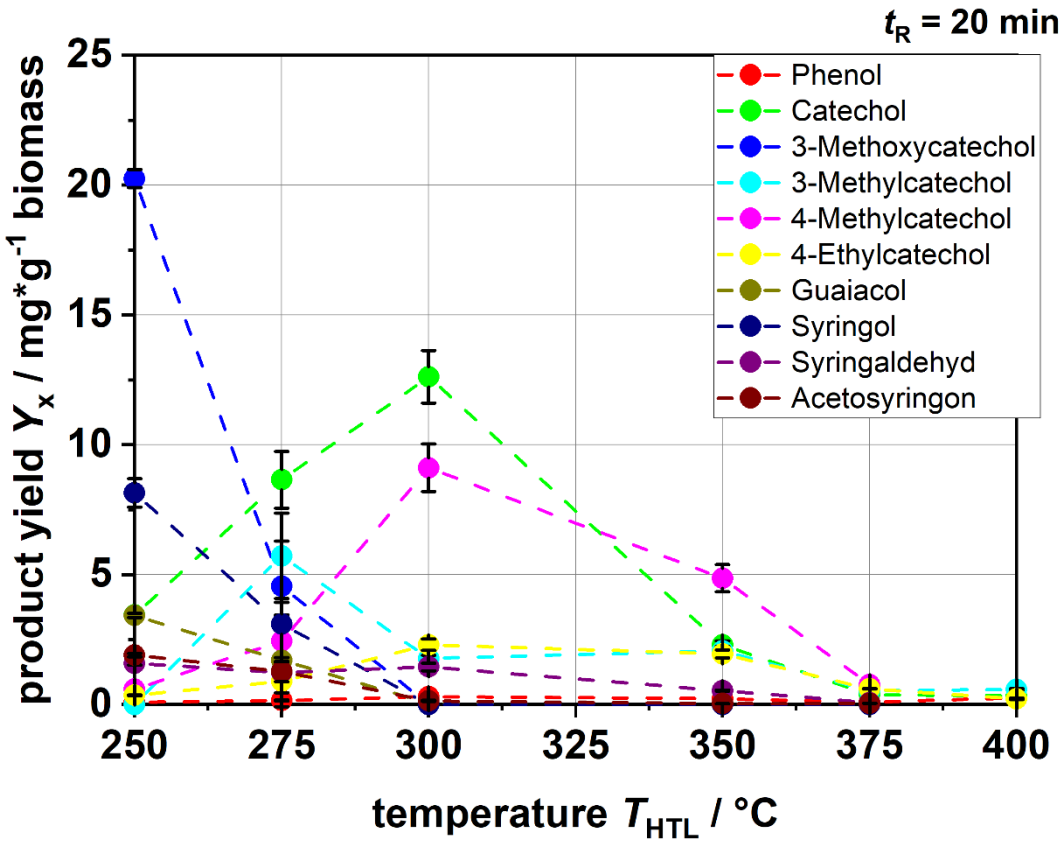
Monomer product yields

Extraction procedure:

- Acidify to pH 3-4
- Extraction with ethyl acetate
- After one hour good phase separation

- Analysis via GC-FID
- Catechol derivates are the main monomer aromatic products
- Yields decrease with higher temperature after reaching maximum



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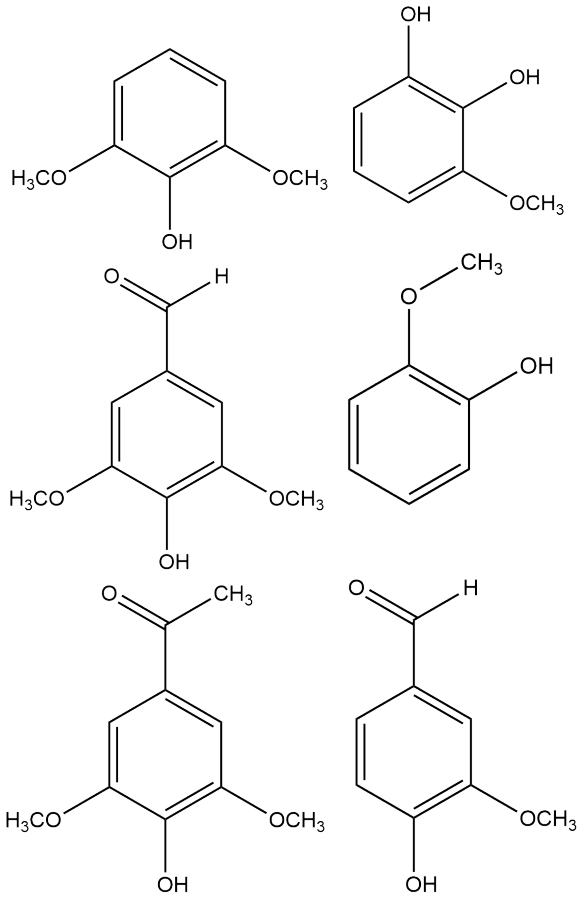
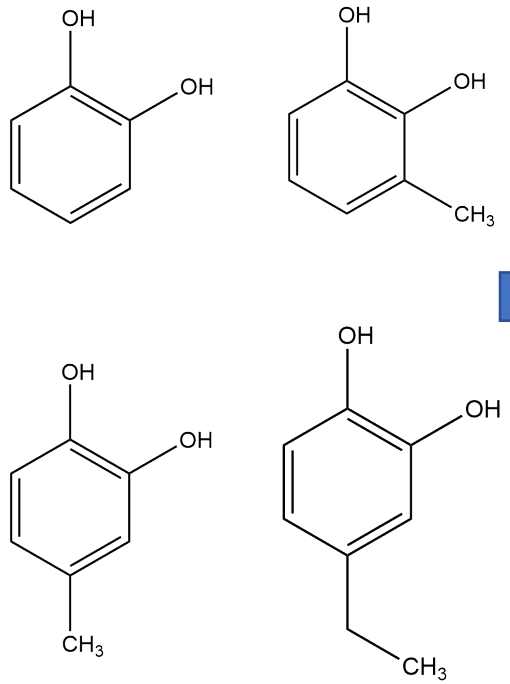
Preliminary reaction pathway

Lignin polymer

Oligomers?



Guaiacol & syringol derivates



Catechol derivates

CO_2, H_2, C_xH_x?

solid residue?

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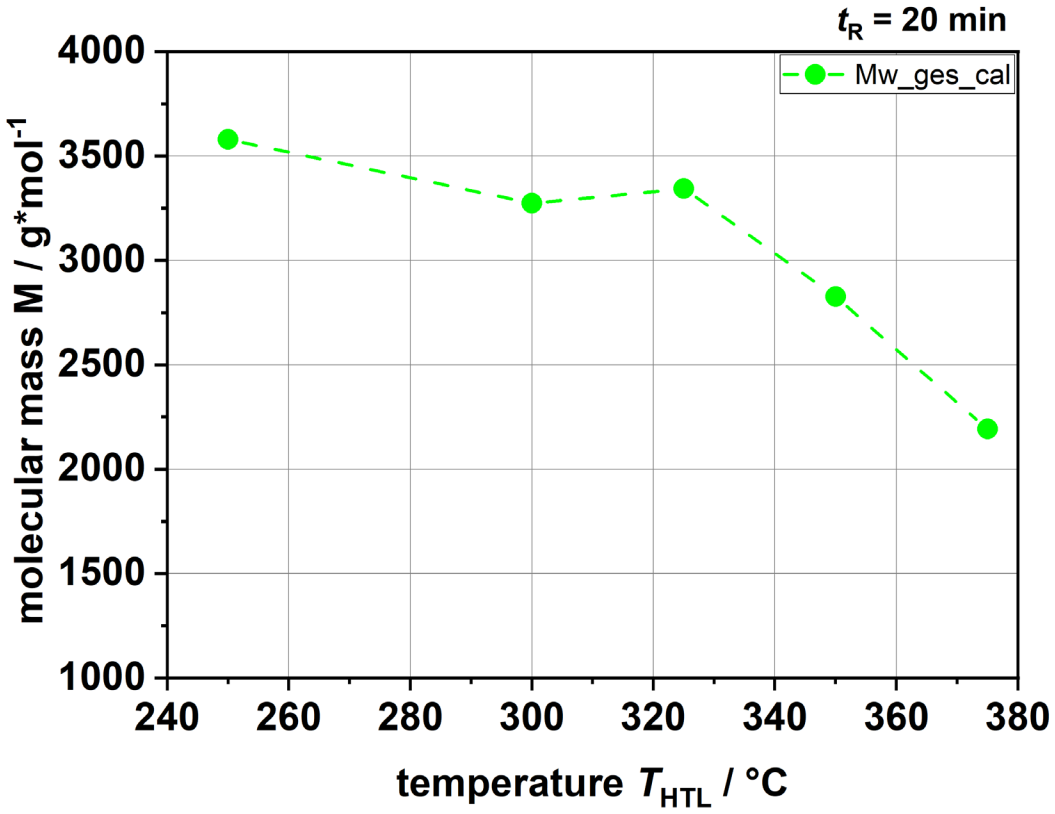
GPC analysis

- Extracted biocrude was analyzed via GPC (dissolved in DMSO)
  - M_w = weight average molecular weight
  - Calibrated range: 250 – 10000 g/mol
  - M_w Lignin before processing: 4217 g/mol

- Decrease of molecular weight with higher temperature from ca. 3500 to 2200 g/mol
- GPC analysis can describe depolymerization of lignin polymer molecule
- The decrease of molecular weight with temperature is slow



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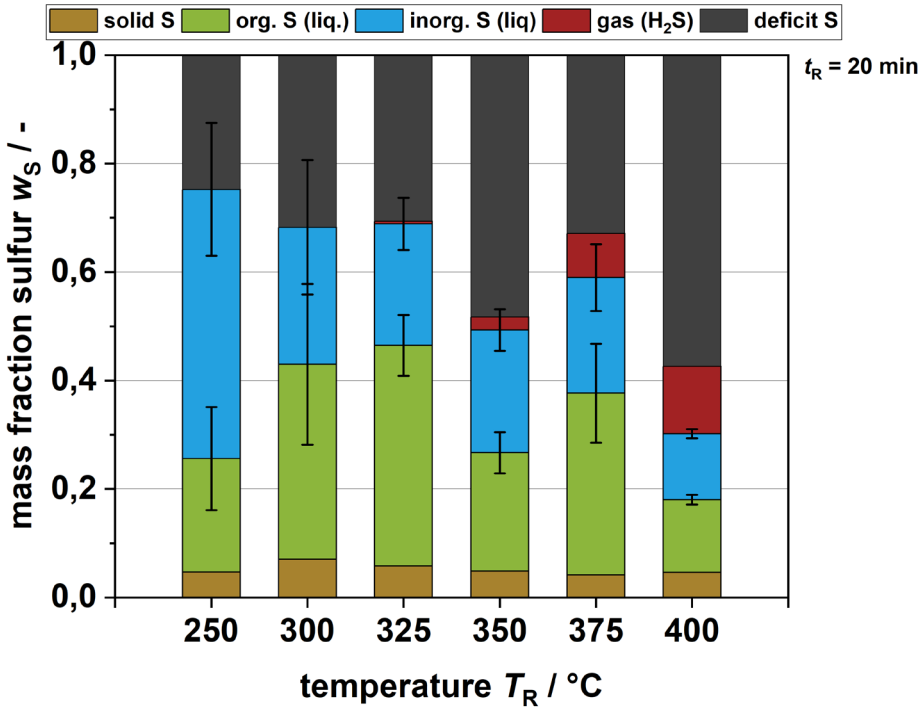
Sulfur mass balance

- Sulfur content in solid phase almost stable, not precipitation effects with higher temperature visible
- Inorganic sulfur in liquid phase is reduced
- Organic sulfur in liquid phase goes through maximum with following decrease



Inorganic sulfur (dissolved salts) → Organic sulfur compounds (liquid) → Non-detectable (organo-) sulfur gas compounds?

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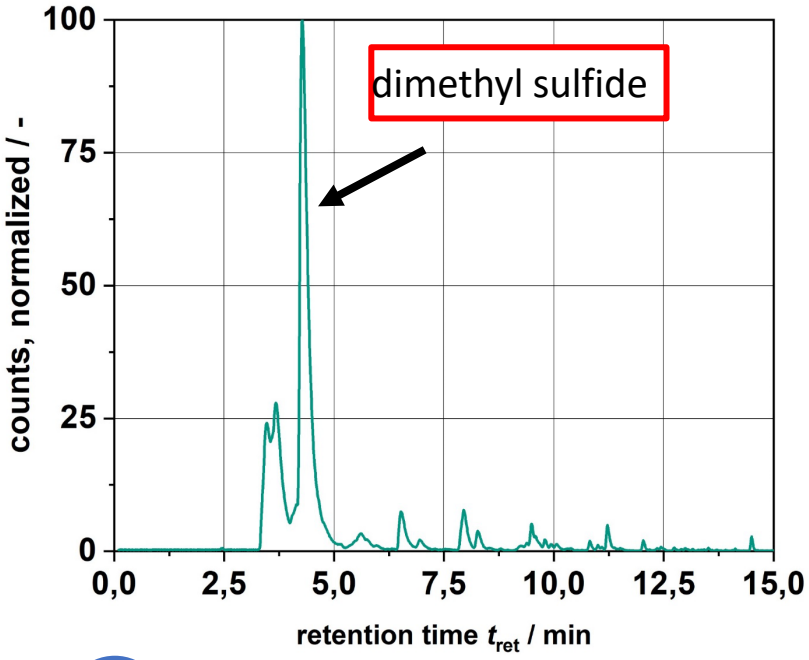
Dimethyl sulfide as missing compound?

- Sulfur mass balance only up to 70 - 80 wt. %
- Loss is expected mainly in gas phase

GC-MS gas analysis to get more insight



- Possible reaction pathway given in Karnofski et al. 1975, *Odor generation in the Kraft process*

$$HS^- + Lig - CH_3O \rightarrow CH_3SH + Lig - O^-$$

Methyl mercaptane

$$CH_3SH + OH^- \leftrightarrow CH_3S^- + H_2O$$

$$CH_3S^- + Lig - CH_3O \rightarrow H_3CSCH_3 + Lig - O^-$$

Dimethyl sulfide

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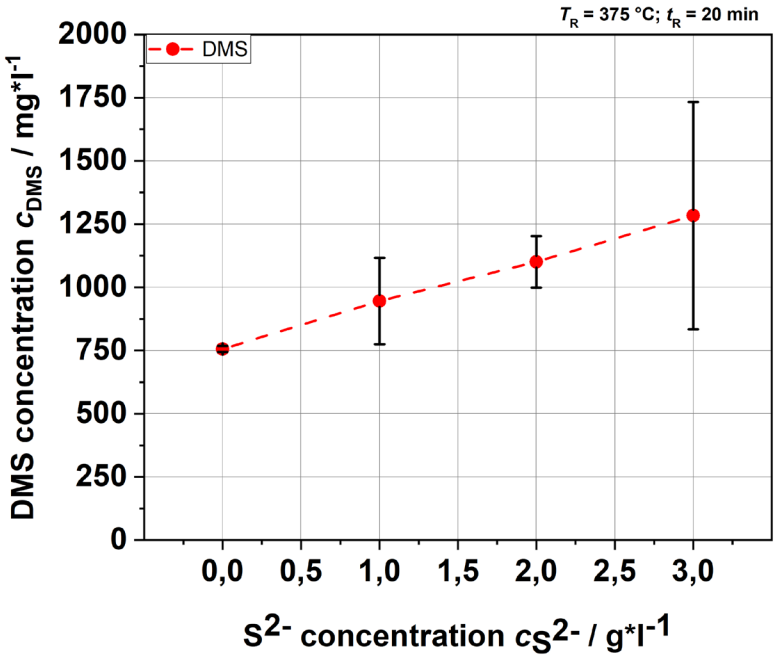
Influence of sulfide (S^{2-}) concentration

- Sulfur mass balance indicates shift from inorganic to organic sulfur
- Shown reaction pathway and found DMS can be possible explanation

model black liquor based on feedstock characterization needed for confirmation

Model BL composition:

- salts: Na_2CO_3, K_2CO_3, Na_2SO_4, Na_2SO_3, $Na_2S_2O_3$, **Na_2S**
- KOH/NaOH for pH adjustments
- Lignin (extracted from BL)



- High DMS concentration observable
- Increasing with higher sulfide concentration in feed shows reaction from inorganic to organic sulfur
- DMS could be main reason for loss in sulfur mass balance
- Concentration values for DMS very uncertain due to difficulties in calibration

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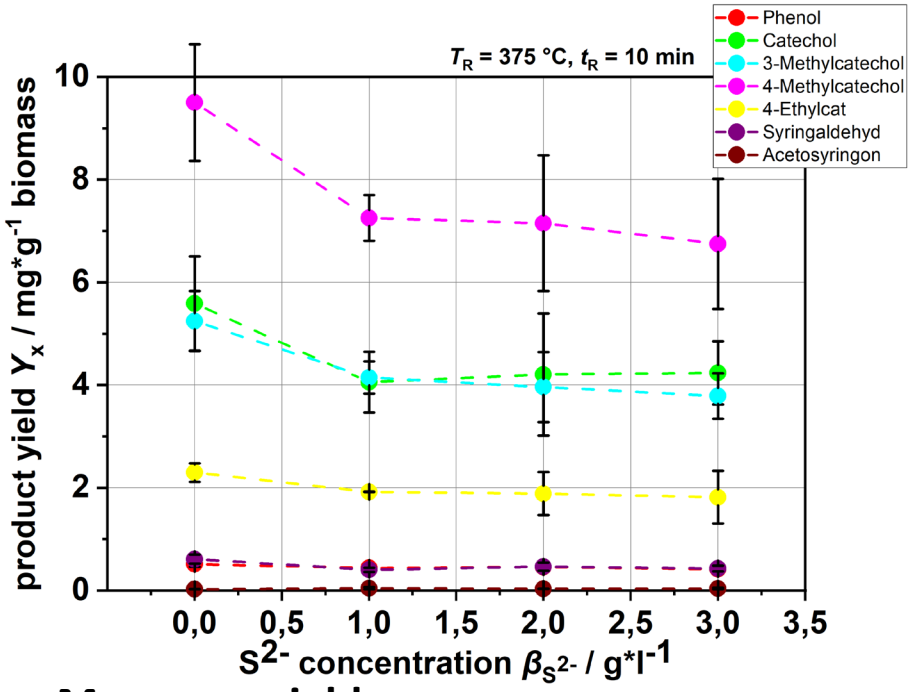
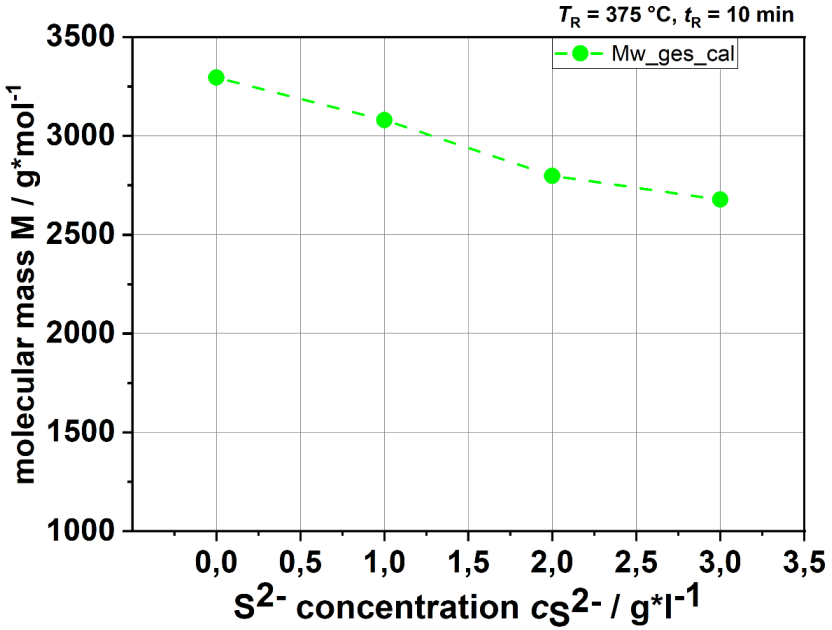


Monomer yields:

Slight decrease with higher sulfide concentration



GPC analysis:

Decrease in molecular weight with higher sulfide concentration

Sulfide (S^{2-}) seems to accelerate depolymerization of lignin

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Summary

- Organic carbon mass fraction is reduced with higher T_R, most of carbon is in solid
- Catechol derivates are the main aromatic monomer products
- GPC analysis shows the depolymerization of lignin by decreasing molecular weight with higher T_R
- Sulfur shifts from inorganic to organic to gaseous sulfur compounds
- Main product in gas is dimethyl sulfide, reaction pathway from literature supports this findings
- Sulfide concentration in the feed leads to slight decrease in monomer yields, but also to a decrease in the molecular weight (acceleration of depolymerization)

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Outlook

- Consistent explanation for results of GPC and GC-FID
- Search for a way to get a better look on the oligomers by improving GPC analysis and/or by using NMR
- Implement sulfur content of dimethyl sulfide in gas phase into the sulfur mass balance
- Start to implement all the results into a kinetic model

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Thank you!

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