Karlsruhe Institute of Technology

Behavior of the sulfur-containing salts during the hydrothermal liquefaction of black liquor

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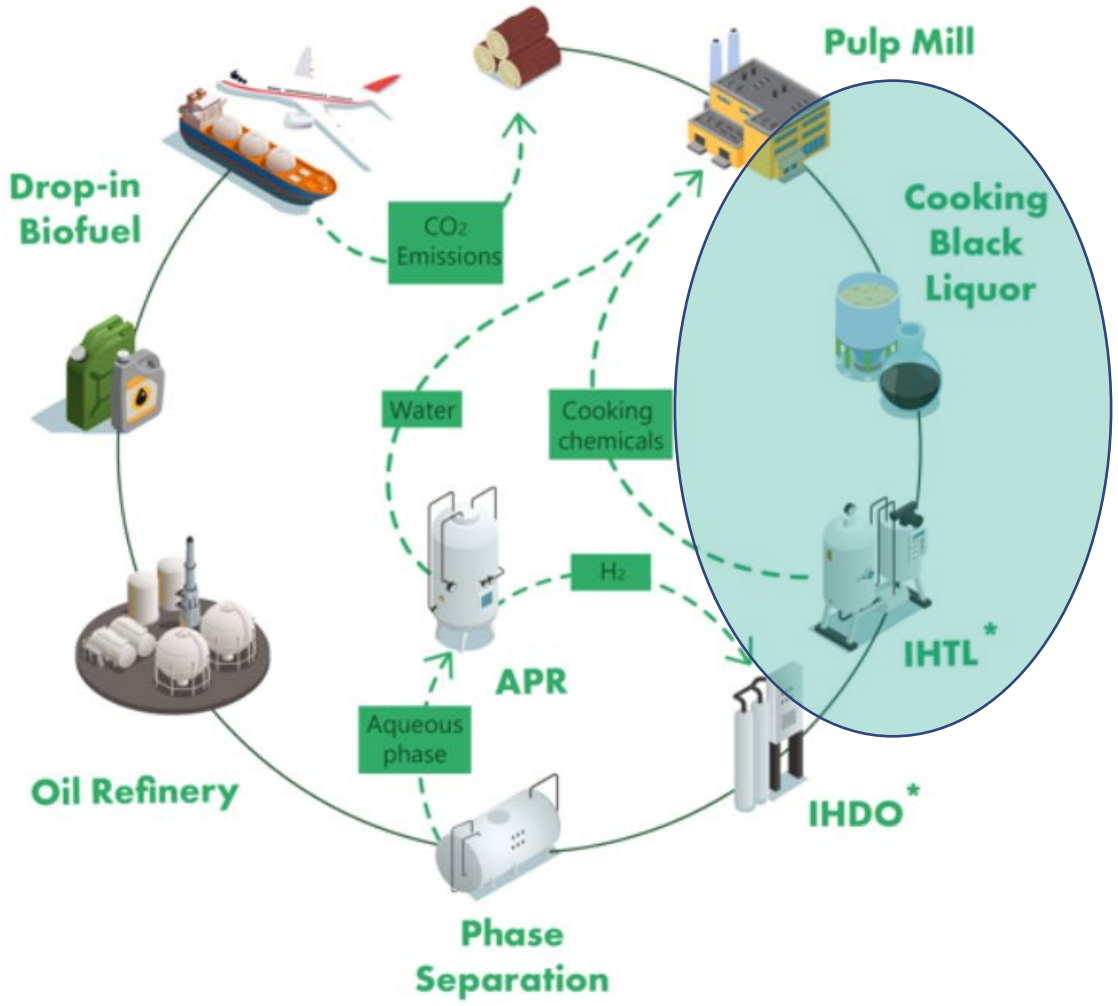
Outline

- General information
  - Black Liquor to Fuels (BL2F)
  - Research on HTL of black liquor/ depolymerization of lignin
- The role of sulfur containing salts
  - Sulfur in different product phases
  - Influence of S^{2-} concentration
- Summary

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

Black Liquor to Fuels project (BL2F)

This project has received funding from the Horizon 2020 programme under the Grant Agreement n°884111.



- Part of European Union Horizon 2020 program
- Production of drop-in biofuels from black liquor
- Valorization/Recycling of every side stream
- Direct use of black liquor

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Black Liquor as feedstock

- By-product of pulping industry
- Alkaline solution (pH > 12)
- Contains:
  - Lignin
  - Hemicellulose
  - Cooking chemicals (e.g. Na_2S)

	C / wt. %	H / wt. %	N / wt. %	S / wt. %	O / wt. %	Na / wt. %	K / wt. %
dry matter (15 wt. %)	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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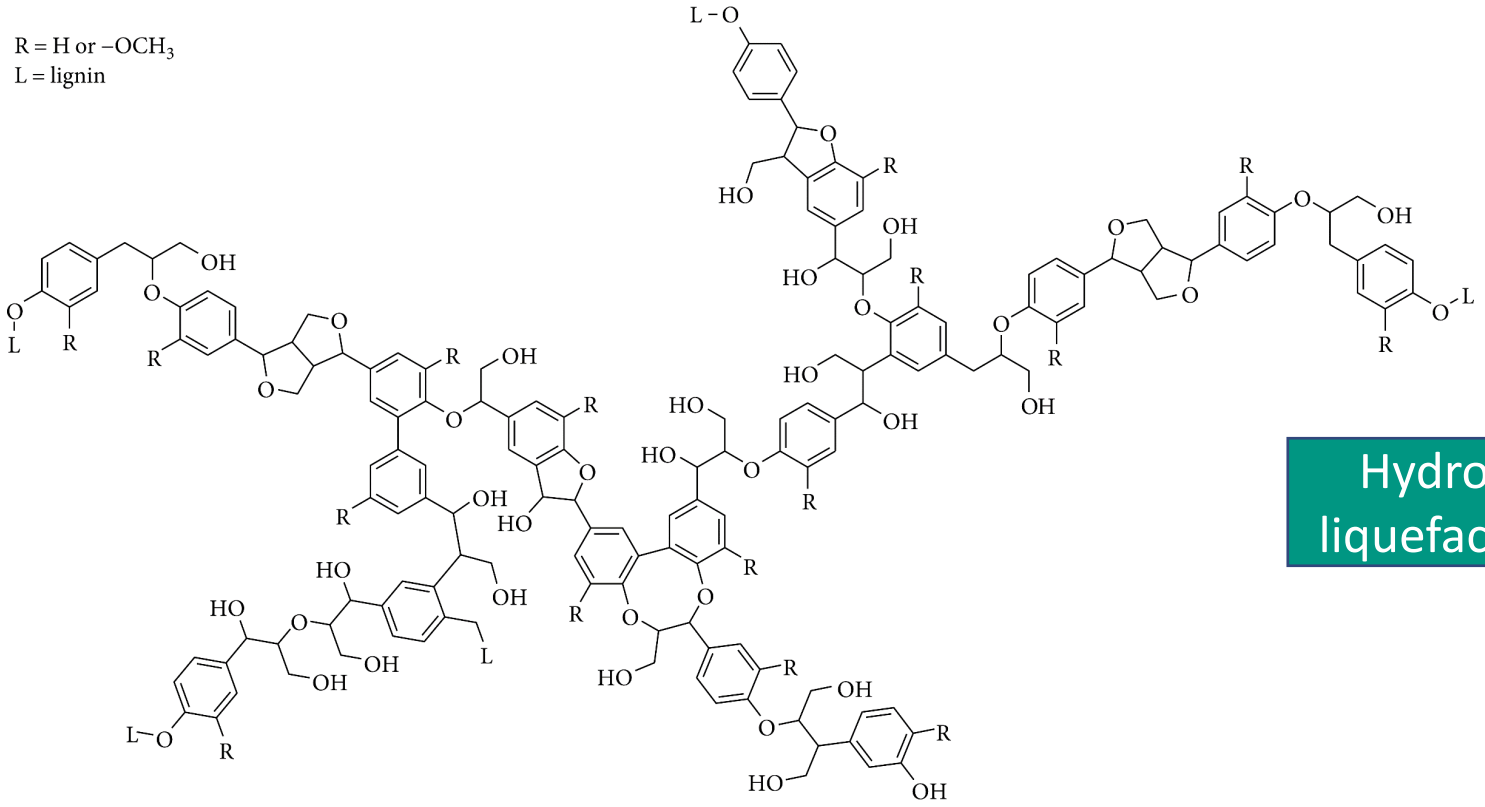
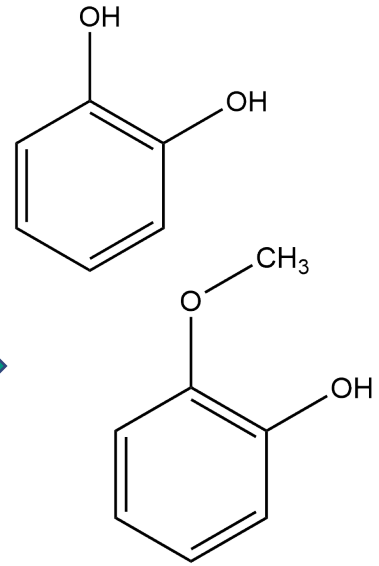
Depolymerization of Lignin



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

- Only natural macro molecule with aromatic content

Hydrothermal liquefaction (HTL)



Products:

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

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Experimental setup

- Batch experiments in micro autoclaves (V = 25 mL)
- Heating process in sand bath
- Investigated parameter ranges:
  - T_R = 250 – 400 °C
  - t_R = 0 – 30 min
- Pressure: around 250 bar (via fill level)

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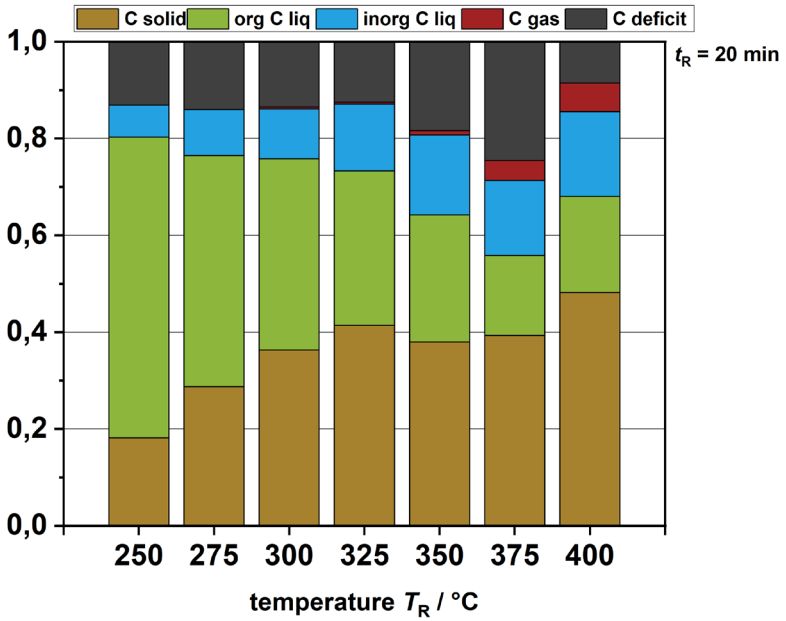
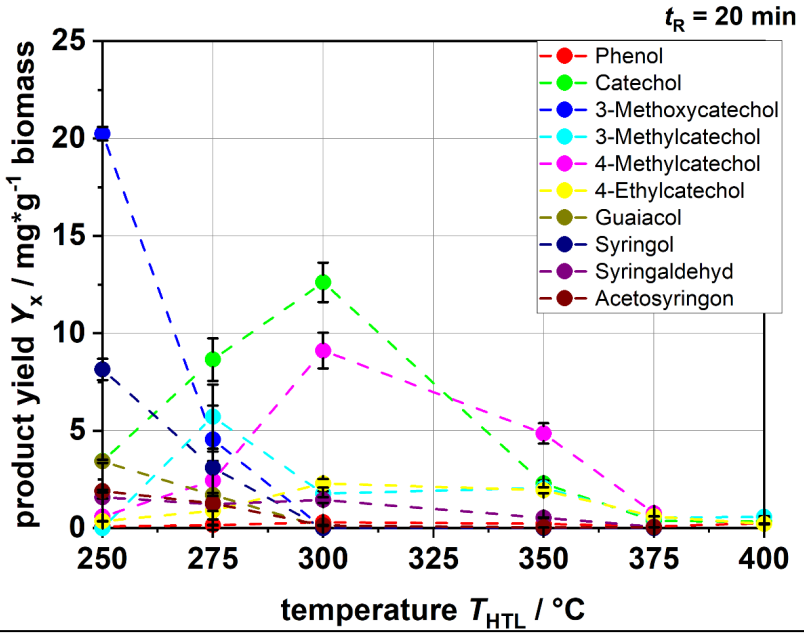
Research on HTL of black liquor

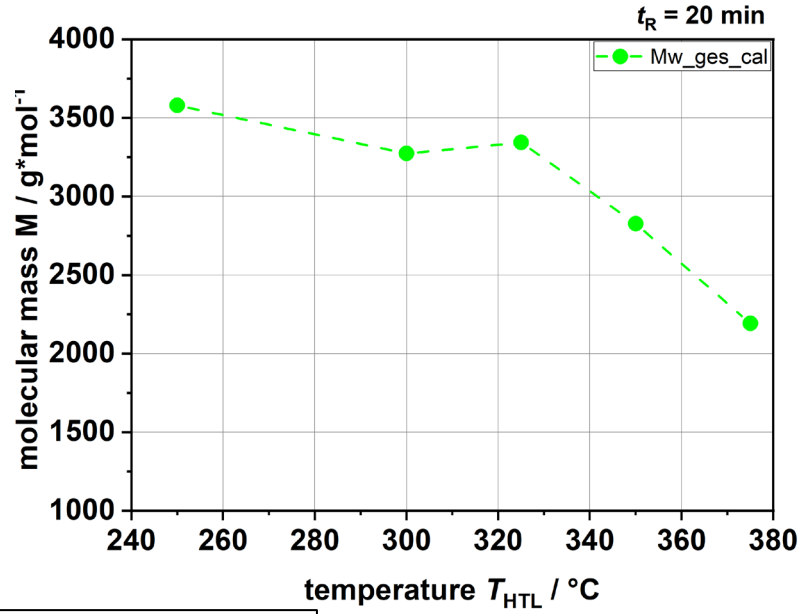
Analysis of all product phases

Organic phase extraction & quantification of monomers

Investigation of lignin depolymerization







Development of a reaction kinetic model based on the obtained data to describe the depolymerization of lignin

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The role of sulfur-containing salts

Cooking chemicals, e.g. Na_2S

Kraft process

HTL

1) Problems for chemical engineering?
2) Environmental & health issues?
3) Influence on depolymerization of lignin?

→ Investigations on behavior of sulfur-containing salts

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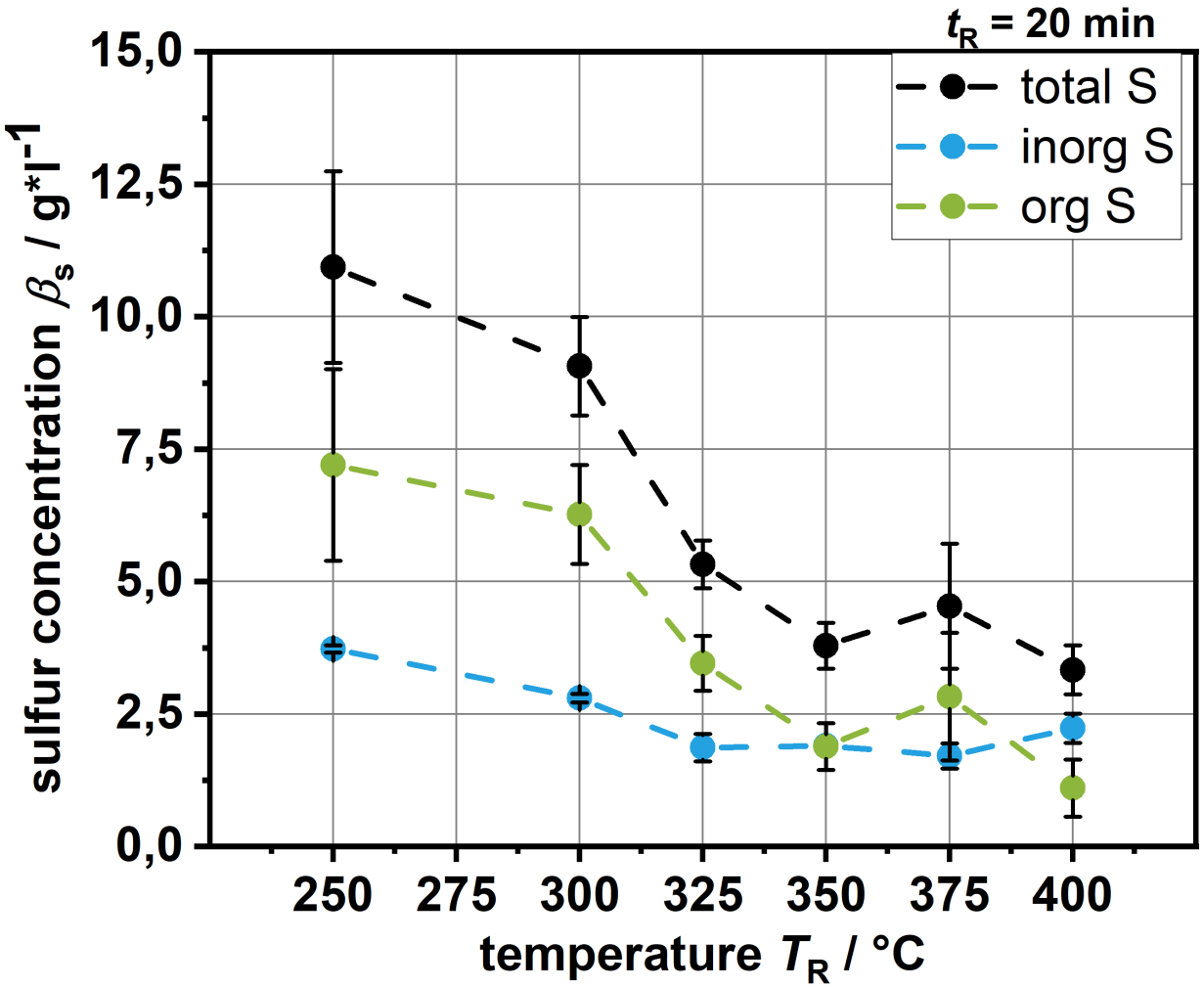
Sulfur in liquid and solid phase

- Sulfur in the solid phase plays only a minor role, less then 10 wt. % of sulfur
- Analysis of liquid phase
  - Total sulfur via ICP-AES
  - Inorganic sulfur via ion chromatography: oxidation of sulfur compounds to SO_4^{2-}
  - Qualification/quantification of some organo-sulfur compounds via GC-SCD
- Inorganic as well as organic sulfur-content are decreasing with T_R↑



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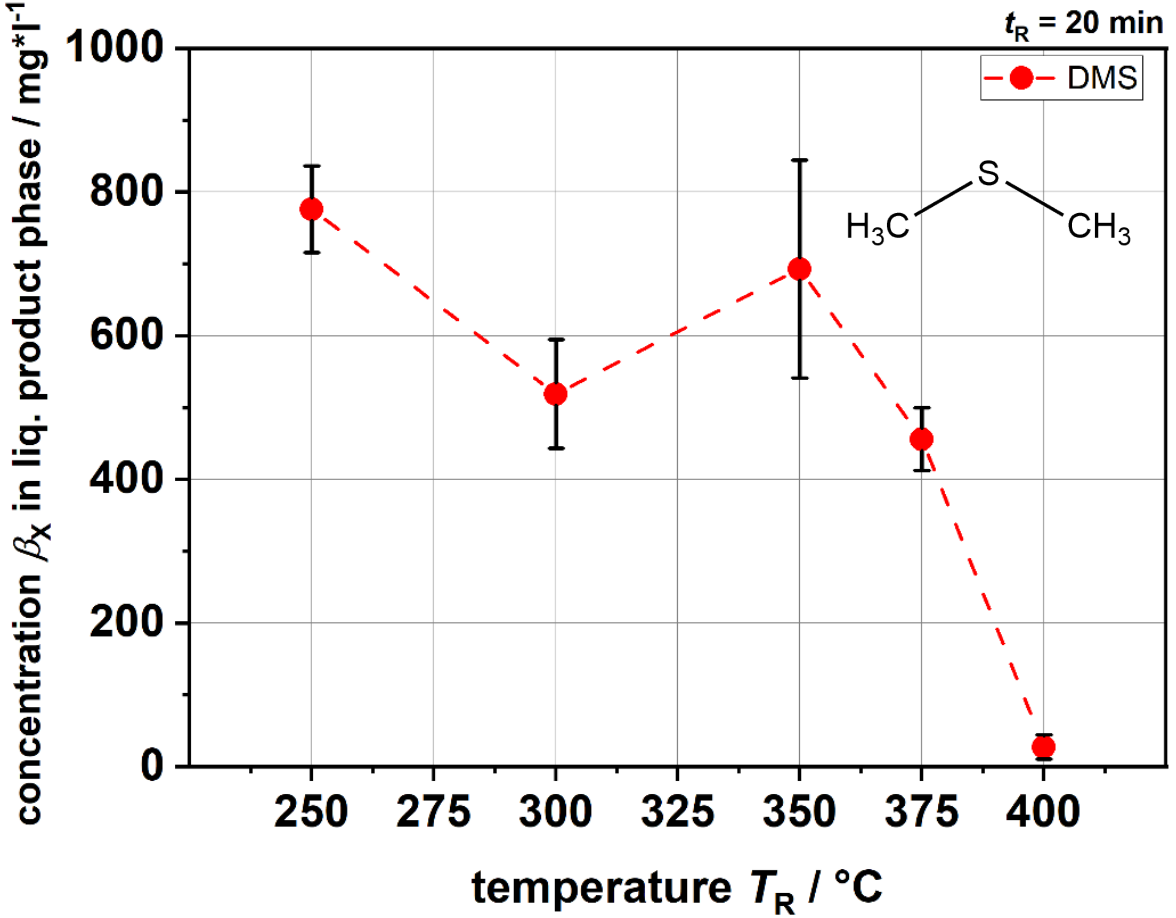
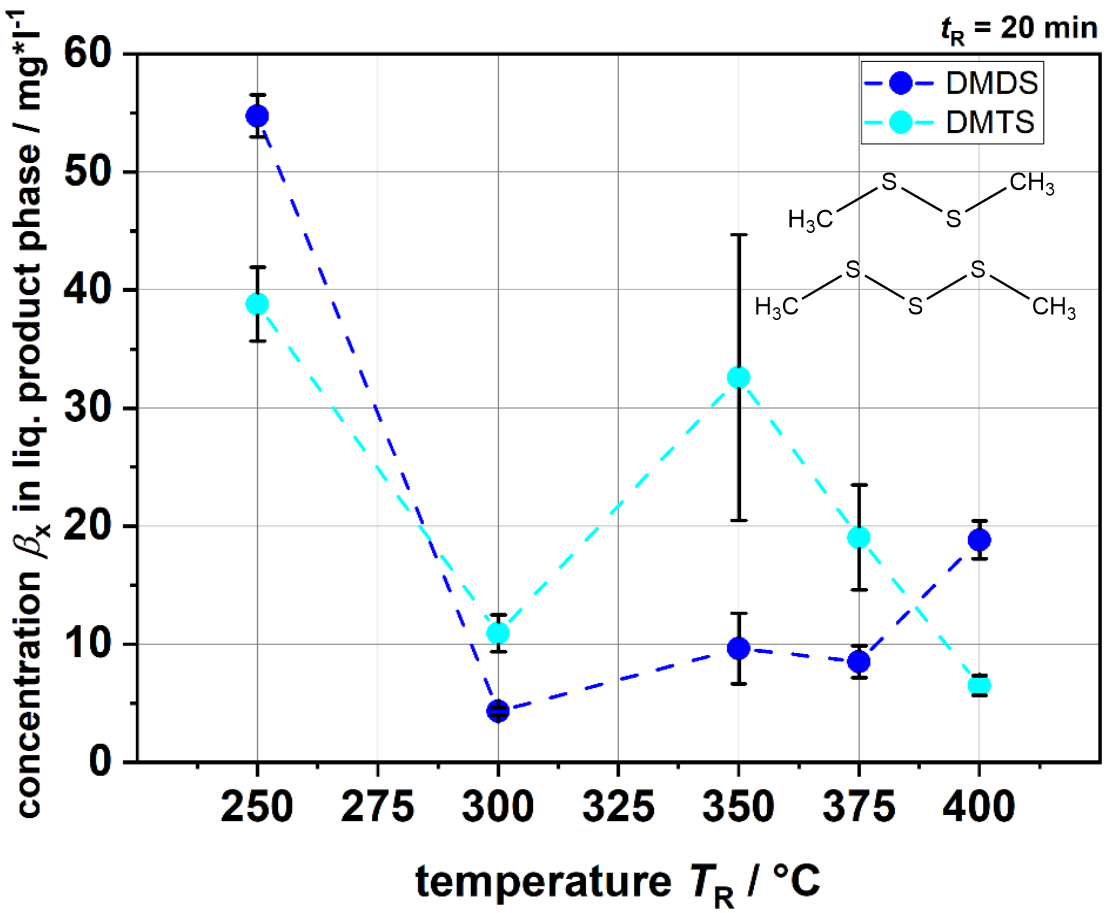
Organo-sulfur compounds in liquid phase





- Mainly organic sulfides, especially DMS
- Other compounds found: (methyl-)thiophene, ethyl mercaptane, methyl mercaptane

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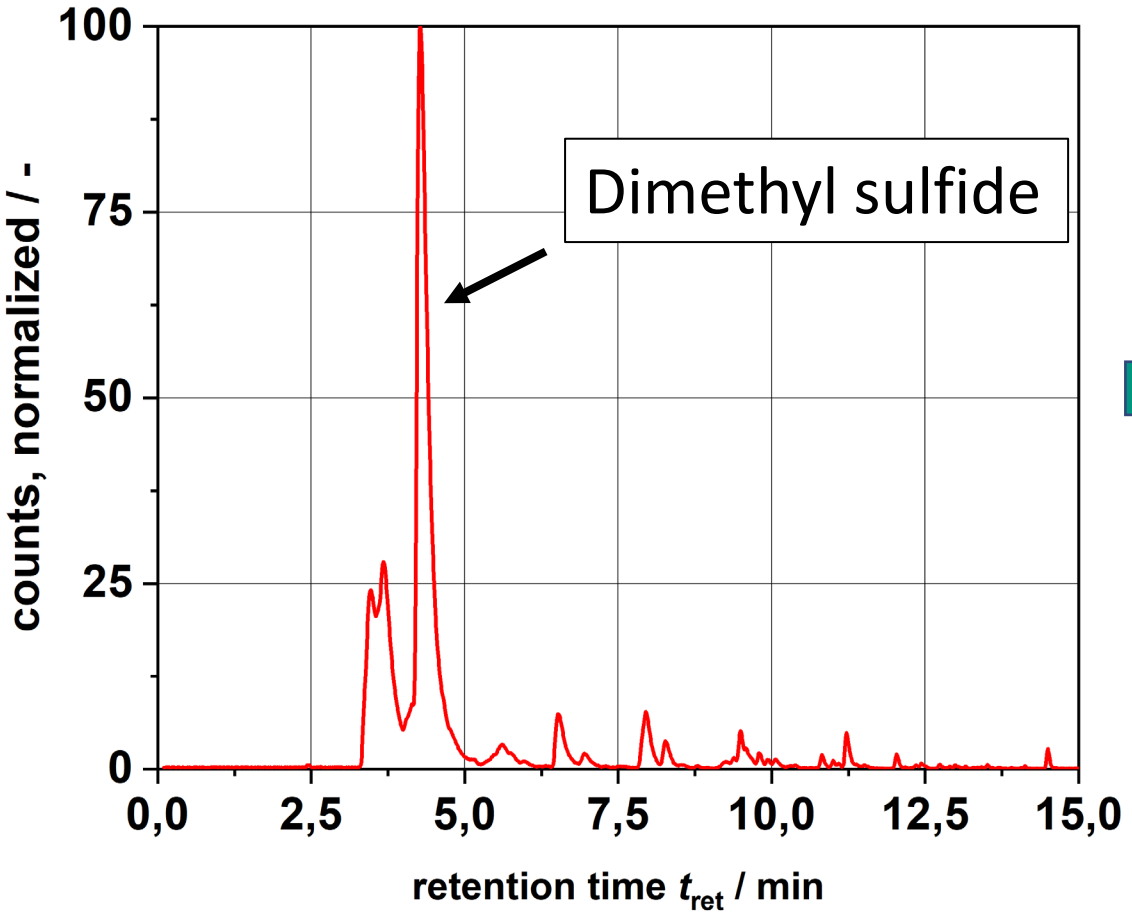
Sulfur in gas phase



Possible reaction pathway from literature:

Methyl mercaptane

$$HS^- + Lig - CH_3O \rightarrow \boxed{CH_3SH} + Lig - O^-$$

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

Dimethyl sulfide

$$CH_3S^- + Lig - CH_3O \rightarrow \boxed{H_3CSCH_3} + Lig - O^-$$

Karnofski et al. 1975, *Odor generation in the Kraft process*

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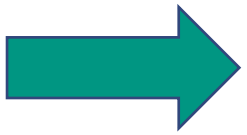
Influence of sulfide (S^{2-}) concentration

- DMS in gas phase could be the reason for the decrease of total sulfur concentration in liquid phase
- Reaction pathway from literature describes connection between sulfide salts and DMS production



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)

- all experiments done at T_R = 375 °C; t_R = 10 min

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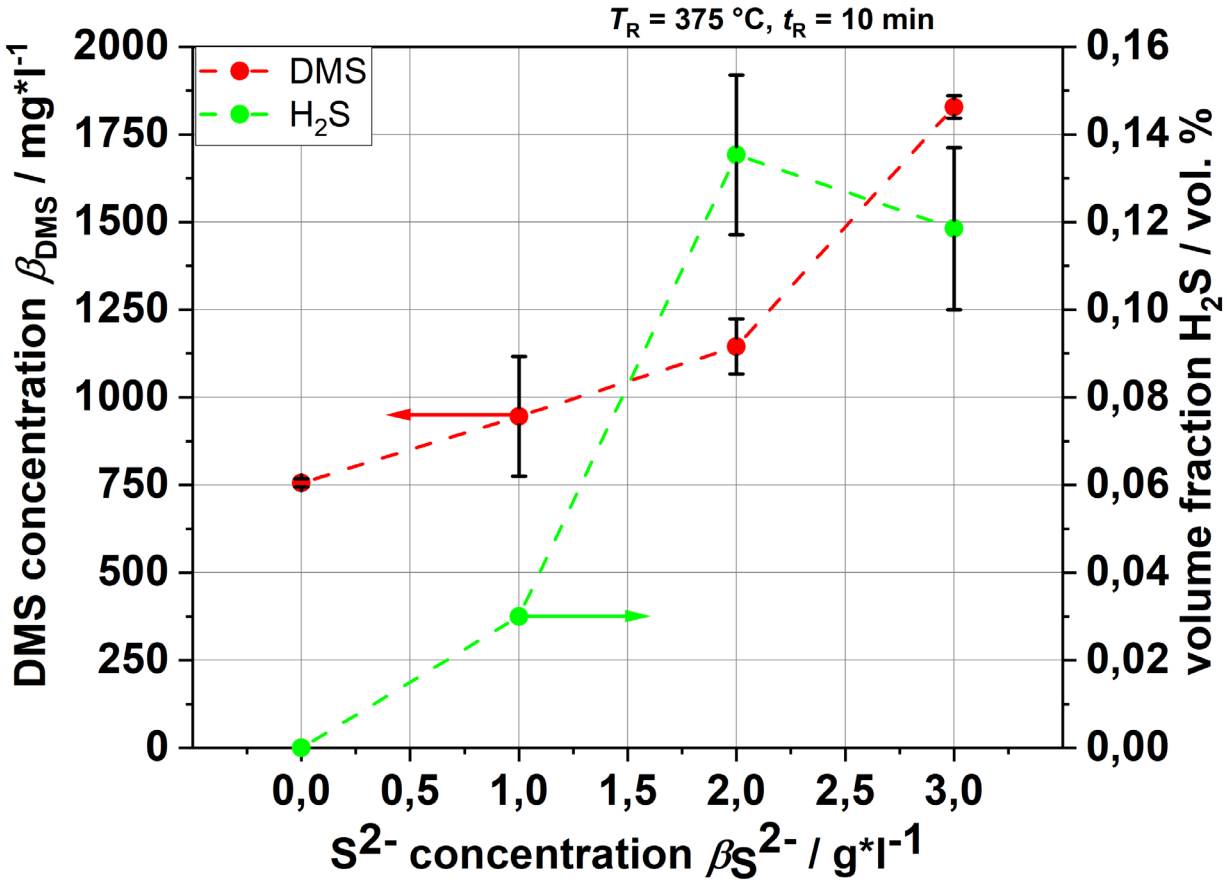
Influence of sulfide (S^{2-}) concentration

- Analysis via GC-FID/WLD
- Clear correlation between sulfide concentration and DMS/H_2S production
- Increase of DMS concentration proves reaction pathway
- Shift from inorganic to organic sulfur-compounds



S^{2-} ions directly involved in HTL process

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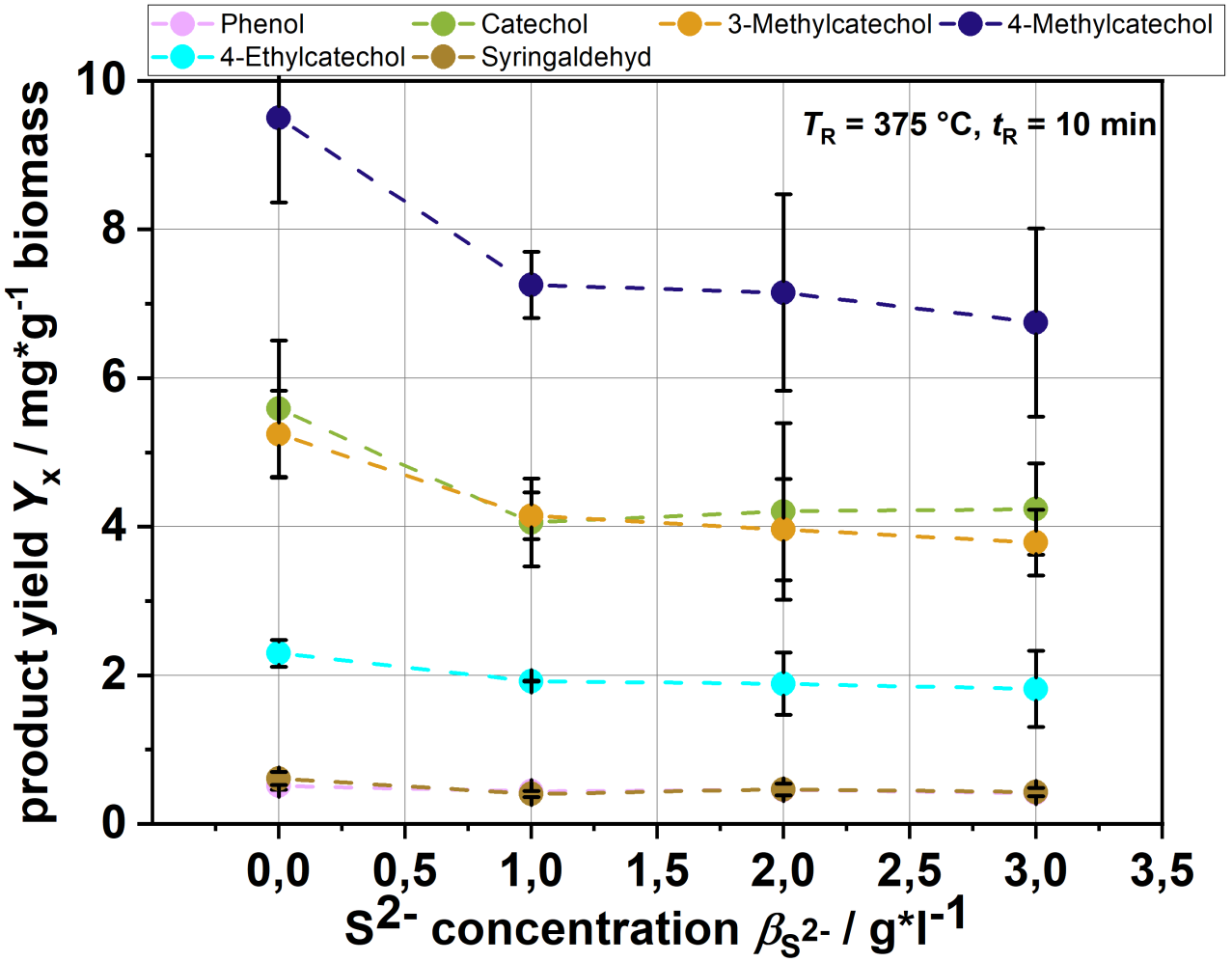
Influence of sulfide (S^{2-}) concentration

- Catalytic/Inhibiting influence on depolymerization of lignin?

→ Observation of typical monomer yields & molecular weight



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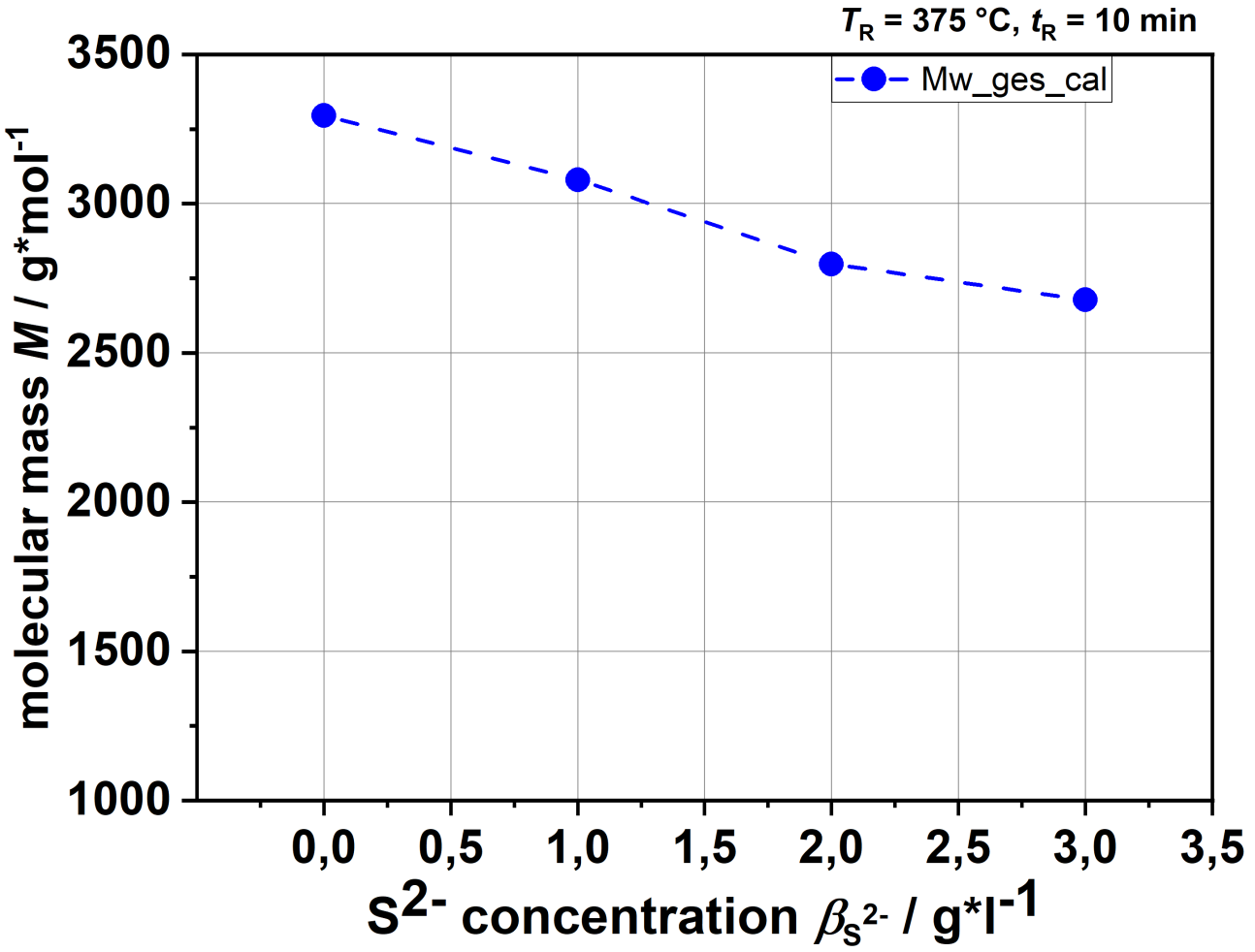
Influence of sulfide (S^{2-}) concentration

- Catalytic/Inhibiting influence on depolymerization of lignin?

→ Observation of typical monomer yields & molecular weight

→ Slight acceleration of lignin depolymerization



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Summary

- Organic as well as inorganic sulfur concentration is reduced with T_R ↑
- most of the sulfur passes into the gas phase, see GC-MS results
- DMS main organo-sulfur compound in gas and liquid phase, H_2S plays minor role
- Correlation between DMS concentration in gas phase and S^{2-} concentration
- S^{2-} concentration affects lignin depolymerization

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Project partners

BL2F
Transforming Black Liquor to Biofuel

KIT
Karlsruhe Institute of Technology

Tampere University

Brunel University London

KIT
Karlsruhe Institute of Technology

SINTEF

PAUL SCHERRER INSTITUT
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THE NAVIGATOR COMPANY

Valmet

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Ranido

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Thank you!

Get in touch with the project:

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