Karlsruhe Institute of Technology

Institute of Catalysis Research and Technology

From Pulp to Aromatic Products – Description of a reaction mechanism for lignin depolymerization during hydrothermal liquefaction (HTL) of Black Liquor

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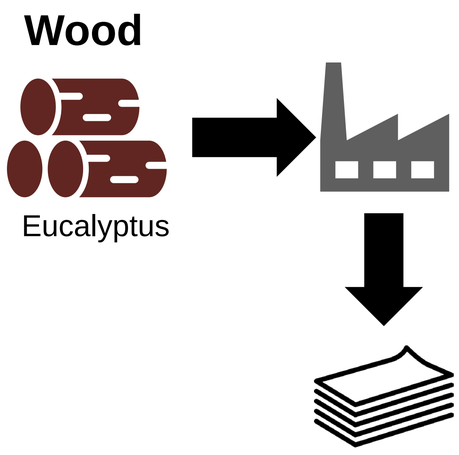
Introduction

- Lignin is a promising resource for production of aromatic compounds
- High Abundancy in form of black liquor (BL) a by-product of the pulp & paper industry
- HTL can depolymerize the lignin molecule by processing the BL directly without prior process steps



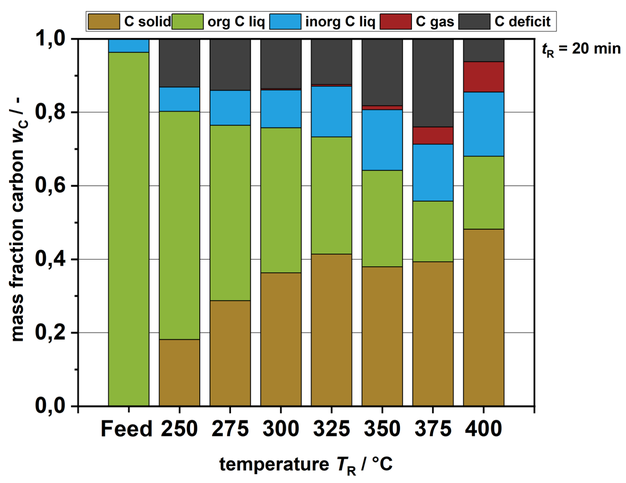
This work

Batch experiments in micro autoclaves

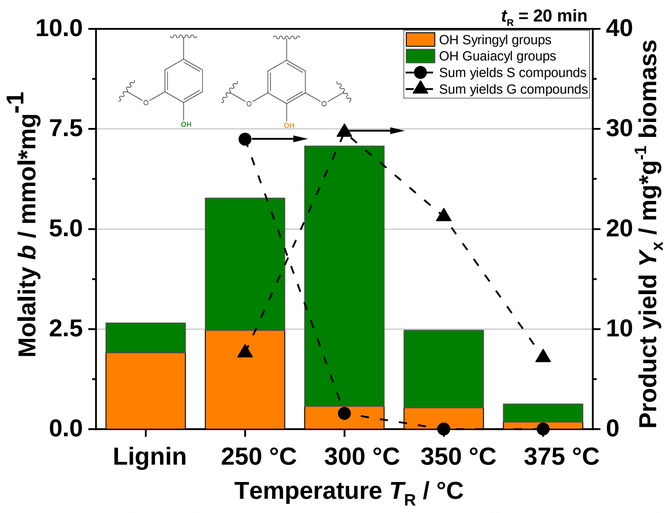
T_R = 250 – 400 °C t_R = 0 – 30 min

Goal: Development of a kinetic model which can describe the potential reactions during lignin depolymerization under HTL conditions under the influence of salts from BL

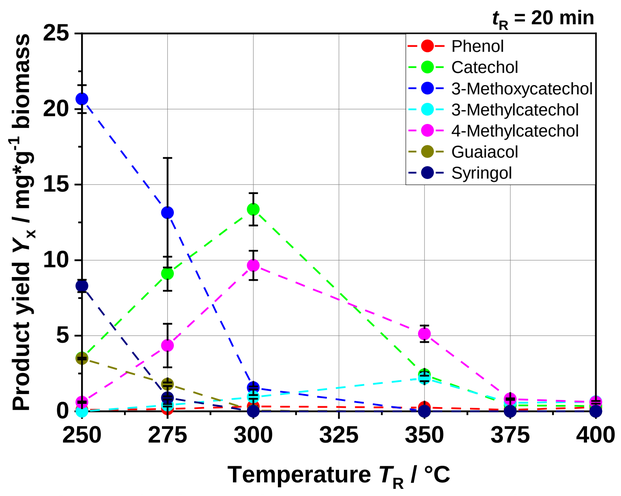
Experimental results



- Lot of carbon in solid phase
- Influence of t_R < Influence of T_R



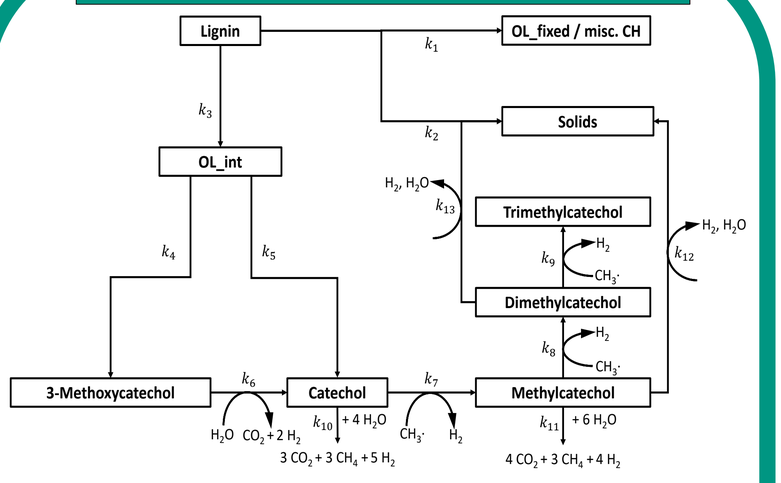
- Syringyl compounds react first to Guaiacyl compounds
- High T_R leads to low yields fast



- Catechols main monomer products
- Slow decrease in yields with increasing t_R,
- -OCH3 → -OH → -OH + -CH3
- Phenol/Cresols not favorized

Wörner M., et al. From Pulp to Aromatic Products—Reaction Pathways of Lignin Depolymerization; Energy and Fuels (2024), 38 (7), pp. 6020 – 6035

Reaction scheme

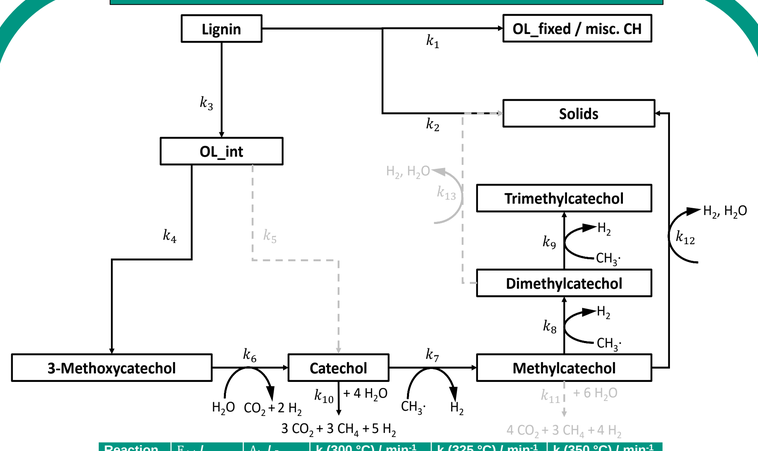


The kinetic parameters of each reaction A_j and $E_{A,j}$ were estimated via minimization of the sum of squared errors via the objective function $f(k)$:

$$k_j = exp\left(A_j - \frac{E_{A,j}}{R}\left(\frac{1}{T_R} - \frac{1}{T_{ref}}\right)\right) \quad [h^{-1}]$$

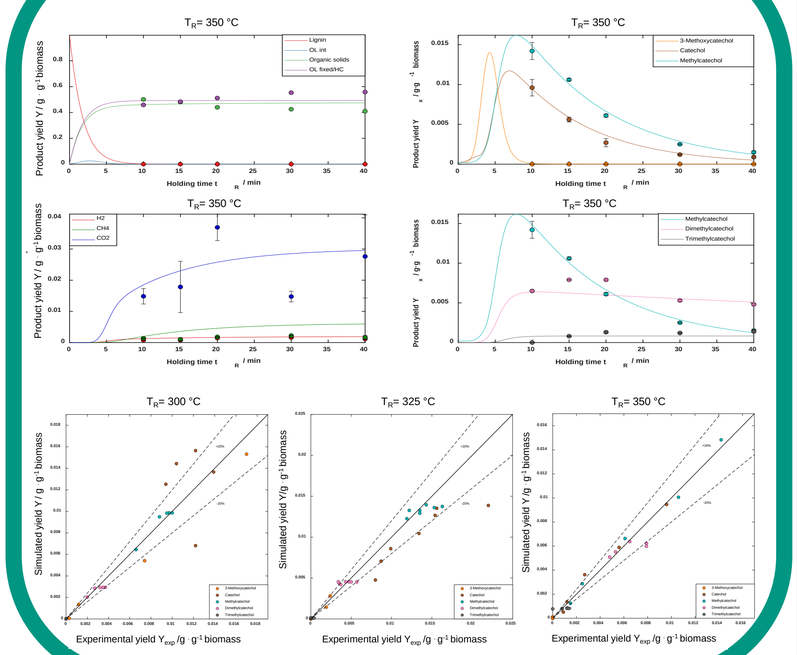
$$\min(f(k)) = \sum_{l=3}^{9}\sum_{l=1}^{q} w_{i,l}\left(\frac{m_{\mathrm{i,l,exp}} - m_{\mathrm{i,calc}}(k)}{m_{\mathrm{i,exp}}}\right)^2$$

Cross validation



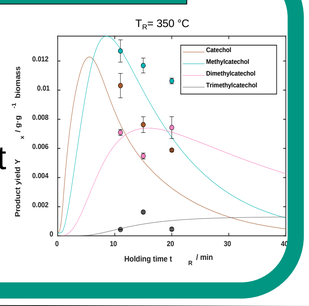
Reaction Number	E_{Aj} / kJ*mol^{-1}	A_j / -	k (300 °C) / min^{-1}	k (325 °C) / min^{-1}	k (350 °C) / min^{-1}
1	0	4.38	$1.33 \cdot 10^{0}$	$1.33 \cdot 10^{0}$	$1.33 \cdot 10^{0}$
2	0	4.30	$1.23 \cdot 10^{0}$	$1.23 \cdot 10^{0}$	$1.23 \cdot 10^{0}$
3	15.54	4.02	$8.10 \cdot 10^{-1}$	$9.28 \cdot 10^{-1}$	$1,05 \cdot 10^{0}$
4	33.12	3.42	$3.81 \cdot 10^{-1}$	$5.10 \cdot 10^{-1}$	$6.66 \cdot 10^{-1}$
6	125.29	4.11	$3.38 \cdot 10^{-1}$	$1.01 \cdot 10^{0}$	$2.79 \cdot 10^{0}$
7	14.85	3.84	$6.78 \cdot 10^{-1}$	$7.72 \cdot 10^{-1}$	$8.71 \cdot 10^{-1}$
8	13.65	2.44	$1.70 \cdot 10^{-1}$	$1.91 \cdot 10^{-1}$	$2.14 \cdot 10^{-1}$
9	234.95	0.69	$4.21 \cdot 10^{-3}$	$3.34 \cdot 10^{-2}$	$2.24 \cdot 10^{-1}$
10	121.46	1.30	$2.11 \cdot 10^{-2}$	$6.12 \cdot 10^{-2}$	$1.63 \cdot 10^{-1}$
12	344.60	-1.17	$2.51 \cdot 10^{-4}$	$5.15 \cdot 10^{-3}$	$8.30 \cdot 10^{-2}$

Simulation



Validation soft wood

- the yields of aromatics from BL based on softwood or hardwood differ only slightly
- since syringyl groups not present route via 3-methoxycatechol is removed



Conclusion

pathway via 3-methoxycatechol with the subsequent methylation of catechol is important for monomer formation of hard wood and can be replaced by catechol for soft wood

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