

COMPARING THE REACTION PATHWAYS OF MONOMERS AND OLIGOMERS DURING HYDROTHERMAL LIQUEFACTION OF LIGNIN

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Lignin is a natural biopolymer built up from aromatic structures. The pulp and paper industry produces around 50 million tons per year [1], in form of black liquor, in which the lignin is dissolved. To valorize the lignin different approaches are studied, among others by hydrothermal liquefaction (HTL). The EU Horizon 2020 project “Black Liquor 2 Fuels” has the aim to integrate an HTL process with subsequent reforming steps into a pulp mill. Black liquor is thus used as feed directly to produce drop-in bio fuels. In order to design the HTL plant in the best possible way, it is necessary to understand lignin depolymerization in more detail.

This work tackles the challenge to picture the reaction pathways of the lignin depolymerization under hydrothermal conditions with focus on the oligomer intermediate compounds. For this, HTL experiments in batch micro autoclaves at different temperatures ($T_R = 250 - 400$ °C) and holding times ($t_R = 0 - 30$ min) were performed. Black liquor as received, extracted lignin in a model salt solution as well as monomer model substances like guaiacol or syringol were used as feedstock. All product phases were analyzed via different analytical methods. To illustrate the reaction pathways for the monomers mainly GC-FID and GC-MS were applied. Looking at catechol, a major product, and its derivatives, we were able to show how the functional groups of the monomers change during HTL. Firstly, methoxy groups are demethylated to hydroxy groups; afterwards, methyl groups bind to aromatic rings possibly by radical or ionic reactions. P-NMR as well as SEC analysis were used to obtain information about the oligomer structures and the depolymerization progress. We were able to picture the course of the molecular weight of the produced organic matter in the liquid phase. Via solid state NMR we could confirm the strong coke formation accelerated by the high content of aromatic structure in the lignin which leads to increased carbon content in the solid product phase [2]. In addition to the batch experiments, we performed experiments in a continuously operated reactor at three different reaction temperatures with black liquor as feed. Besides the comparison with the batch experiments the larger quantities of product enables us to perform a 2D-NMR analysis. This improved our insight into the structural changes of the oligomers at different reaction temperatures. Overall, we were able to elaborate similarities and differences between the depolymerization process on the oligomer and monomer side. These results will ultimately end up in a kinetic model, which describes the lignin degradation during the HTL.

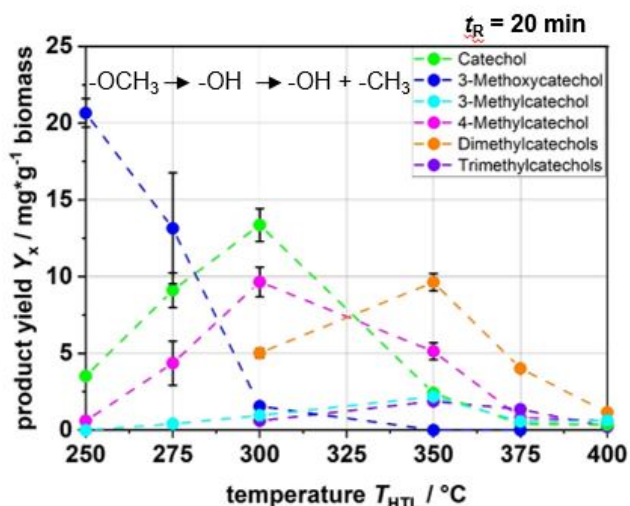


Figure 1 – product yields of catechol and derivatives with increasing reaction temperature

References:

1. José Borges Gomes F, Souza RE de, Brito EO et al. (2020) A review on lignin sources and uses. JABB:100–105. <https://doi.org/10.15406/jabb.2020.07.00222>
2. Wang C, Fan Y, Hornung U et al. (2020) Char and tar formation during hydrothermal treatment of sewage sludge in subcritical and supercritical water: Effect of organic matter composition and experiments with model compounds. Journal of Cleaner Production 242:118586. <https://doi.org/10.1016/j.jclepro.2019.118586>