

From pulp to aromatic products - Understanding the lignin depolymerization during hydrothermal liquefaction (HTL)

Maximilian Wörner, Alexandra Barsuhn, Dr. Ursel Hornung, Prof. Dr. Nicolaus Dahmen

Karlsruhe Institute of Technology (KIT) – Institute of Catalysis Research and Technology (IKFT)
Herrmann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen

Lignin is a naturally occurring biopolymer that provides stability and durability to plants and trees. At the same time, it holds enormous potential for reducing the consumption of fossil resources in the chemical industry. The molecule contains a high density of aromatic rings, which is otherwise only found in coal or crude oil. Since aromatics are of significant importance for a wide range of applications, it is necessary to find alternative production routes for these substances as part of the shift to renewable resources. Lignin therefore offers itself as a possible feedstock. Around 50 million tons per year of Lignin are produced in large quantities as a by-product in the paper industry. Up to now, this lignin has largely been used energetically. In addition to the above-mentioned need to substitute fossil resources, the material valorization of lignin also holds economic potential.

A suitable process for depolymerizing the lignin molecule is hydrothermal liquefaction (HTL). In this process, the changing properties of the water near or above the critical point of water (374 °C, 221 bar) are utilized. This makes it possible to break down the lignin into many smaller monomers and oligomers. These are essential aromatic platform chemicals that can be of importance in various sectors of the chemical industry. By using the HTL process, it is also possible to use feedstock with a high water content. This makes it suitable for the use of lignin from the pulp industry. The most commonly used wood pulping process is the Kraft process. Here, the lignin is present dissolved in the black liquor, a by-product. The HTL allows the direct use of the black liquor as feedstock without having to extract the lignin first.

One problem in the depolymerization of lignin is the complexity of the reaction network. The typical aromatic monomer compounds such as catechol are formed on the one hand directly from the lignin molecule and on the other hand via oligomers. In order to better understand and optimize the process, it is important to have more detailed information about the reactions that take place and the intermediates that are formed. This study is about an advanced characterization of oligomers as well as the breakdown of possible reaction pathways. For this purpose, HTL experiments were performed in micro autoclaves as well as in a continuous tube reactor. Experiments were carried out in the range of 250 to 400 °C and holding times of 1 to 30 minutes and a pressure of around 25 MPa. Black liquor as well as various model substances were used. The continuous experiments were performed with black liquor and/or under a feed flow between 1.4 and 2.0 kg/h at 325, 350 and 375 °C and 24 MPa. The organic phase was extracted from the liquid product phase obtained by HTL and analyzed by various analytical methods (H-NMR, C-NMR, HSQC, GC-FID, GC-MS, SEC, ...).

SEC analysis show clear differences in the molecular weight of the oligomers at different reaction temperatures and holding times. Interestingly, the SEC analysis leads to constant high molecular weights at higher temperatures, around 4000 g/mol. A hypothesis is that large molecules do not degrade further. Additional NMR results show changes in the functional groups over time and temperature. Regarding the reaction pathways, we are introducing an extended reaction pathway involving different intermediate and final monomer products as well as larger molecules.

All results together lead to a reaction scheme, which can describe the depolymerization of lignin in more detail.