

Lignin depolymerization from subcritical to supercritical water

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Lignin is a 3-dimensional amorphous polymer consisting of methoxylated phenyl propane units. Despite the considerable scientific effort, there has been limited commercial success in recovering usable aromatics from lignin. The complex polymer structure changes with biomass origin, so lignin depolymerization components also depend on biomass source (with guaiacol type units being more prevalent in softwood, syringol units in hardwood for example).

Subcritical water hydrolysis of lignin rapidly produces a large mixture of compounds with very low selectivity that makes the process technically and economically unfeasible to product aromatic building blocks [1].

Reactions of lignin in supercritical water (SCW) lead a phenolic char as the dominant product in the majority of literature studies, as well as a minor yield of aromatic hydrocarbons. Char is formed through crosslinking of phenolic units and formation of recalcitrant C-C aromatic to aromatic bonds. These condensation reactions take place too fast, and it is not possible to control them in conventional reactors.

Whilst poor selectivity is common to both sub- and SCW, there are some significant differences between the reaction media – most notably the difference in ionic product of water, thus favoring ionic reactions at subcritical water conditions vs the radical reactions that are prevalent under SCW conditions. Furthermore, the SCW is a non-polar reaction media where the depolymerized products could be dissolved. Therefore, providing the char production is avoided, lignin depolymerization in SCW would open new ways to develop processes to produce selective aromatics building blocks from lignin.

In this contribution, an experimental study about the use of ultrafast reactors to control the char production in SCW is described. Supercritical temperatures were achieved by mixing the lignin feed with a hot stream of SCW. Reaction time was kept below 1 s thanks to a rapid cooling step by sudden depressurization. Optimization of reaction time was done so that the amount of char formed is minimized while obtaining a high yield of aromatic oil.

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