

Abstracts

Chemical Lignin Crushing Based on the FENTON Mechanism

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Objective

The beginning of the formaldehyde discussion has triggered developments aiming at formulating alternative gluing systems. Such developments include the approach to synthesise resins on the basis of lignin. One possibility of its application as an alternative formaldehyde-free bonding agent results from, if possible, selective fractioning of the lignin matrix into uniform compounds and their subsequent networking. Such disintegration is caused by dry rot and other brown rot fungi due to the so-called FENTON mechanism, which is a non-enzymatic reaction mechanism. The fungi generate hydroxyl radicals by means of variegated acid and induced ferro-reduction, which then split the lignin up into smaller components. This degradation is focused at for biomimetic application, as there is reason to assume that this natural degradation process yields uniform fragments that are catabolised by further mechanisms, such as in dry rot. The assumption is based on the fact that, in nature, the avoidance of disorder or diversity of metabolic processes is of primary importance. Hence, this research project comprised investigations on the suitability of the FENTON mechanism as an approach for the chemical fragmentation of lignin before the background of an application as an adhesive for wood and wood-based materials.

Materials and Methods

The project started out from morphologically investigating the grain size distribution and from determining the chemical parameters of buffer capacity and pH-value.

Preliminary tests at the IHD were able to prove a clear decrease in the medium molar mass (MN) of kraft lignin acc. to the FENTON reaction (Fig. 1). Based on those results, various differentiations in performing the reactions were applied in the course of the project.

- variation of the amount of hydrogen peroxide added,
- impact of the iron salt,
- variation of the reducing agent.

Subsequently, by using selected preferential variants, the networking of the FENTON products was investigated by means of ABES (Automated Bonded Evaluation System). Networking options using glutaraldehyde and pMDI (polymeric diphenyl methane diisocyanate) were investigated for that purpose.

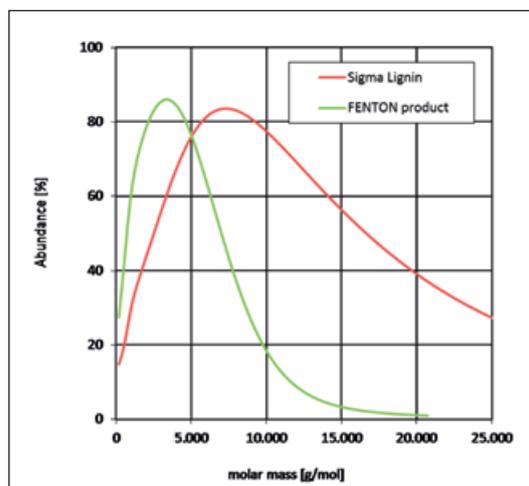


Fig. 1: Molar mass distribution of kraft lignin, of sigma lignin and of the respective product after fractioning by way of the FENTON mechanism in a preliminary test (determination of the GPC).

Findings

Chemical crushing of lignin

Proof of the impact of the performed approaches onto the fractioning process was provided by determining the medium molar mass by means of the GPC. The two initial lignins used in the project were of a medium molar mass of between 5,500 g/mol and 6,200 g/mol. A variation of the amount of hydrogen peroxide yielded lignin of medium molar masses of around 10,000 g/mol. After fragmentation, the fragments aggregated. By varying the iron salt and the reducing agent, no significant crushing could be observed in the process. Adjustments in the performance of the reactions then resulted in slightly lower medium molar masses in the range around 5,500 g/mol.

The determination of the oxygen content in selected products revealed a higher oxygen content in the FENTON macromolecule as compared to the initial lignin.

Investigations on the efficient networking of FENTON degradation products

Networking tests were performed on selected FENTON products. For that purpose, lignins were treated using the dialdehyde glutaraldehyde and the diisocyanate pMDI. The reactivity with a view to its suitability as an adhesive component

for wood was investigated and evaluated by way of ABES. A comparison with the referential lignins used did not reveal any substantial increases in reactivity. A comparison with industrially applied UF resins did not allow for deriving substantial adhesive potential either.

Summary

The results of lignin fragmentation can be summarised by the following items:

- a decrease in the medium molar mass could not be achieved;
→ hence, a molar-mass-dependent increase in reactivity was not achieved by crushing;
- adjustments in the reaction conditions were able to push back verifiable aggregation of the lignin molecules to form larger macromolecular agglomerations;
- the oxygen content at the macromolecule and thus the share of functional groups containing oxygen were increased by applying the radical FENTON mechanism;
→ an increase in reactivity can be deduced from that.

Moreover, it could be shown that kraft lignin allows to be networked by both dialdehydes and diisocyanates. The findings of the study generally show that there is a networking potential in lignins.