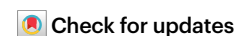


Cleavage of challenging chemical bonds in lignin enables biofuels

Elena Subbotina & Joseph S. M. Samec



Lignin contains both C–O and C–C bonds, where C–C bonds are highly resistant to cleavage. Now, a bifunctional catalyst enables the cleavage of the challenging C–C bonds in lignin to produce biofuels.

Wood consists of carbohydrates (up to 70 wt%) and lignin (up to 30 wt%). To enable a wood biorefinery, both carbohydrates and lignin must be valorized¹. While valorization of wood carbohydrates into, for example, pulp and paper is well established, lignin is currently burnt to a low value in these industries² despite being a source of highly desirable aromatic compounds³. During the past decade, there has been a strive to develop methods to valorize lignin in addition to the pulp, termed the 'lignin-first approach'⁴. To convert lignin macromolecules into fuels or commodities, its complex structure needs to be cleaved into smaller compounds (monomers; Fig. 1a). Lignin is a heterogenous polymer built up by random polymerization of phenolic propenols leading to both C–O and C–C bonds connecting the aromatic groups² (Fig. 1b). The C–C bonds that are native in lignin are: 5–5', β -5', β - β' and β -1' (Fig. 1a). In addition to these bonds, new aryl–aryl and aryl–alkyl bonds are formed by undesired reactions during lignin isolation. So far, the main research focus has been to cleave the most abundant C–O lignin ether bonds that have bond dissociation energies of around 60–70 kcal mol⁻¹. Even though the content of these bonds can be as high as 70%, cleavage of all C–O bonds in lignin will only lead to 49% of monomers (theoretical maximum yield; Fig. 1c). Besides C–O ether bonds, lignin contains C–C bonds that have higher bond dissociation energies of up to 334–502 kJ mol⁻¹, and these linkages are not cleaved using most current strategies. Thus, the by-products from cleaving C–O bonds in lignin are dimers and oligomers comprising C–C bonds that are difficult to further valorize.

Now, writing in *Nature Chemical Engineering*, Emiel Hensen, Rui Xiao, Zhicheng Luo and co-workers report a bifunctional catalyst able to cleave C–C bonds in lignin⁵. The catalyst (Pt/H-MOR) comprises platinum that shuffles hydrogen and a zeolite with Brønsted acid sites (H-MOR) that can activate and cleave the generated C=C bonds. The combination of these two sites is thus powerful to activate and cleave C–C bonds in lignin. By carefully studying the mode of activation and screening the reactivity, the authors have developed a catalytic system that can activate the C–C bonds 5–5', β -5', β - β' and β -1', and achieve high yields of 5- and 6-membered hydrocarbons that are desirable as components in gasoline and jet fuel (Fig. 1d).

By measuring reaction kinetics of model compounds combined with density functional theory (DFT), they found that hydrodeoxygenation of bisphenols (representing 5–5' lignin linkage) was fast, leading to either phenylcyclohexane or bis-cyclohexane intermediates. The cleavage of the former can be directly achieved by only the acidic site

of the zeolite (activation barrier of 134 kJ mol⁻¹). However, a pathway via dehydrogenation to phenyl-cyclohexene over Pt followed by protonation by H-MOR and subsequent cleavage was found to be more feasible (activation energy of 86 kJ mol⁻¹), which demonstrates the necessity of two catalytic sites. Regarding the cleavage of bis-cyclohexane, it was experimentally found that it could not be transformed by only the zeolite or platinum, indicating a presence of an intermediate, which was found to be cyclohexylcyclohexene. Supported by DFT studies and experiments, the rationale behind the observations was that Pt performs a dehydrogenation of the cyclohexyl group to form an olefin as a reactive intermediate. This olefin is then protonated by the zeolite to generate a carbenium ion that facilitates C–C bond cleavage to generate 5- and 6-membered hydrocarbons, with the activation energy of 117 kJ mol⁻¹. Based on experimental and computational results, the pathway via phenylcyclohexane was found to be the most favorable. A spatial proximity of two catalytic sites in the Pt/H-MOR catalyst is crucial, since the rate of the C–C cleavage using physical mixtures of Pt/SiO₂ and H-MOR was considerably lower.

Model studies were performed to demonstrate cleavage of C–C bonds in various compounds targeting 5–5', β -5', β - β' and β -1' motifs, disclosing high yields of monomeric compounds from aryl–aryl, aryl–alkyl and alkyl–alkyl C–C bond cleavage, where the cleavage of β -5', β - β' and β -1' structures resulted in more complexed product mixtures.

The transformation was then applied to real lignins. In a conclusive experiment, a previously established transformation targeting only C–O bonds in birch wood lignin was first performed to give a monomer yield of 42.3%, corresponding to the theoretical maximum yield. The lignin oil comprising monomers, dimers and oligomers was then reacted with the bifunctional Pt–zeolite at 300 °C and 40 bar H₂ to produce a total of 76.9% monomers, of which 34.6% resulted from C–C bond cleavage. Thus, the yield of monophenols was increased by an impressive 82%. Application of the strategy to lignins obtained via industrial processes also showed improvement compared with previous methods, but led to lower yields of monomers (16.8–21.5%). Given these figures, it is not surprising that the performed techno-economic analysis as well as the life-cycle assessment showed economic and environmental sustainability.

This study opens new avenues for C–C bond cleavage that can be applied to substrates beyond lignin, such as plastics. Especially noteworthy is the elegant finding of the essential dehydrogenation step to generate the intermediate containing the C=C bond and the presence of Brønsted acid sites of the catalyst to facilitate events leading to cleavage of the bonds. This leads to higher yields than the previous report⁶.

While this work considerably advances the field, it brings questions for further investigations. The authors performed thorough experimental and computational studies of the mechanism of the cleavage of 5–5' model compounds; however, the mechanisms of transformations of the β -5', β - β' and β -1' motifs were not covered. Since

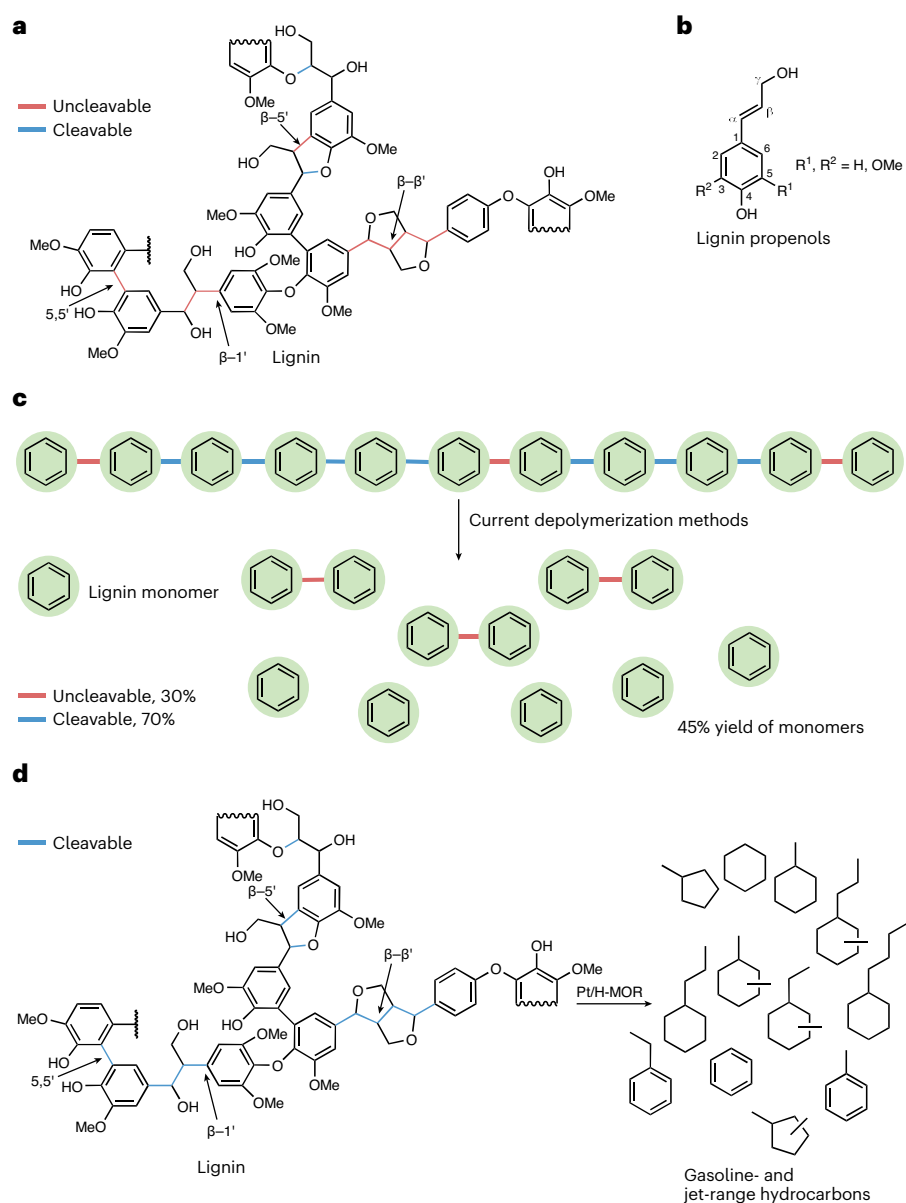


Fig. 1 | Cleavage of C–C bonds in lignin. **a**, Schematic representation of lignin structure and major types of lignin interunit linkages. Methods for nearly quantitative cleavage of C–O linkages is well established. However, C–C lignin linkages generally are not cleaved by most common current lignin valorization methods. **b**, Lignin building blocks: *p*-coumaryl, coniferyl and sinapyl alcohols. The names of the interunit linkages in lignin stem from the corresponding positions that are connected by a particular bond. **c**, Visualization of the

theoretical maximum yield of lignin monomers, containing 70% of cleavable C–O bonds and 30% of uncleavable C–C bonds. **d**, The approach used in the highlighted work allows to generate lignin monomers in 76.9% yield, which exceeds the yield of lignin monomers by previous methods (42.3%) by 82%. The additional monomers are formed via C–C bond cleavage in addition to C–O bond cleavage. The developed method delivers 1,079.1 tons gasoline- and jet-range hydrocarbons from 2,000 tons of lignin.

these models resulted in more complex mixtures of products, such studies would help to further improve selectivity of the process. One potential strategy is to study different morphologies of zeolites, which can improve product selectivity via shape-selective catalysis⁷. Another limitation of the process is the still relatively low yields from industrial lignins. A further investigation of the structure–reactivity relationship will be needed for these lignin sources.

Elena Subbotina^{1,2} & **Joseph S. M. Samec**³

¹Center for Green Chemistry and Green Engineering, Yale University, New Haven, CT, USA. ²Department of Fibre and Polymer Technology, Wallenberg Wood Science Center, KTH Royal Institute of Technology, Stockholm, Sweden. ³Department of Organic Chemistry, Stockholm University, Arrhenius Laboratories, Stockholm, Sweden.

✉ e-mail: elena.subbotina@yale.edu; joseph.samec@su.se

Published online: 11 January 2024

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Competing interests

The authors declare no competing interests.