

Designing lignin depolymerization by Ni/C-assisted β -ether cleavage and kinetic modeling

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Highlights

- Correlating β -O-4 bond cleavage for efficient lignin depolymerization.
- Higher temperature increases monomer yield and suppresses cross-linking reactions.
- Structural complexity challenges complete prediction of lignin behavior.
- Insights from the lignin model compound support efficient lignin depolymerization.

1. Introduction

The alteration towards environmentally friendly and sustainable production of fuels, polymers and chemicals has driven the exploration of alternative feedstocks, particularly bio-based components, as substitutes for petroleum-based resources. Lignin, an aromatic component of lignocellulosic biomass, is a promising biomaterial for conversion into valuable aromatic products. However, its depolymerization presents a challenge due to the complexity of the resulting multicomponent and multiphase products [1].

Microkinetic studies on lignin depolymerization often face limitations in estimating the kinetic parameters for a small number of components and predicting the structure of oligomeric intermediates. To solve this problem, lignin model compounds have been introduced that simplify the estimation of kinetic parameters by reducing the complexity and difficulty of the reaction. Lignin model compounds, which have well-characterized structures and defined bond types, provide valuable insights into the behavior of lignin under different reaction conditions [2,3]. In the broader context of kinetic modeling of lignin depolymerization, the study has been focused on the use of 2-phenoxy-1-phenylethanol, a representative lignin model compound with a β -O-4 bond. The objective has been to screen operating conditions for selective cleavage of the ether linkage to convert the β -O-4 bond into phenolic monomers while preventing undesired complete saturation of the phenolic ring by hydrogenation.

To elucidate the kinetics of lignin depolymerization, a comprehensive model will be developed that relates the composition of the reaction mixture, the structure of the lignin and the operating conditions. This modeling will not only refine our understanding of the complexities of lignin depolymerization but will also serve as a basis for the prediction and optimization of reaction pathways. The research is expected to contribute to the development of more efficient and sustainable strategies for lignin utilization and represent a crucial step towards a bio-based economy.

2. Methods

The experiments were carried out in six parallel batch reactors (75 mL) with a magnetic stirrer. The lignin model compound 2-phenoxy-1-phenylethanol (2P1PE) and organosolv ethanol-lignin were dissolved in ethanol (1:20 w/v), and the experiments were performed at temperatures of 175-275 °C and 0.5-1.5 MPa hydrogen pressure with a Ni/C catalyst (1:5 w/w). The liquid samples of 2P1PE cleavage were analyzed by gas chromatography coupled with mass spectrometry and flame ionization detector (GC-MS/FID), while the product distribution of lignin depolymerization was presented as solid carbon residue, oligomeric lignin fragments, and lignin monomers [3].

The kinetic model is based on the reaction mechanism of the lignin model compound, the concentration of the individual components and transport phenomena. Individual steps within the reaction mechanism are considered in the kinetic model to determine the contributions to the kinetic rates of the lignin model compound [1,2]. For the description of the SEC spectra, a new numerical algorithm was developed to

evaluate the depolymerization rate of the lignin macromolecule. The model contains the scission of different bonds within the lignin and the change in structural features. The latter is important, because the algorithm for the SEC description can be coupled with first-principle kinetics. The differential equations were solved using Matlab R2022a software.

3. Results and discussion

To understand lignin depolymerization, a lignin model compound that mimics the lignin structure was used. However, the results of 2P1PE and the organosolv lignin indicate dissociation and not complete compatibility. On the other hand, the lignin model compound provides insights into the reactivity of the β -O-4-lignin bond and the kinetic rate parameters of bond cleavage can be easily calculated.

During the experiments, we found that the temperatures used for the lignin model compound are not sufficient for lignin. In order, to suppress recondensation to solid carbon residue and to achieve more efficient depolymerization in the form of monomeric/oligomeric products, the reaction temperature for organosolv lignin had to be increased. While the lignin model compounds provide some insight into the behavior of lignin, we cannot fully predict lignin depolymerization and the exact conditions required for efficient lignin depolymerization.

With the combination of the kinetic model and SEC numerical model, there will hopefully be a clear correlation between the reaction rates for the resulting monomers and the structure of lignin. Moreover, the model will explain how the change in lignin molecular weight affects the concentration of each monomeric product at different process conditions (temperature, time, reactant to catalyst ratio, etc.).

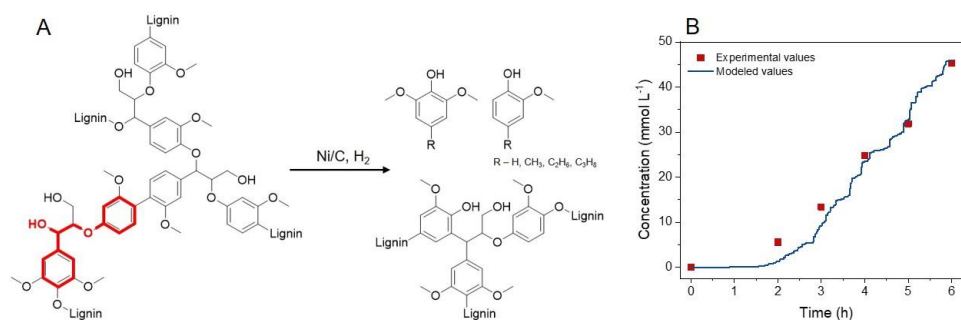


Figure 1. Proposed lignin depolymerization mechanism (A) and SEC numerical model (B).

4. Conclusions

In our study, we attempted to correlate β -O-4 bond cleavage, product distribution and reaction conditions using a lignin model component and an actual lignin sample. The kinetics of bond cleavage for the lignin model compound could be easily described by reaction rate parameters and activation energies. While the lignin model compound provides insight and predictability for the β -O-4 bond cleavage rates, the structural complexity of lignin prevents a full prediction of its behavior under different conditions. Nonetheless, the insights gained from the lignin model components provide a valuable basis for the development of more efficient lignin depolymerization strategies.

Acknowledgements

This research was funded by Slovenian Research Agency (research core funding P2-0152 and research projects J2-2492, N2-0316 and L2-50050).

References

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Keywords

Lignin model compound; lignin depolymerization; Ni/C; kinetic modeling.