Kinetic assessment of reductive depolymerization of hydrolysis lignin on a Pd catalyst

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Highlights

- Activation energies for main catalytic pathways in reductive lignin depolymerization.
- Fundamental description of the reactivity of monomers through key reaction families.
- Specific descriptors to extend the modeling strategy to other lignin valorization routes.

1. Introduction

Being the largest resource of renewable aromatics, lignin holds major, yet presently untapped, potential for the sustainable production of chemicals and materials. Unfortunately, lignin depolymerization, a key step in all lignin valorization pathways, is highly complex due to the large number of components and reactions involved. Therefore, developing kinetic modeling strategies capable of capturing the complexity of lignin while accurately describing the formation of targeted aromatics with a reasonable computational effort remains critical for advancing lignin valorization technologies. In this work, we present a novel modeling framework that combines key aspects of molecule-based modeling [1] with the continuum theory of lumping [2].

2. Methods

The lignin stock solution was prepared by dissolving 1.0 g of dried hydrolysis lignin (HL) at room temperature in 10 mL of ethanol/water (70/30 vol%) mixture. The catalytic depolymerization of HL was investigated over a commercial 5 wt% Pd/γ-Al_2O_3 catalyst and 10 bar H_2 in a batch reactor set-up. The reactions were performed at temperatures between 150 to 200 °C for durations ranging from 1 to 6 h. The resulting lignin oils were then characterized *via* Gel Permeation Chromatography (GPC), 2D Nuclear Magnetic Resonance (2D NMR) spectroscopy and Gas Chromatography-Mass Spectrometry (GC-MS). More detailed information on the experimental procedures has been published in a previous work from our group [3]. Following a similar procedure, other combinations of feedstock and solvent mixtures were also tested in the absence of a catalyst to isolate lignin-solvent interactions, see below.

Continuous lumping models account for the reactivity (k-space) of species in complex mixtures as a function of a continuous characteristic such as the molecular weight. The reactivity can also be characterized in a more elementary manner, e.g., through key reaction moieties such as β-O-4 bonds and hydroxyl groups. Moreover, lignin-solvent interactions can be quantified through the Flory coefficient (χ), which is a function of the cohesive energy density (CED) of the solvent and the feedstock. In this work, the CED is obtained through thermodynamic calculations or literature correlations. In the reductive catalytic depolymerization of lignin, however, the presence of a catalyst requires to account for additional phenomena, i.e., mass transfer, catalytic pathways, as well as the role of H_2. In this way, four reaction families have been identified: vinyl and carbonyl hydrogenation, HDO and isomerization; each being kinetically described through specific parameters, i.e., a rate coefficient and activation energy using Brønsted-Evans-Polanyi (BEP) relationships $\left(E_{a,i} = E_{a,i}^{0} + \gamma\, \Delta H_{rxn}\right)$. Both $E_{a,i}^{0}$ and γ are seen as kinetic descriptors, whereas the number of active sites is considered a catalyst descriptor.

3. Results and discussion

The mass transfer assessment was found to be important for reactions involving bulky lignin species, see Fig. 1a. This is mostly attributed to the size of the molecules, which results in lower diffusional rates.

Simultaneously, due to their higher absolute number of reactive centers, these polymeric structures are more prone to undergo depolymerization. The combination of these two phenomena results in effectiveness factors (η) much lower than one [1]. Moreover, lignin species can be larger than the average pore size of the catalyst, which should slow down effective reaction rates even further, see Fig. 1b. This is in agreement with calculated η values lower than 0.1 at those conditions. Fig. 1c shows the experimentally observed and simulated monomer ratios at different reaction times based on a proposed reaction mechanism [3]. Accordingly, monomers are characterized based on the functionality of the side-chain in the *para* position with respect to the phenyl -OH group in lignin building blocks. By means of BEP relationships, the following activations energies per reaction family are obtained: $E_{a,HDO}$ = 150, $E_{a,vinyl\text{-}hyd}$ = 110, $E_{a,\ carb.\text{-}hyd}$ = 98 and $E_{a,iso}$ = 87 kJ mol^{-1}. Fig. 1d shows the robustness of the model in simulating the molecular weight distribution of many operating conditions as obtained experimentally *via* GPC. To that aim, the model is reparametrized using specific functions with the Flory coefficient of each configuration as independent variable. This approach enables lignin-solvent interactions to be directly linked to specific model parameters, facilitating the application of the model to different feedstock/solvent configurations. Finally, this methodology enables a physical interpretation of the value of parameters responsible for describing the stoichiometry in continuous lumping models [2].

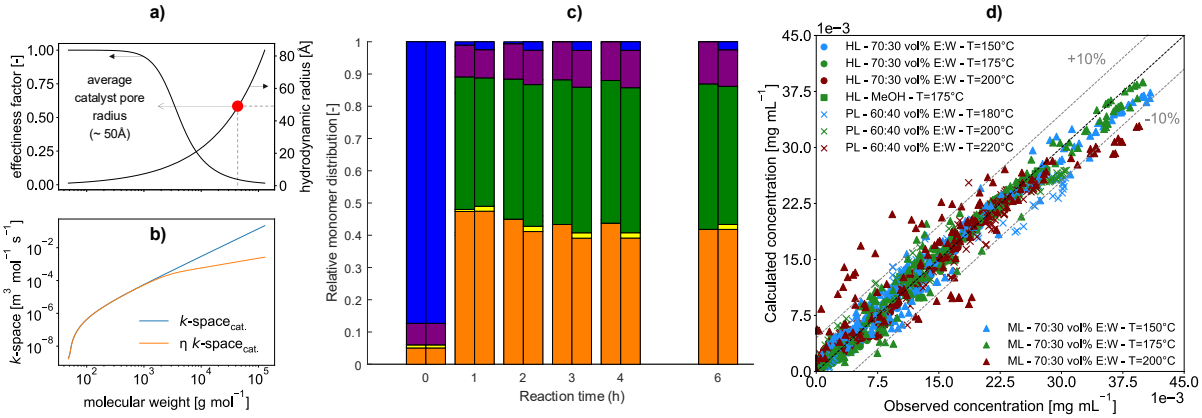

Figure 1. **a)** Effectiveness factor profile as a function of the molecular weight of lignin species and **b)** *k*-space profiles. **c)** Experimental and simulated relative monomer distribution from HL depolymerization under 5 wt% Pd-γAl_2O_3 catalyst at 175 °C showing experimental (left-hand side bars) and simulated (right-hand side bars) values. Side-chain functionalities of monomers: alkane (orange), alkene (yellow), alcohol (green), ketone (purple) and aldehyde (blue). **d)** Parity plot showing the model performance in terms of concentration values from molecular weight distributions for different feedstock/solvent mixture configurations. Abbreviations in the legend: HL: hydrolysis lignin, PL: poplar lignin, ML: soda miscanthus lignin, E:W: ethanol/water, MeOH: pure methanol.

4. Conclusions

A novel strategy that combines features of fundamental kinetics and the continuum lumping theory is presented for modeling the reductive catalytic depolymerization of lignin. On the one hand, kinetics of complex reactions mixtures are simulated *via* continuous lumping, i.e., reactions involving polymeric and oligomeric lignin species. On the other hand, the formation of functionalized monomers are described *via* specific catalytic pathways classified into reaction families, which involves defining both catalyst and kinetic descriptors, such as the number of active sites and BEP parameters, respectively. This methodology can ultimately be extended to other catalytic configurations by making use of said descriptors to describe, and potentially extend, the reaction mechanism that relates the monomeric lignin species involved in the process.

References

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Keywords

Lignin valorization; catalytic depolymerization; kinetic modeling.