

Solvolytic transformations of soda miscanthus lignin: an experimental and modelling assessment of de- and repolymerization kinetics *via* continuous lumping

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Highlights

- Experimental elucidations of soda lignin solvolysis for model validation.
- Continuous lumping modelling for assessing lignin de(re)polymerization kinetics.
- Fundamental description of the reactivity of species through key reaction families.

1. Introduction

Lignin depolymerization via solvolytic routes, a key step in lignin valorization, is a complex chemical transformation which involves a significantly large number of species and reactions. Aiming for process optimization and reactor design, research efforts are targeting the development of kinetic models to simultaneously cope with the heterogeneity of the feedstock and vast reaction mechanisms. Accordingly, a novel modelling strategy based on the continuum theory of lumping [1] is presented.

2. Experimental methods

Miscanthus x giganteus lignin, isolated in a pilot scale Soda extraction [2], was utilized as feedstock. The lignin stock solution was prepared by dissolving 3 g of dried miscanthus lignin in 20 mL ethanol/water (70/30 vol.%) mixture. The solution was then stirred at room temperature for c.a. 12 h and filtered. Solvolysis experiments were conducted in a stirred batch set-up consisting of 7 individual reactor vessels of 25 mL [3]. In a typical experiment, a reactor was loaded with 2.5 mL of lignin stock solution and 8 mL of the ethanol/water solvent mixture. Subsequently, the reactor vessel was pressurized up to 10 bar with H₂ and heated to the set temperature. Within this work, experiments were conducted at 200 °C in a reaction time span ranging from 1 to 6 h. The lignin oil samples were characterized through Gel Permeation Chromatography (GPC) equipped with a refractive index detector (RID) and UV/VIS detector, as well as *via* two-dimensional nuclear magnetic resonance (2D-NMR) spectroscopy.

3. Model development

In its simplest formulation, purely in the direction of depolymerization, continuous lumping models account for the reactivity of species (k -space) as a function of a single continuous characteristic, e.g., the molecular weight. In lignin solvolysis, however, repolymerization reactions should typically not be ignored, primarily in the monomer and light oligomer region of the considered species. Moreover, even though the molecular weight is a suitable continuous variable to characterize the reactivity space (k -space), a more fundamental representation of the reactivity should also include information about key reactive moieties, such as β -O-4 linkages, characterized through 2D-NMR analysis.

From the modelling perspective, two reactivity spaces are then proposed to describe the kinetics of depolymerization (k -space_{de}) and of repolymerization (k -space_{re}). The second continuous characteristic proposed in this work, namely the concentration of β -O-4 linkages, allows for a non-unique dependence of the reactivity on the molecular weight. As a result, the k -space evolves as a function of the reaction time/conversion. The system is hereby characterized through pseudo-components (pcs), the reactivity of which is not only defined by their size, but also by relevant chemical sub-structures. Another important aspect of the proposed model is the yield distribution function (YDF), which represents the stoichiometry of the system. A skewed-gaussian distribution is adopted because of its flexibility for representing the physical phenomena involved. With respect to depolymerization, it can describe from middle-chain up to terminal-chain cracking; whereas for repolymerization, it allows for condensation

reactions from the monomeric region onwards. The proposed continuous lumping model comprises 10 model parameters, 4 of which correspond to kinetic parameters and 6 shape parameters, which describe the stoichiometry. These model parameters are estimated *via* regression to the experimental data.

4. Results and discussion

The experimental data reveal the formation of three groups of species in the monomer-to-trimer region of the molecular weight spectrum, see the dashed lines in Figure 1 A. Note that the relative amount of species from the second group, i.e., the monomer/dimer region, decreases after 2 h of reaction. This effect can be attributed to repolymerization of those species into heavier ones, as the absence of an stabilizing agent, i.e. a heterogenous catalyst, can lead to unstable depolymerized species. Moreover, the shift towards heavier species was further confirmed by GPC-UV/VIS deconvolution [3]. The 2D-NMR analysis reveals that the concentration of β -O-4 linkages in the lignin stock solution amounts to 36 % and decreases to 11 % after 6 h of reaction, as shown in Figure 1 B. With respect to the main C-C lignin inter-linkages, i.e. β - β , β - β' , β -5, their concentrations remain practically constant, indicating that depolymerization undergoes primarily *via* β -O-4 cleavage at the investigated operating conditions.

The regression analysis indicates that all model parameters are statistically significant, and the model performance is depicted in Figure 1 A. The model is able to capture well the depolymerization products in the low molecular weight region, and the extent of it is confirmed by the weight-average (M_w) and number-average (M_n) molecular weight profiles, see Figure 1 C. The slight increase in the M_n values at longer reaction times suggests that repolymerization might take place in the low molecular weight region, as this parameter is more sensitive to changes in the latter. This stresses the need for assessing the repolymerization effect in the model. Furthermore, the more fundamental formulation of the k -space_{de} enables the estimation of the β -O-4 concentration, see Figure 1 B. The resulting β -O-4 profile is calculated through proportionality relationships with respect to the instantaneous reaction rates of depolymerization, which is in agreement to the lack of reactivity associated to C-C linkages.

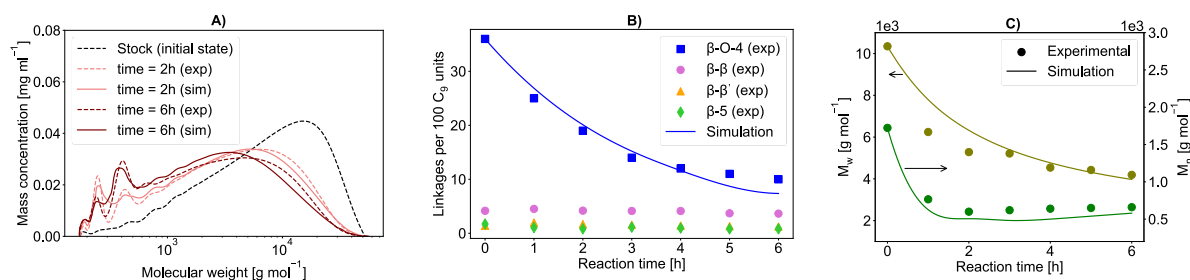


Figure 1. Experimental and simulation results. A) Molecular weight distributions at different reaction times, including the lignin stock solution. B) Concentration profiles of main lignin linkages. C) M_w and M_n profiles.

4. Conclusions

A novel continuous lumping model has been developed to describe lignin depolymerization and repolymerization kinetics. An experimental investigation of soda miscanthus lignin solvolysis has been conducted as proof-of-concept for model validation, generating statistically significant results. The β -O-4 moieties have been identified as a key descriptor for the reactivity towards depolymerization, which can be ultimately extended to other reaction families, e.g. C-C bonds, if corresponding depolymerization routes are proven experimentally.

References

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Keywords

Continuum theory of lumping; kinetic modelling; reaction families; lignin solvolysis.