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Modelling of ultrafast lignin depolymerization kinetics under supercritical conditions

Aim

In this thesis the kinetics of an innovative ultrafast lignin depolymerization process under supercritical conditions will be investigated, aiming to develop and experimentally validate a comprehensive kinetic model.

Justification

Lignocellulose is recognized as the most abundant and cheapest inedible biomass. Moreover, one of its main constituents, i.e., lignin, is considered to be the most scalable and economically viable source of bio-aromatics, which can ultimately serve as building blocks towards the production of novel materials and fuels. In recent years, several methods have been attempted to depolymerize lignin where high monomer yields were sometimes achieved, for example under reductive conditions ¹. These processes typically involve specific catalysts for stabilizing reactive intermediates and preventing them to undergo repolymerization. Moreover, the resulting monomer yields are heavily dependent on the initial lignin structure, particularly on the relative amount of reactive β -O-4 linkages, and reaction times can go up to a few hours.

Compared to the current state-of-the-art, lignin depolymerization under supercritical conditions represents a promising and innovative pathway towards lignin valorization. Accordingly, this method does not require a catalyst, while the supercritical water induces depolymerization reactions at remarkably fast rates (reaction times ranging from milliseconds to seconds). Lignin depolymerization under such conditions necessarily involves vast reactions networks, even more complex than other approaches where the primary depolymerization pathways is associated to the cleavage of β -O-4 linkages.

Kinetic models based on the continuum theory of lumping have been developed for simulating the chemistry of complex reaction mixtures ². Applied to lignin, such models allow for capturing experimentally observable characteristics, such as the molecular weight distribution, the ratio of different linkages and the number of functional groups. The continuous representation of these characteristic lignin features can be used within a fundamental single-event microkinetic (SEMK) methodology. The basic idea of SEMK is that chemical transformations pertain to reactive moieties rather than to individual molecules. Hence, a vast number of elementary steps, is classified into a limited number of reaction families. Such a model will ultimately allow for optimizing process conditions to steer the product yields towards targeted aromatics.

Program

- Literature survey on lignin depolymerization under supercritical conditions, kinetic modelling of complex mixtures (continuous lumping and SEMK) and analytical methods to characterize lignin oils;
- Apply and extend available in-house kinetic models using experimental datasets form the literature;
- Conduct experiments at a wide range of operating conditions (residence time, temperature and pressure) and feedstock properties (MW distribution, inter-unit linkages and functional groups);
- Comprehensive characterization of the depolymerized lignin oils and kinetic assessment.
- Model validation using in-house experimental data.

References

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