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Kinetic modeling of lignin catalytic hydroconversion in a semi-batch reactor

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Introduction

Lignin which represents almost 30 wt% of lignocellulosic biomass could be the most relevant and abundant bioresource to produce aromatic compounds due to its natural polymeric structure composed by phenylpropane units with ether linkages¹. One potential way is the catalytic hydroconversion to depolymerize lignin and produce aromatic compounds². In our work, a upgraded batch reactor is used, open for gas phase with a continuous feeding of H₂, and equipped with a condensing reflux followed by cooled traps to remove continuously light products and water from the reacting mixture and recycle the solvent (Fig. 1a). Firstly, a lumped reaction network of lignin conversion was established on the basis of experimental observations (Fig. 1b). Secondly, kinetic parameters were estimated using a nonlinear least-squares regression on the product yields and the outlet gas dynamics.

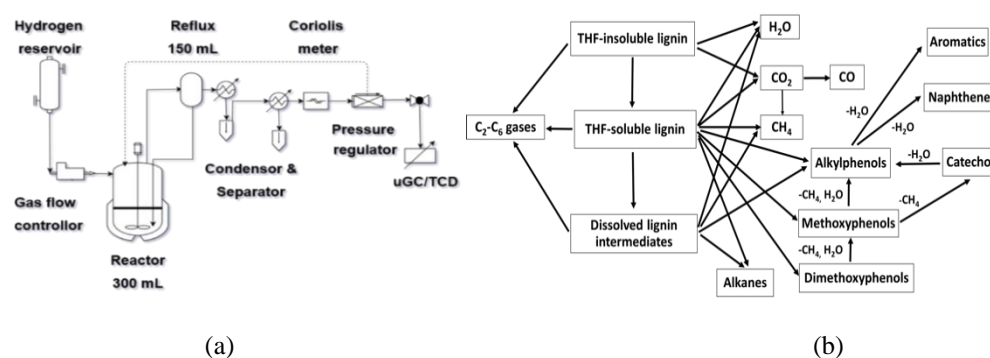


Figure 1: (a) Experimental setup of lignin conversion (b) Proposed reaction network in our work

Methods

Wheat straw soda lignin (30 g) was introduced with tetralin (70 g) and CoMoS/ γ -Al₂O₃ (3 g) in a 0.3 L Parr autoclave reactor. For all hydroconversion experiments, the reactor temperature of 350 °C, the reflux temperature of 160 °C, stirring rate of 800 rpm, pressure of 8 MPa and H₂ inlet flow of 40NL/h were kept constant. Kinetic experiments were carried out at several residence times (0-13 h). The residence time was measured from the instant the reaction temperature was reached, defined as time zero. During the experiment, a part of relative light liquids was collected in cold traps and outlet

gases were analyzed and quantified online thanks to a μ GC-TCD and Coriolis meter (Fig. 1a). After reaction and cooling, liquids and solids were separated by centrifugation. The solids were extracted with THF. The so-called “residual lignin” is the THF-soluble fraction corresponding to partially converted lignin, and was analyzed by GPC and NMR (^{13}C , ^{31}P). The two fractions of liquids were mainly characterized by GC \times GC-MS and quantified by GC \times GC-FID.

Results and Discussion

In order to get a more accurate description of the intrinsic kinetics, the gas hydrodynamic behavior and the liquid-vapor mass transfer between phases need to be taken into account. The gas RTD experimental results show that the reactor and the reflux can be modeled as CSTRs and the other parts of the semi-batch pilot (condensers and tubes) as PFRs at reaction conditions. The hydrodynamic model of the gas phase was coupled to the mass balance of each unit of the semi-batch pilot. The liquid-vapor mass transfer between phases in the kinetic model was calculated by a driving force model ($k_{\text{LA}}\Delta C$), to take into account the vaporized fraction of reactants and products at reaction conditions. Interface concentrations (C^*) were estimated for each lumps from partition coefficients (K) found with flash calculations by Prosim Plus, with a group contribution equation of state called PSRK using a PSRK mixing rule coupled with a UNIFAC method. Assuming first-order reactions with respect to each lump, experimental data corresponding to the solid and liquid samples and dynamic outlet gas flow were used to estimate 31 parameters corresponding to the rate constant (k) and stoichiometric coefficients (ν) for a set of 11 reactions in the reaction work. Our kinetic model (lines) fits well with experimental data (makers) (Fig. 2).

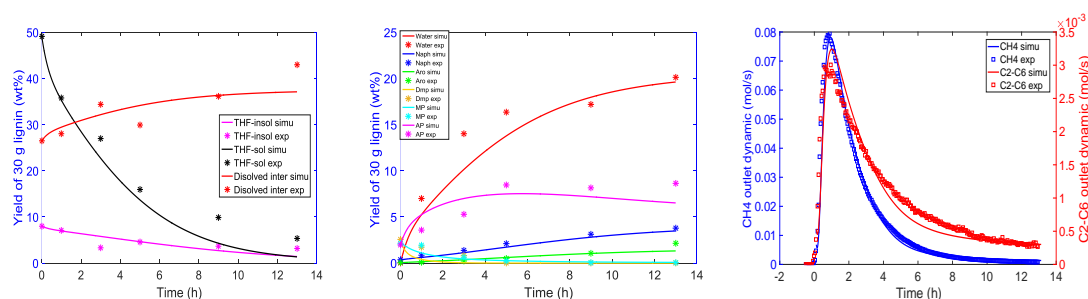


Figure 2: The comparisons between experimental data and simulation results

Conclusion

The proposed detailed chemical scheme reveals the complete pathways from lignin to specific lumped compounds, and corresponding kinetic parameters of each step have been achieved by nonlinear regression technique.

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