Modeling study of lignin catalytic hydroconversion in a semi-batch reactor

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Abstract: The hydroconversion of lignin was studied in a semi-batch reactor, with a CoMoS/γ-Al_2O_3 catalyst under H_2 pressure at 350 °C. Based on the product evolutions versus residence time, it allows the mapping of the complete pathway from lignin to specific target lumped compounds, such as alkylphenols and aromatics. Moreover, a lumped kinetic model was proposed, taking into account liquid-vapor mass transfer and equilibrium. Stoichiometric and rate coefficients were estimated with experimental results.

Keywords: Lignin hydroconversion, Transformation scheme, Kinetic modeling.

1. Introduction

Lignin which represents almost 30 wt% of lignocellulosic biomass is the most relevant and abundant bioresource to produce aromatic compounds due to its original polymeric structure composed by phenylpropane units with ether linkages[1,2]. We propose the catalytic hydroconverison as a mean to depolymerize lignin and produce aromatic compounds. A new upgraded batch reactor is used, open for gas phase with a continuous feeding of H_2, a condensing system followed by cooled traps to remove continuously light products and water from the reacting mixture and recycle the solvent (Fig. 1). The advanced reaction system has been demonstrated to be powerful compared to a traditional batch system previously used[3]. Here, our study focuses on three parts: reactor hydrodynamic characterization, catalytic tests at different residence times with product characterization and quantification, and reaction scheme building with corresponding kinetic modeling.

2. Experimental

Wheat straw soda lignin (30 g) was introduced with tetralin (70 g) and CoMoS/γ-Al_2O_3 in a 0.3 L Parr autoclave reactor open for gas phase and equipped with condensing system. After evacuation of air, the reactor was continuously fed with H_2 (40Nl/h) and the temperature increased up to 350 °C under stirring of 800 rpm. 80 bars of total pressure was kept during the whole reaction. During the experiment, a part of relative light liquids was collected in cold traps and gases were analyzed and quantified online thanks to a µGC and Coriolis meter (Fig. 1). After reaction and cooling, liquids and solids were separated by centrifugation. The solid were extracted with THF. The so-called “residual lignin” is the THF-soluble fraction corresponding to partially converted lignin, and were analyzed by GPC and NMR (^{13}C, ^{31}P). The two fractions of liquids were mainly characterized by GC×GC-MS and quantified by GC×GC-FID. Catalytic tests at various residence time between 0h and 13h were performed. After reaction, four different fractions were found: insoluble solids, residual lignin, gases and liquids (Fig. 1).

3. Results and discussion

For getting a more accurate description of the intrinsic kinetics, liquid-vapor equilibrium (LVE), hydrodynamics and mass transfer characteristics need to be taken into account. First of all, hydrodynamic characterization of the semi-batch reactor was performed by gas Residence Time Distribution (RTD) measurements using pulse injections of N_2, as a tracer in H_2 flow. A physical model composed of ideal reactors (CSTRs and PFRs) can correctly simulate the behavior of gas mixing inside the whole set-up. Secondly, a series of tests at different residence time were performed under operating conditions, using a mixture of lignin model compounds instead of lignin. With an accurate thermodynamic model calculating the LVE, the cumulated quantity of different compounds in cold traps versus time can be well predicted, and was validated experimentally.

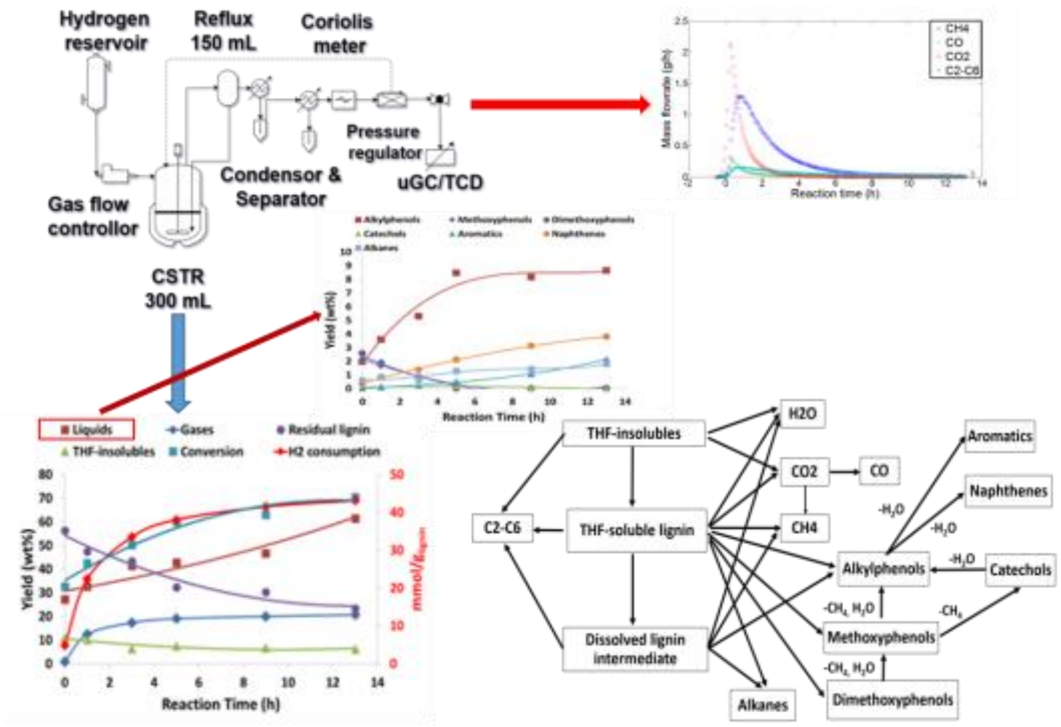

Figure 1. Scheme of semi-batch reactor; Dynamic gas outlet flow versus reaction time; Evolutions of main products and H_2 consumption versus time; Evolution of monomers in the liquid phase versus time; Proposed reaction network in our work

Thirdly, based on the experimental observations of lignin conversion versus time, the residual lignin was continuously converted to liquids and gases versus time. The characterization on residual lignin showed deep cleavage, thus decreasing its average molecular mass, and chemical transformation via deoxygenation reactions. In the liquids, main families of monomers were quantified for each experiment (Fig. 1). The same type of deoxygenating reaction towards alkylphenols and aromatics was clearly observed. It allows us to map the complete pathways from lignin to specific lumped compounds[4] (Fig. 1). A kinetic model was proposed, taking into account LVE and liquid-vapor mass transfer. A set of experimental points at different residence times was used to estimate rate coefficients *k* and stoichiometric coefficients *v*.

4. Conclusions

The use of this new system is powerful to perform catalytic hydroconversion of lignin and follow the reactions occurring. Based on experimental product evolutions, a reaction network of lignin hydroconversion was proposed. Meanwhile, a step-by-step approach of kinetic model was undertaken, with the consideration of hydrodynamics, mass transfer characteristics and thermodynamic model.

References

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