An experimental and modeling study of lignin catalytic hydroconversion

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Highlights
- A wheat straw soda lignin was converted using a CoMoS supported catalyst.
- A deep characterization of lignin conversion products was undertaken.
- The evolution of different fractions was implemented to understand the reaction scheme.
- A tentative kinetic model on the basis of experimental data is proposed.

1. Introduction

Nowadays, because of the fossil fuels depletion and environmental concerns, transformation of lignocellulosic biomass is becoming a great challenge in order to provide biofuels and biochemicals in a near future. Lignin which represents almost 30 wt% of lignocellulosic biomass is the most relevant and abundant bio-resource to produce aromatic compounds due to its original polymeric structure composed by phenylpropane units with ether linkages[1,2]. In this context, the use of lignin as a precursor of aromatic compounds has attracted lots of attention thanks to its low cost and high availability.

In order to find a catalytic way to valorize lignin coming either from pulp industry or biorefineries, we propose here the catalytic hydroconversion as a mean to depolymerize lignin and produce aromatic compounds. The reaction takes place in tetralin, a H-donor solvent, which allows to avoid condensation reactions between the radical fragments and also improve hydrogen diffusion into the liquid phase where the catalytic process occurs. A new upgraded batch reactor is used, opened 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. The advanced reaction system has been demonstrated to be powerful compared to a traditional batch system previously used[3,4], as the hydrogen is fed during the whole process and water and light products are separated avoiding long contact of catalyst with water and over-conversion of lights to gas. Here, we presents the evolution of the conversion and selectivities for a CoMoS/γ-Al$_2$O$_3$ catalysts versus residence time and a proposed reaction mechanism.

2. Methods

Wheat straw soda lignin (30 g) is introduced with tetralin (70 g) and CoMoS/γ-Al$_2$O$_3$ (3 g) in a 0.3 L Parr autoclave reactor open for gas phase and equipped with condensing system. After evacuation of air, the reactor is continuously fed with H_2 and the temperature is increased up to 350 °C under stirring of 800 rpm. 80 bars of total pressure was kept during the whole reaction. During the experiments, a part of the liquids are collected in cold traps and gases are analyzed online thanks to a μGC. After reaction and cooling, liquids and solids are 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 were analyzed by GPC and NMR (^{13}C, ^{31}P). The liquids were mainly characterized by GC×GC-MS and quantified by GC×GC-FID.

3. Results and discussion

Firstly, 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. The built gas flow model can represent the behavior of gas mixing inside of the whole set-up. In order to build a kinetic model

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based on experimental results, we performed the hydroconversion of lignin over extrudate $CoMoS/\gamma\text{-}Al_2O_3$ at various residence times: 0, 1, 3, 5, 9 and 13 h. A previously implemented products recovery procedure was followed[3] and the mass cloture reached higher than 95 wt%. Thanks to appropriate analytical techniques, the characterization of the gas, solid, and liquid products was undertaken for each residence time.

Lignin catalytic hydroconversion led to four different fractions: gases, residual lignin, insoluble solids and liquids. Regarding the liquids, the yield reached 60 wt% after 13 h. Concerning the residual lignin, it was continuously converted to liquids and gases versus time (Fig. 1a). The characterization on residual lignin showed deep cleavage, thus decreasing its average molecular mass, and chemical transformation via deoxygenation reactions. In the liquid fraction, main families of monomers (alkylphenols, methoxyphenols, aromatics, and naphthenes…) were quantified for each experiment (Fig. 1b). The same type of deoxygenating reactions towards alkylphenols and aromatics was clearly observed.

(a)   (b)
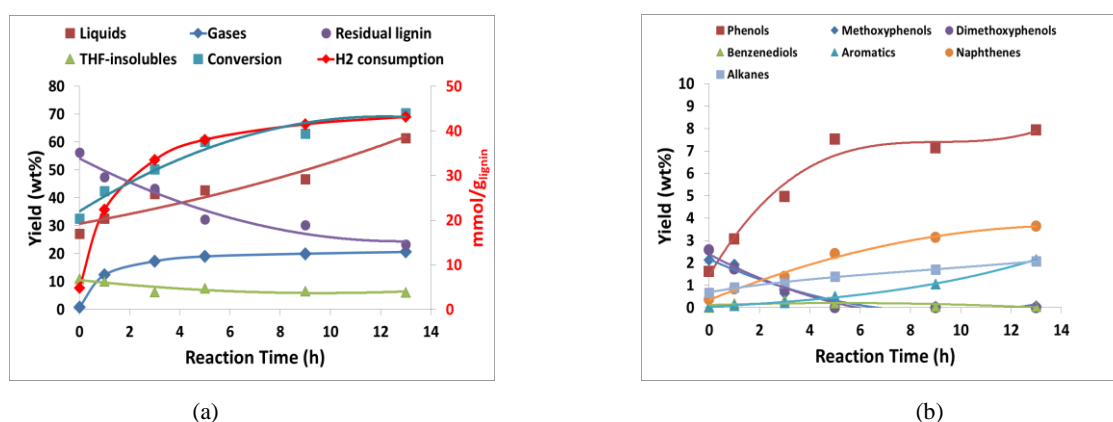
Figure 1. (a) Evolution of lignin conversion, yield of the different fractions and H_2 consumption as a function of residence time; (b) Evolution of monomers in the liquids as a function of residence time

The evolutions of these molecules and residual lignin allow us to understand the various reactions occurring to lignin itself and its products, then a transformation scheme was established. The proposed scheme reveals the degradation process of lignin into low molecular weight fragments by cleavage and deoxygenation pathways, as well as various reaction pathways of monomers in the liquid fraction. The experimental data are used to implement a kinetic model to simulate the complex process.

4. Conclusions

The use of this new system is powerful to perform catalytic hydroconversion of lignin and follow the reactions occurring. The quantification of all the products is done thanks to a tool of well-chosen analytical techniques. Based on the evolutions of products, a tentative kinetic model is proposed with a multi-step reaction mechanisms.

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