COMPOSITION AND REACTION MODELING FOR THE SIMULATION OF LIGNIN CONVERSION

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Abstract

To convert lignocellulosic biomass into liquids (bio-oils), a large spectrum of thermochemical processes, such as pyrolysis, hydroconversion and catalytic cracking, are currently being developed. However, the high structural complexity of lignocellulosic materials hampers its accurate analytical characterization, as well as the understanding of the conversion mechanisms and their kinetics. In the current work, a stochastic methodology has been developed for the modeling of the conversion of lignin. A probabilistic representation of lignin, the most complex biomass compound, was used and a kinetic Monte Carlo approach was developed for biomass conversion. In the modeling of lignin hydroconversion, a good agreement was obtained between simulated and experimental data for the composition and characteristics of the initial lignin. The kinetic model correctly predicts the composition and some of the physical characteristics of the conversion products.

Keywords

Lignin conversion, composition modeling, kinetic Monte Carlo, stochastic simulation.

Introduction

The concept of biorefineries arises from the need of achieving sustainable growth by replacing fossil or mineral-based products for products from renewable resources, such as biomass. Different chemical, thermochemical and biological processes have been proposed for the conversion of lignocellulosic biomass into liquids (bio-oils). In order to optimize these conversion processes, information concerning biomass composition and its conversion mechanisms should be known. However, the high structural complexity of lignocellulosic materials hampers its accurate analytical characterization, as well as the understanding of the conversion mechanisms and their kinetics. In the current work, a stochastic methodology has been developed for the modeling of the conversion of lignin.

Methodology

The first step of our methodology transforms the available analytical information on the lignin into a set of molecules that has the same average properties. In the second step, the effect of the reactions on the generated set of molecules is simulated using a variable time step kinetic Monte Carlo simulation method.

Representation of the lignin structure

Owing to its structural complexity, a molecular structure cannot be directly obtained from the available analyses. Hence, these samples are generally characterized by many different analytical techniques, which all highlight different characteristics of the sample.

Klein et Virk (2008) represented lignins by means of a 6x8 matrix of probabilities of occurrence for different types of aromatic units in the structure. Each row of the matrix is a specific type of methoxyphenol and each column a type of 3-carbon-atom side chain or inter-unit linkage. Each matrix element a_{jk} represents an aromatic unit composed by a ring equal to the type j of methoxyphenol and a lateral chain of the type k. The probability of occurrence of this specific unit is equal to the product of the occurrence of its components. The values of each element in the matrix offer a concise

probabilistic description of a lignin polymer. During lignin conversion, however, other structures start to appear. In our work, this representation for the initial lignin has therefore been extended to a 44x22 matrix by including additional lignin moieties and additional linkages to account for the various structures formed during lignin conversion. From this probability matrix, a representative set of molecules can be created by sampling the matrix.

Stochastic reaction modeling of lignin conversion

After sampling, the generated set of molecules is used as input for the molecule-based kinetic modeling of the hydroconversion of lignin. From this representation of the initial lignin and a list of possible reactions, the transformation of the lignin was simulated by means of a kinetic Monte Carlo (kMC) algorithm, described elsewhere (Pereira de Oliveira *et al.*, 2012). Such a method describes the reaction system at the molecular level by following the transformations of a discrete population of molecules. The corresponding reaction parameters are determined from model compounds in literature with a similar structure to that of the elements in the matrix.

Results and discussion

The above-described method was applied to a wheat straw soda lignin (Protobind 1000). The Protobind 1000 lignin was characterized by Gel Permeation Chromatography, elemental analysis, ^{1}H-NMR, and ^{13}C-NMR. After phosphitylation, a ^{31}P-NMR analysis was also performed. Detailed information on these techniques and their results can be found elsewhere (Joffres *et al.*, 2013). For this lignin, an average molecular weight of 4915 g/mol was obtained. The elemental analysis showed that the lignin contained 65 wt% of carbon, 28 wt% of oxygen, 6 wt% of hydrogen and 1 wt% of nitrogen.

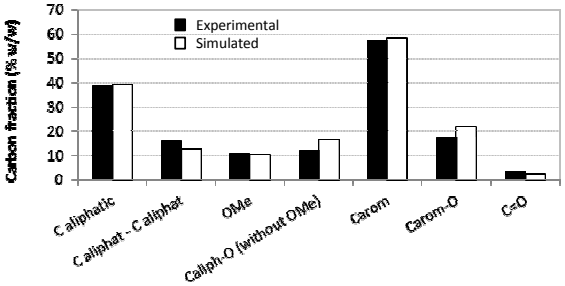

Figure 1. ^{13}C NMR families for native lignin: analytical (black) vs. reconstructed (white).

From these analytical data, a matrix of occurrence probabilities was created. After resampling, the set of molecules closely represents the Protobind 1000, as illustrated in Figure 1 for ^{13}C NMR. For the molecular weight and polydispersion index, a similar agreement is obtained, while the elemental analysis matches exactly.

The kMC algorithm was used to simulate the conversion of the lignin, and allows to accurately predict the fractions of gas, liquid and solid (Figure 2), the gas composition, the composition (elemental analysis, functional groups) of the bio-oil, and the molecular weight and polydispersion index of the residual lignin.

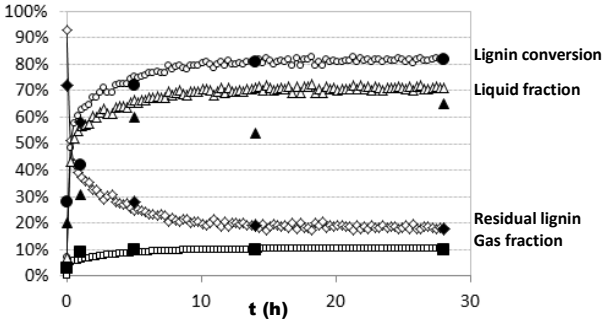

Figure 2. Evolution of the lignin conversion and the product fractions: experimental (black) vs. simulated (white).

Conclusions

A stochastic procedure has been described for the modeling of the conversion of lignin. A probabilistic representation of this complex biomass compound was used based on a matrix that reflects the probability of occurrence of a set of structural elements. Two types of elements were required to represent the initial lignin: 16 aromatic rings and 6 inter-unit linkages, whose combination leads to 96 substructures. The number of available substructures was increased to 968 by extending the matrix with chemical moieties produced during the conversion of lignin. By sampling this matrix of probabilities, a representative set of molecules was created and used as input for the kinetic modeling. The hydroconversion of lignin was then simulated by means of a molecule-based kinetic Monte Carlo method.

This methodology was shown to be a valid tool for the representation of lignin polymers, providing a set of realistic structures of this complex co-polymer whose average properties accurately fit to the information from experimental analyses. Kinetic Monte Carlo techniques have also given interesting results in their application on the simulation of the hydroconversion of lignin. Besides, the simulation of the reactions does not require a pre-defined kinetic network since it is generated as the reactions proceed.

References

Joffres B., Lorentz C., Vidalie M., Laurenti D., Quoineaud A.-A., Charon N., Daudin A., Quignard A., Geantet C. (2013) Catalytic hydroconversion of a wheat straw soda lignin: Characterization of the products and the lignin residue. *Appl. Cat. B: Environmental* 145 (2013) 167–176.

Klein, M. T.; Virk, P. S. (2008) Modeling of lignin thermolysis. *Energy Fuels* 22, 2175–3182.

Pereira de Oliveira, L., Verstraete, J.J., Kolb, M. (2012) A Monte Carlo modeling methodology for the simulation of hydrotreating processes. *Chem. Eng. J.* 207-208, 94–102.