P08

Semi-Detailed Chemical Kinetic Modeling of Primary Pyrolysis of Lignin for Process Optimization

Yuki Furutani[1*], Yuki Dohara[2], Shinji Kudo[3], Jun-ichiro Hayashi[3], Koyo Norinaga[3]
[1] *Interdisciplinary Graduate School of Engineering Sciences, Kyushu University*
[2] *Faculty of Engineering, Kyushu University*
[3] *Institute for Materials Chemistry and Engineering, Kyushu University*

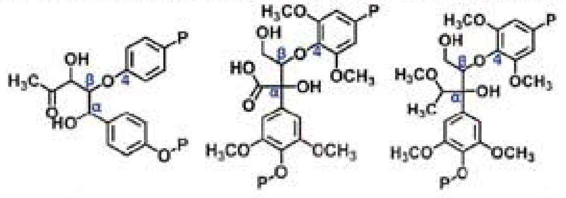
Abstract

Product distribution derived from primary pyrolysis of three types of lignins (EHL, OEL, KL) was estimated with both the two-stage tubular reactor and the kinetic modeling. For EHL, numerical results of char and H2O yields at all temperature agreed well with experimental data. Numerical simulation overestimated tar yield and underestimated CO yield at high temperature probably due to the absence of secondary vapor-phase cracking. Char and tar yields of EHL, OEL and KL at 923 K evaluated by numerical simulation were qualitatively agreed with experimental ones.

1. Introduction

Lignin is a highly cross-linked amorphous copolymer of three randomly polymerized phenylpropane units, and accounts for up to 35wt% of dry biomass, and carries the highest specific energy content of the three principal components of biomass. In addition to its significant presence in biomass, lignin is a byproduct of the pulp and paper industry, and of biorefinery processes that focus on utilizing the more easily convertible polysaccharide fractions of biomass (e.g. sugar fermentation to ethanol). Today, most lignin is burned for process heat, however, processes like pyrolysis, gasification, combustion, and liquefaction are available to convert lignin or biomass into useful products. Of these, pyrolysis is the most promising method for converting lignin into lower molecular weight liquid and gas products. A longstanding goal is the development of predictive models to optimize fast and slow pyrolysis processes that produce renewable fuels and aromatic chemicals from lignin; unfortunately, existing models lack sufficient detail to be useful for this type of optimization.

As a step toward a more mechanistic model, we explore the use of a semi-detailed kinetic model for lignin pyrolysis to predict the compositions of gases and tar components from the pyrolysis of lignin over a wide range of slow and fast pyrolysis conditions. Our kinetic scheme is based on that proposed by Faravelli et al.[1] Challenges characterizing lignin and defining its structure are well documented, and in this work we follow the approach of Faravelli et al[1] in choosing model components to approximate different possible lignin structures.Three model components (LIGC, LIG-H, LIG-O, following the naming conventions of Faravelli et al.) based on a β-O-4 skeleton are chosen to characterize the initial lignin structure (Figure 1).



LIC-C ($C_{17}H_{16}O_5$) LIC-O ($C_{20}H_{22}O_{10}$) LIC-H ($C_{22}H_{18}O_9$)

Figure 1. Reference dimer units in lignin structure. The solid residue start with P.

2. Experiment

Three types of lignin (EHL, OEL and KL) were employed in this study. Samples used in this experiment were smaller than 150 μm of particle sized under vacuum overnight. Pyrolysis mechanism of benzenediols was investigated by a two stage tubular reactor (TS-TR)[2] connected with GC. TS-TR consists of two zones divided by a quartz wool filter. The sample was dropped into the bottom of the first hot zone and vaporized at 773 – 1223 K with residence time (tr) of 0.1 s. Then, volatiles were flown into the secondary zone with helium carrier gas at 241 kPa. Passing the secondary zone, volatiles were directed into GC column and further identified by GC detector.

3. Computational Method

In order to verify and validate the capacity of these reference species to characterize the natural lignins, Figure 2 described the lignins (EHL, OEL and KL), their elemental analysis and the equivalent composition in terms of the three reference components. The kinetic model for lignin pyrolysis involving ~100 species and 400 reactions is presented which is capable of predicting the temporal evolution of molecules and functional groups during lignin pyrolysis. A heating rate is assumed as 1, 10, 100 K/s.

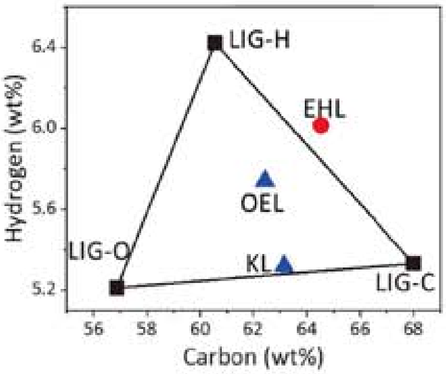


Figure 2. Lignins and equivalent compositions

4. Results

In Figure 3 we compare model predictions for char, tar, CO, H_2O and CO yields derived from EHL primary pyrolysis to the experiments at 773 – 1223 K. The kinetic model shows excellent temporal agreement with char and H_2O yields. The temperature effect on mass loss rate was quite well captured. In the range of high temperature, the kinetic model underestimated the tar yields, while overestimated the CO yields probably due to the lack of secondary gas-phase reactions.

Figure 4 shows the comparison of EHL, OEL and KL between the simulation and experiment. For char and tar yields, the trends were captured.

5. Conclusion

The volatile compositions derived from the primary pyrolysis of three types of lignins (EHL, OEL, and KL) was estimated with two-stage tubular reactor. Simulation with kinetic modeling of lignin primary pyrolysis was performed at the heating rate of 1, 10 and 100 K/s to predict the volatile compositions. The results between experiment and simulation were compared to evaluate the effect of the heating rates and lignin types.

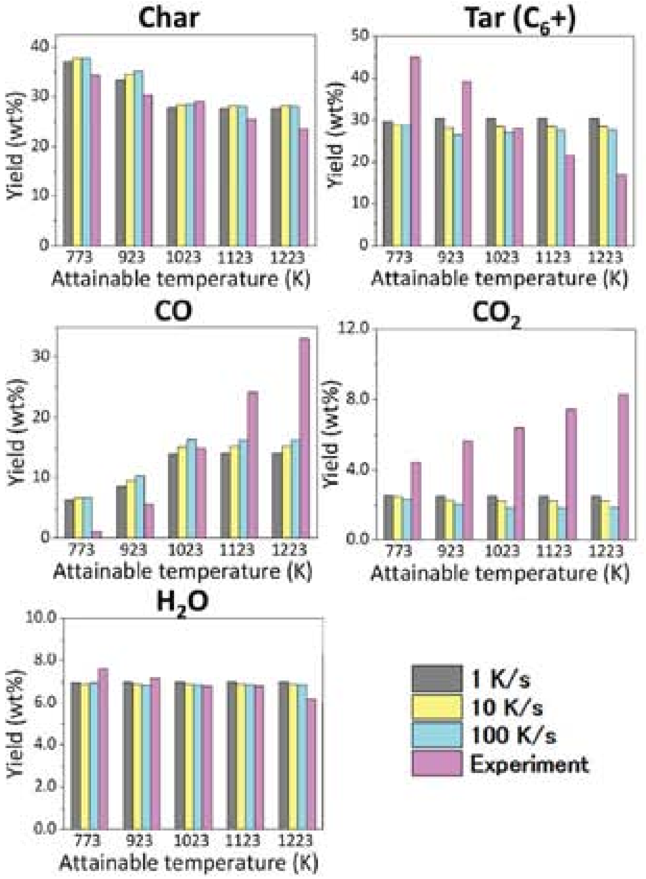


Figure 3. The difference in yields of char, tar, CO_2, H_2O and CO between simulation and experimental values at different attainable temperature.

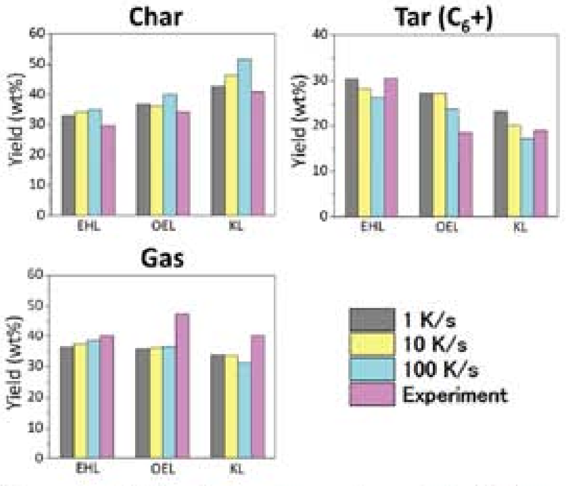


Figure 4. Yields of char, tar and gas derived from EHL, OEL, KL at 923 K.

References:

[1] Faravelli, T. *et al*, Biomass & Bioenergy, **34**, 120 (2014).

[2] Yang, H. *et al.*, Ind. Eng. Chem. Res, **54**, 6855 (2015)

Email: 3ES15008R@s.kyushu-u.ac.jp