

Coupling the detailed chemical kinetic models of primary and secondary pyrolysis of lignin

Yuki Furutani¹

¹Interdisciplinary Graduate School of Engineering, Kyushu University

1. Introduction

Lignin pyrolysis is divided into two stages: (a) primary pyrolysis, where volatiles escape from biomass particles; and (b) secondary vapor-phase reactions, where the produced volatiles undergo further cracking, combine, or condense in the vapor phase. Our research group has developed a detailed chemical kinetic model (DCKM) based on elementary reactions provide information on the pyrolysis behaviors of individual components.¹⁾ However, the DCKM has been limited to the secondary vapor-phase reaction and used the experimentally-measured volatile composition derived from primary pyrolysis as a boundary condition. The purpose of this study is to develop the DCKM predicting both primary pyrolysis and secondary vapor-phase reactions.

2. DCKM of primary pyrolysis

Initial lignin structure was characterized by linear combination of three model components (LIG-C, LIG-H, and LIG-O)²⁾ based on a β -O-4 skeleton as shown in Fig. 1. Hough et al.²⁾ proposed the kinetic model consisting of 96 species and 404 elementary reactions.

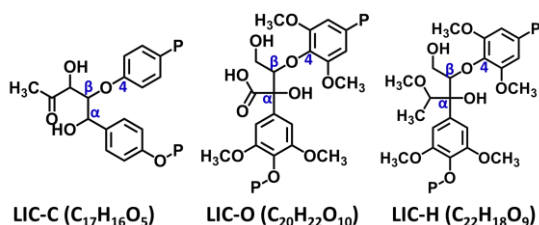


Fig. 1: Three model components. The solid residue start with P.

We employed this kinetic model to simulate the primary pyrolysis of enzymatic hydrolysis lignin under heating rate of 10^3 K/s and attainable temperature of 773 – 1223 K, and predict the volatile composition derived from primary pyrolysis. Fig. 2 predicts that 3-hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)propan-1-one (HHDPP)

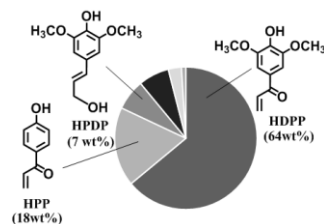


Fig. 2. Tar (+C6) composition at 1223 K

accounted for 64 wt% of total tar (+C₆) species generated from primary pyrolysis.

3. DCKM of secondary vapor-phase reaction

Our established DCKM¹⁾ did not involve the kinetic database on vapor-phase reaction of monolignols as shown in Fig. 2. Thus, the pyrolytic pathways of all monolignols as shown in Fig. 2 were proposed, and the Arrhenius parameters ($k=AT^n\exp(-E/RT)$) for each elementary reaction step were calculated based on quantum chemical calculation and transition state theory. Total 340 elementary reaction rate constants were added into the original kinetic database¹⁾. By using the volatile composition predicted by the DCKM of primary pyrolysis as a boundary condition, the simulation was performed at residence time of 0.1 and temperature of 773 – 1223 K.

Fig.3 shows the comparison of the model prediction of the yields for various chemical species with the experiment of Yang et al.¹⁾ Our numerical results of char, CO, H₂O, C₆H₆, C₆H₅OH, C₂H₄, C₃H₆ and CH₃OH yields agreed well with the experimental measurement. The model prediction underestimated the yields of CO₂ and CH₄, and overestimated the yield of H₂. These differences could result from the use of too simple a definition for characterizing the initial lignin structures.

P-02

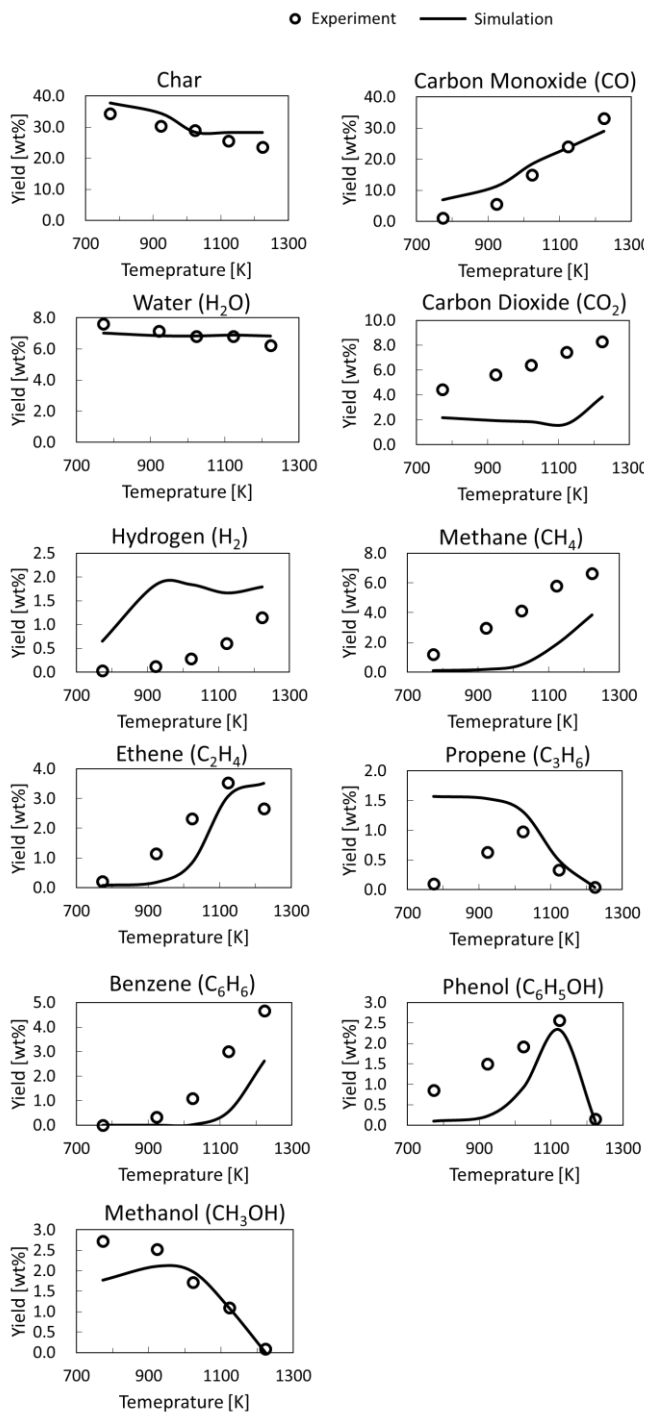


Fig.3: Comparison of predicted yields for various chemical species with experimental data¹⁾

References:

- 1) Yang, H. et al., *Ind. Eng. Chem. Res.*, **54**, 6855 (2015)
- 2) Hough, B. R. et al., *Ind. Eng. Chem. Res.*, **55**, 9147 (2016)