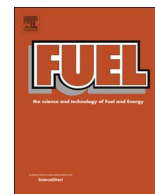




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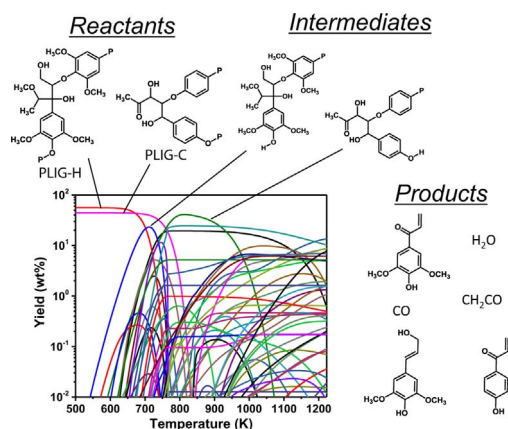
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Full Length Article

Predicting molecular composition of primary product derived from fast pyrolysis of lignin with semi-detailed kinetic model

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GRAPHICAL ABSTRACT



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ABSTRACT

A numerical approach is presented for predicting the yields of char and volatile components obtained from fast pyrolysis of three types of lignin (enzymatic hydrolysis lignin, EHL; organic extracted lignin, OEL; and Klason lignin, KL) in a two-stage tubular reactor (TS-TR) at 773–1223 K. The heating rate of lignin particle in the TS-TR was estimated at 10^2 – 10^4 K/s by solving the heat transfer equation. The pyrolytic behavior of lignin and the formation of products in the temperature rising process were predicted using a semi-detailed kinetic model consisting of 93 species and 406 reactions, and the predicted yields of 8 primary products (*i.e.*, char, tar, CO, CO₂, H₂O, CH₃OH, C₂H₆, and C₃H₆) were compared with experimental data for the critical evaluation. For EHL, the predicted yields of char and H₂O were in good agreement with the experimental results at all temperatures. However, the numerical simulation overestimated tar yield and underestimated CO yield at high temperature probably due to a lack of the kinetic model of the tar cracking reaction. The predicted yields of CH₃OH, C₂H₆, and C₃H₆ were close to the experimental values at high temperature by adding the detailed chemical kinetic model of the secondary vapor-phase reaction. Moreover, the model reproduced the experimental observation that among the three types of lignin the char yield increased in the order of EHL < OEL < KL, whereas the tar yield decreased.

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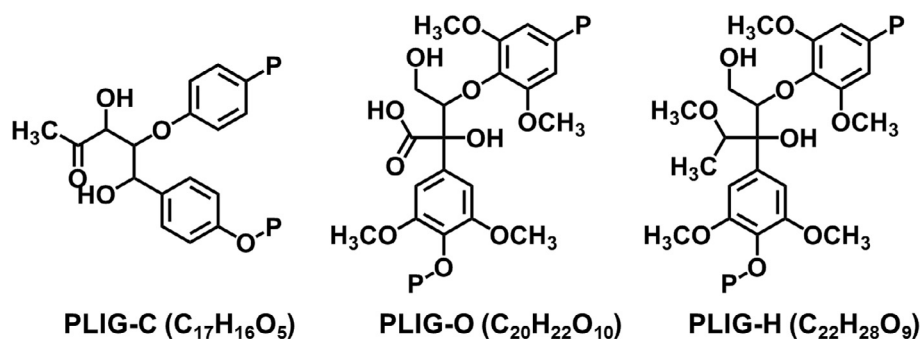


Fig. 1. Virtual compounds used to characterize initial lignin structures [47].

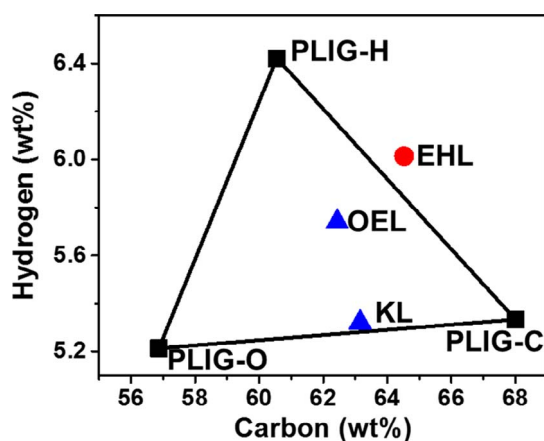


Fig. 2. Elemental compositions of the six lignins.

1. Introduction

After cellulose, lignin is the second most abundant component in biomass [1,2]. As a residue of the pulp and paper industry, huge amounts of lignin are available at low cost [2]. Although currently most lignin is burned to produce heat, thermal conversion processes, including pyrolysis, gasification and liquefaction, can be used to convert lignin or biomass into useful products, such as gas, char, liquid fuels and chemicals as well as heat [3–6]. Among these thermal conversion processes, pyrolysis is known as a common step to cause fragmentation of the lignin or biomass structure [7]. 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.

A lot of studies have been carried out to identify the pyrolysis products generated from secondary vapor-phase reactions and to establish lumped kinetic models [7–10]. Caballero et al. [10] established a lumped kinetic model for the global secondary reaction of Kraft lignin by assuming a first-order reaction. However, lumped kinetic models established based on global product categories, such as char, tar, and gases, cannot describe the formation mechanisms for specific products at the molecular level.

A detailed chemical kinetic model (DCKM) of vapor-phase reactions based on elementary reactions [11–30] has been developed to overcome the limitations of the lumping approach and provide information on the pyrolysis behaviors of individual components. Our group revealed that the DCKM was able to reproduce not only the yields of major products but also those of minor products such as aromatic hydrocarbons, which were obtained with a two-stage tubular reactor (TS-TR) connected to a gas chromatograph (GC) [11–13]. However, the DCKM has been limited to secondary vapor-phase reactions. Thus, the molecular composition of the volatiles derived from fast pyrolysis has to be obtained as a boundary condition with the TS-TR setting a residence

Table 1
Elemental compositions and equivalent compositions of EHL, OEL, and KL.

	Elemental composition (wt%)			Equivalent composition (wt%)		
	C	H	O	PLIG-C	PLIG-O	PLIG-H
EHL	63.3	5.9	28.9	44.1	0.0	55.9
OEL	62.0	5.7	31.6	36.8	23.3	39.9
KL	62.9	5.3	31.4	55.3	41.3	3.4

time of 0.1 s for vapor-phase reactions [11–13]. In order to enhance the versatility of the DCKM, it is necessary to expand the DCKM to include the primary pyrolysis stage.

For primary pyrolysis of lignin, lumped kinetic models of the decomposition reaction have been extensively reported in the literature [31–35]. However, these models did not allow prediction of the molecular composition of gases and tar components. Recently, Xiong et al. [36] performed computational fluid dynamics (CFD) simulations coupled with distributed activation energy mode (DAEM) reaction kinetics for lab-scale bubbling bed biomass pyrolysis reactor, and revealed that the coupled CFD–DAEM system does not significantly increase computational overhead. A reliable kinetic model, which predict the yields and the molecular composition of gas and tar as accurately as possible, has been required with the development of highly efficient CFD methods [36–45] and the increase of computational resource. Faravelli et al. [46] explored a semi-detailed kinetic model, which characterizes lignin structures using three virtual compounds and involves approximately 100 species and 400 reactions, to predict the molecular compositions of products derived from primary pyrolysis. Recently, Hough et al. [47] added eight reactions into the kinetic models established by Faravelli et al. [46], and compared the integral yields of char, tar, and gases predicted by the model and observed for slow pyrolysis experiments by thermogravimetric analysis (TGA) [48]. However, the model predictions have not yet been compared with the molecular compositions of volatiles derived from fast pyrolysis experiments, such as TS-TR experiments. This comparison is also an important step to optimize fast pyrolysis process, which generates much amount of volatile products from biomass and produces “bio-fuel” [5].

The purpose of this study is to examine whether the semi-detailed kinetic model established by Hough et al. [47] could reproduce the molecular composition of the primary products generated from fast pyrolysis with TS-TR experiments. First, characterization of lignin structures was described using virtual compounds. Second, the heating rate for lignin samples in the primary pyrolysis zone of the TS-TR was estimated. Finally, based on the estimated heating rate, the yields of char and volatiles were predicted using the semi-detailed kinetic model and compared with TS-TR experimental results [13] for the critical evaluation. This estimation would help to integrate the DCKM of both primary pyrolysis and secondary vapor-phase reactions.

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