Mechanistic study on the gas phase reactions of multi-component mixtures derived from fast pyrolysis of cellulose and lignin

楊，華美

氏　　名：楊　華美

論文題名：Mechanistic study on the gas phase reactions of multi-component mixtures derived from fast pyrolysis of cellulose and lignin（セルロースとリグニン急速熱分解生成物の気相反応機構に関する研究）

区　　分：甲

<div align="center">論　文　内　容　の　要　旨</div>

Ligno-cellulosic biomass is expected to be a reliable source for the sustainable production of carbon-based fuels, chemicals, and materials. Thermo-chemical conversion of biomass is one of the most promising routes to add value to low- or negative-value biomass by converting it into marketable fuels, heat, and chemicals. At temperatures higher than 773 K, typically 75–90 wt% of biomass is converted into volatiles which continue cracking in vapor phase. This high conversion into volatile products suggests that vapor-phase reactions have an important role during biomass pyrolysis, determining the final products distribution. And the complex compositions of the volatiles lead to a very complex reaction network of the vapor-phase reactions in the pyrolysis of biomass. Full understanding of the kinetic and chemical mechanism of vapor-phase reactions is significant and helpful for the design and optimization of biomass thermochemical conversion processes. Hence, this study focuses on the understanding the mechanism of the vapor-phase cracking of volatiles derived from the pyrolysis of cellulose and lignin which are the main components of biomass.

The purpose of this thesis is to understand the mechanism of the vapor phase reactions of volatiles derived from the pyrolysis of cellulose and lignin experimentally and numerically, which is significant for the development and advanced operation conditions of the biomass pyrolysis process. The vapor-phase reactions of volatiles derived from the pyrolysis of cellulose and lignin were investigated by a two stage tubular reactor, and simulated with a detailed chemical kinetic model. Good agreements between the experimental observations and prediction profiles encouraged us to draw a reaction network to describe the vapor-phase reaction pathways leading to aromatic hydrocarbons. To improve the detailed chemical kinetic model and establish a more comprehensive model for the simulation of biomass conversion, model compounds were pyrolyzed to give a deeper understanding of decomposition sub-mechanism of phenols derived from lignin pyrolysis. At the same time, rate coefficients of radical addition to substituted benzenes are studied systematically based on ab initio calculation, which permits us to find the rule for the estimation of rate coefficient

of unknown aromatic reactions.

The thesis consists of five chapters and a brief summary of each chapter is given as follows:

Chapter 1 generally introduced the progress and developments of biomass pyrolysis, reviewed the investigation of cellulose and lignin pyrolysis, and summarized the application of the detailed chemical kinetic model.

Chapter 2 describes the experimental and numerical study on vapor phase cracking of volatiles derived from cellulose pyrolysis. The pyrolysis of cellulose was conducted in a two stage tubular reactor at 400 to 900 ℃ with the vapor phase cracking time from 0.2 s to 4.3 s. The products of alkyne and diene were identified from the primary pyrolysis of cellulose even at low temperature range 500 – 600 ℃. These products include acetylene, propyne, propadiene, vinylacetylene, and cyclopentadiene. The vapor phase reactions were numerically simulated with a detailed chemical kinetic model consisting of more than 8000 elementary step like reactions with over 500 chemical species. Good agreements were obtained for products between experiment observation and numerical predictions. Based on the model, reaction pathway analysis was conducted to understand the formation of aromatic compounds via the alkyne and diene from primary pyrolysates of cellulose. C_3 alkyne and diene are primary precursors of benzene at 650 ℃, while combination of ethylene and vinylacetylene produces benzene dominantly at 850 ℃. Cyclopentadiene is a prominent precursor of naphthalene. Combination of acetylene with propyne or allyl radical leads to the formation of cyclopentadiene. Furan and acrolein are likely important alkyne precursors in cellulose pyrolysis at low temperature, whereas dehydrogenations of olefins are major route to alkyne at high temperatures.

Chapter 3 describes chemical structures and primary pyrolysis characteristics of lignins obtained from different preparation methods. Three different types of lignin samples were prepared through enzymatic hydrolysis, organosolv extraction, and klason procedure. The structures of the three lignin samples were charactered by FT-IR and solid state ^{13}C-NMR. The three lignin samples were pyrolyzed in a tubular reactor at 923 K, and pyrolysis products were analyzed with gas chromatographs on-line. Aromatic structure favors the formation of char. High H content can reduce the char formation and enhance the tar formation. Substituents especially oxygen substituents enhanced the formation of non-alkyl phenols.

Chapter 4 describes experimental and numerical study on vapor phase reactions of volatiles derived from lignin pyrolysis. Lignin residue after enzymatic hydrolysis was pyrolyzed in a two-stage tubular reactor at 773–1223 K. The nascent volatiles formed in the first stage underwent vapor-phase reactions in situ in the second stage. A detailed chemical kinetic model that consists of more than 500 species and 8000 elementary reactions was used to simulate the vapor-phase reactions of volatiles derived from fast pyrolysis of lignin. The contribution of tar in the vapor-phase reactions was

considered in global reactions, which improves the predictive capability of the kinetic model. The experimental data and numerical predictions of 31 products were compared and analyzed to understand the mechanism of vapor-phase reactions of lignin. The model predictions were in good agreements with the experimental observations. Reaction pathway analysis for the formation of aromatic hydrocarbons is performed. Cyclopentadienyl radicals produced by phenol decomposition were suggested as important intermediates in the formation of aromatic hydrocarbons during lignin pyrolysis.

Chapter 5 investigated thermal decompositions of lignin model compounds: catechol, hydroquinone, and resorcinol. In this study, the three model compounds were pyrolyzed in a Curie-point pyrolyzer at 650 and 750 ℃ and a two stage tubular reactor at a residence time of up to 3.6 s and a temperature ranging from 650 to 950 ℃. p-Benzoquinone was the primary product from hydroquinone pyrolysis, while no o-benzoquinone and m-benzoquinone were detected from the pyrolysis of catechol and resorcinol. For light hydrocarbons, hydroquinone generated mainly C_2 and C_4 hydrocarbons, and catechol yielded mainly C_4 hydrocarbons, while the selectivity of C_1-C_5 hydrocarbons generated from resorcinol are not so much different. Compared with catechol and hydroquinone, resorcinol produced much more C_1, C_3, and C_5 hydrocarbons. CO was the main gas with yields of 24.3 wt%, 25.1 wt%, and 19.4 wt% formed from hydroquinone, catechol and resorcinol, respectively. A much higher yield of CO_2 (15.5 wt%) were generated from resorcinol than from hydroquinone (1.0 wt%) and catechol (0.8 wt%). Reaction pathways were analyzed to describe the pyrolysis of catechol, hydroquinone, and resorcinol.

Chapter 6 systematically studied radical addition reactions to substituted benzenes and the reverse beta-scission reactions with the ab initio calculation at CBS-QB3 level. The effects of addition or eliminated radicals and substituents of benzene ring located at ipso, ortho-, meta-, and para-position were analyzed on the rate coefficients of radical addition reactions and beta-scission reactions. 27 chemical groups were considered as addition or eliminated radicals and substituents of benzene ring located at ipso position, and 6 groups were tested as substituents located at ortho-, meta-, and para-position. The rate coefficients strongly depend on the nature of addition or eliminated radicals, and rather independent of the substituents of benzene ring. The rate coefficients of the addition reaction reduces in the order of highly energetic vinyl and phenyl radicals > sp^3- hybridized radicals> resonantly stabilized radicals such as allyl, benzyl, and propargyl radicals, while the rate coefficients of beta-scission reactions reduce in an opposite order. The activation energy increases with heat of reaction with a increasing parameter of 0.5 for radical addition reactions and 0.6 for beta-scission reactions.

Chapter 7 summarizes the general conclusions of this study.