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A mechanistic study on the reaction pathways leading to benzene and naphthalene in cellulose vapor phase cracking

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ABSTRACT

The reaction pathways leading to aromatic hydrocarbons such as benzene and naphthalene in gas-phase reactions of multi-component mixtures derived from cellulose fast pyrolysis were studied both experimentally and numerically. A two-stage tubular reactor was used for evaluating the reaction kinetics of secondary vapor phase cracking of the nascent pyrolysates at temperature ranging from 400 to 900 °C, residence time from 0.2 to 4.3 s, and at 241 kPa. The products of alkyne and diene were identified from the primary pyrolysis of cellulose even at low temperature range 500–600 °C. These products include acetylene, propyne, propadiene, vinylacetylene, and cyclopentadiene. Experiments were also numerically validated by a detailed chemical kinetic model consisting of more than 8000 elementary step-like reactions with over 500 chemical species. Acceptable capabilities of the kinetic model in predicting concentration profiles of the products enabled us to assess reaction pathways leading to benzene and naphthalene via the alkyne and diene from primary pyrolysates of cellulose. C₃ alkyne and diene are primary precursors of benzene at 650 °C, while combination of ethylene and vinylacetylene produces benzene dominantly at 850 °C. 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.

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1. Introduction

Ligno-cellulosic biomass, such as wood, straws, and agricultural residues, 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 [1–4].

Tar formation is one of the major problem during biomass thermo-chemical conversion like gasification for power generation [5–9]. Biomass tar mainly consists of stable aromatic compounds such as benzene and polycyclic aromatic hydrocarbons. Tar condenses at reduced temperature and results in blocking and fouling of engines and turbines. A deep understanding of the chemical reactions that are responsible for the tar formation is expected to offer a better solution towards the development and advanced operation technology of the biomass gasification process.

Carbohydrate polymers such as cellulose and hemicellulose, and lignin (an aromatic polymer) compose the lingo-cellulosic biomass. The presence of single ring aromatic structures in the lignin is likely responsible for the tar formation during the gasification of biomass. The importance of the competition of cracking and polycondensation of lignin oligomers was identified in the secondary vapor phase reactions of wood biomass [10]. However, it is well known that the benzene and toluene are also produced in thermal decomposition of cellulose, which is free from aromatic structure [11–13]. Even though the aromatic hydrocarbons are minor products in the cellulose pyrolysis, their impacts on the continuous operation of the gasification process is significant as they can condense and accumulate at the syngas cooler which lead to blockage of the particulate filter and product gas line downstream. The kinetic modeling study and mechanistic interpretation on the formations and consumptions of the aromatic hydrocarbons are of great importance in understanding and predicting the tar formation characteristics in the biomass thermochemical conversion, which will contribute better design of the process and optimization of the operation.

Although the pyrolysis of cellulose has been studying extensively [14,15], there are very limited studies dealing with the secondary pyrolysis using an experimental approach sequencing the complex reactions of solid fuels and simplifying them for the kinetic analysis. We developed a two-stage tubular reactor (TS-TR) in which biomass particles are fast-pyrolysed, and the generated volatile constituents are separated immediately from the char. These volatiles are introduced to a reaction zone in which residence time can be controlled by changing the volume of the subsequent reaction zone [13,16,17].

It is also attempted to develop an elementary reaction-based kinetic model to describe the secondary pyrolysis of cellulose [13]. A number of reactions are included in the kinetic model to account for the cellulose gas-phase pyrolysis. The detailed chemical reaction model, which consists of more than 500 species and more than 8000 elementary step-like reactions, is developed based on an existing literature data

[18–28] as well as by using a tool for the automatic reaction generation [29]. The newly developed kinetic model is critically validated with our experimental data of more than 20 products. The model prediction generally agreed for the experimental concentration profiles of major species such as H_2 , CO, CO_2 , CH_4 , and C_2H_4 . The model predictions of minor products such as acetaldehyde, acetic acid, acetone, hydroxyl acetone, furan, benzene, and toluene are also fairly good. These validations are performed without adjusting any parameters in the kinetic model, such agreements are always encouraging. A better understanding and the use of the reliable mechanistic model will help the operations of thermo-chemical conversion process in most profitable and safest way.

Reaction pathway analysis also conducted for aromatic species such as benzene [13]. It is suggested that there are two dominating routes to benzene; the first one is the decomposition of toluene, and the second is from C_3 hydrocarbons such as propadiene and propyne. Toluene is formed almost exclusively by the combination of cyclopentadienyl radicals and acetylene. Cyclopentadienyl radicals are mainly formed by the combination of allyl radicals with acetylene. Allyl radical is formed from butane and propylene, both of which are major constituents of the primary pyrolysis products of cellulose. Acetylene is produced mainly during secondary pyrolysis from the dehydrogenation of ethylene. Benzene formation from C_3 hydrocarbons is divided into two routes, which include the combination of propargyl radicals and the reactions between propadiene and propargyl radicals. Propargyl radicals are generated from propyne and propadiene, and also from decomposition of furan. Propyne and propadiene are produced from allyl radicals.

Even though the aromatic hydrocarbons are minor products in the cellulose pyrolysis, their impacts on the continuous operation of the gasification process is significant as they can condense and accumulate at downstream facility such as syngas cooler, which also lead to blockage of the particulate filter and product gas line. The kinetic modeling study and mechanistic interpretation on the formations and consumptions of the aromatic hydrocarbons are of great importance in understanding and predicting the tar formation characteristics in the biomass thermochemical conversion, which will contribute better design of the process and optimization of the operation.

Although our study mentioned above strongly suggests the importance of the alkyne and diene compounds as precursors for the aromatic hydrocarbons, their formation profiles were not monitored experimentally. The present study was thus conducted to provide experimental proof for the formation of these alkyne and diene products. It also offers the evaluations of the capability of the proposed detailed chemical kinetic model in predicting the formation and consumption profiles for these important intermediates for further strengthening the value of our approach. In this study, analytical pyrolysis experiments for cellulose were conducted with improved setup for the product analysis detecting the alkyne and diene compounds to confirm their formations and validate the proposed reaction mechanism. The numerical simulations with the detailed chemical kinetic model are also conducted to obtain mechanistic insights into chemical reactions leading

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