**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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Keywords

Cellulose; Biomass; Pyrolysis; Chemical kinetics; Tar formation; Aromatic hydrocarbons.

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 thermochemical 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 C₃ 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 C₃ 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 to aromatic hydrocarbons in the vapor phase cracking of multi-component mixtures derived from cellulose fast pyrolysis.

2. Experimental

A schematic representation of the experimental rig used for cellulose (Microcrystalline powder, Sigma-Aldrich, USA) pyrolysis is shown in Fig. 1. A U-shaped two-stage tubular reactor (TS-TR) was made-up of quartz and divided into two zones by a quartz wool filter, one for the fast pyrolysis of the cellulose and the other one for the secondary pyrolysis of nascent volatiles in the gas phase. The inner diameters of the first portion and the second portion were 6 and 4 mm, respectively. Approximately 1.0 mg of the sample was wrapped by a sheet of stainless (SUS316) wire mesh (15 x 15 mm) with a mesh opening of 45 μ m and dried in vacuum at room temperature overnight. The mass of the wrapped sample was measured immediately after the

drying to determine the exact dry mass of the sample. The wrapped sample was held by a hook made of a steel wire. The hook was located at the upper part of the reactor with the help of a magnet outside of the reactor. The TS-TR was then connected to the streamline of GC or GC/MS with a carrier gas such as helium or nitrogen with a flow rate of $45 \text{ cm}^3 \text{ min}^{-1}$ (stp of 298.15 K, and 101.35 kPa). Due to the pressure drop provided by the GC columns, the TS-TR was slightly pressurized to 241 kPa. After stabilizing the heated section of the TS-TR at the desired temperature, the sample was dropped into the bottom of the first tube by removing the magnet, where the sample was fast-pyrolyzed. The furnace is well insulated and the temperature of the position where cellulose sample is held (before dropping) is always below 323 K, even when the furnace temperature is set to be 1173 K. The nascent volatiles formed by pyrolysis were swept off into the second zone. The residence time of the volatiles in the second zone was varied from 0.2 to 4.3 s by adjusting the effectively heated volume of the second reactor, which can be achieved by moving the furnace vertically. The product streams were directed to the GC or GC/MS. The compositions of the products were quantified individually by two GCs, i.e., only one GC is used at each run. The GC/MS was also used for chromatogram peak assignment based on the library reference mass spectral data for the identification of compounds through the fragmentation of their ions generated by electron ionization with a voltage of 70 eV. The analytical conditions are summarized in Table 1. In the analytical pyrolysis experimental setup, in which a tubular reactor is connected within the gas stream line for the gas chromatography (GC), an identical gas has to be used for pyrolysis and GC analysis. Helium was used for most of the experiments, but nitrogen was also used for the experiments using VZN-1 GC column packing, that separates not only alkyne and diene compounds but also hydrogen that is monitored with TCD. Thermal conductivity of hydrogen and helium is very near, then we had to choose

nitrogen as a carrier gas only for the experiments with the VZN-1. The pyrolysis temperatures are generally 400, 500, 550, 600, 650, 700, 750, 800, 850, and 900 °C. Only the data at 400 and 550 °C obtained at the GC setups with VZN-1 and PoraBOND columns, respectively, were not available. The quantifications of the products were conducted based on the external calibration method which uses response vs amount functions that are subsequently used to estimate amounts of analyte in a separately analyzed sample as long as the standard compounds for the target products were available. The effective carbon number concept [30] was also employed for estimation of the amounts of products of which standards were unavailable. The mass of the sample after the pyrolysis was measured to evaluate char yield. It was found that the char yield mass fraction was generally small under rapid heating at 1 % to 4 % in the temperatures range used. The repeatability examinations for the analytical pyrolysis experiments revealed that the relative errors of the product yield generally within ± 10 %. The detailed experimental procedure and product analysis were given in elsewhere [13,16,17].

<Fig. 1 here>

<Table 1 here>

3. Detailed chemical kinetic modeling

Numerical simulations were conducted using the DETCHEM^{BATCH} code that was designed for computational analysis of time-dependent homogeneous reaction systems [31]. In this program, the input includes forward reaction-rate parameters and thermodynamic polynomials for all participating species, in addition to temperature, pressure, and reactant concentrations. The

program calculates the rate constant of the backward reaction for every given reversible reaction. It can be considered that the cellulose produces spontaneously volatiles under the rapid heating at first stage. The volatile cloud is directed to GC with a carrier gas. The residence time for the secondary cracking of the molecules contained in the volatiles is thus determined based on the volume of the second reactor and flow rate of the carrier gas. It is possible to consider this situation as a problem to solve time dependent change in the composition of the multi-component gas mixtures at isothermal condition. Thus we chose a batch reactor model. The compositions of the primary pyrolysis products at different pyrolysis temperatures were approximated similarly with our previous study [13] to provide the input information for the batch reactor simulation, and listed in Table 2. It should be noted that the kinetic model starts not with cellulose but with multi-component gas mixture included in volatiles derived from the primary pyrolysis. Computations were performed under isobaric and isothermal conditions. The reaction mechanism used here is same with that used in the previous work [13]. The reaction mechanism consists of 548 species and 8159 reactions. It is noteworthy that our challenge is that not to provide a kinetic model which can temporarily be used to explain the experimental results at limited conditions but to offer a comprehensive kinetic model. This is the reason why that we fixed the kinetic model. To demonstrate that the previously proposed kinetic model can predict the new experimental results is another important issue of this study. The reaction pathway analysis was also performed according to the method described elsewhere [32–34].

<Table 2 here>

4. Results and discussion

4.1. Detections of alkynes and dienes in the pyrolysis products of cellulose

Typical GC/FID chromatograms obtained with the GC equipped with the packed columns, along with the assignments of peaks, are shown in Fig. 2. Based on our previous work [13], Gasukuropak 54, consists of polymer beads with highly cross linked styrene-divinylbenzene copolymer, can able to separate the products from cellulose pyrolysis. However, this column cannot separate acetylene with ethylene. Another packed column (VZN-1) was employed to separate and quantification of the alkyne and dienes. As shown in right side of Fig. 2, good resolutions for alkyne and diene are observed and acetylene, propyne, and propadiene are successfully separated and identified by the retention time matching with the standard gases.

<Fig. 2 here>

Since the packed columns have limitations in separating high molecular mass compounds, these compounds were quantified with GC equipped with capillary column (CP PoraBOND). As shown in Fig. 3, this setup enabled us to detect compounds larger than toluene such as alkylbenzene, phenol and naphthalene. It is also possible to get more detailed information on the C₄ and C₅ hydrocarbons, and oxygen containing compounds. For example, the separation of furan and acetone is insufficient with the packed column (Fig. 2 left) whereas, these compounds are successfully separated by the capillary column. Most of the peaks were assigned by retention time matching, but several compounds such as vinylacetylene, 1,3-butadiene, and cyclopentadiene, of which standard gases and molecules are not available. These compounds

were identified with the aid of the results of the GC/MS equipped with the identical capillary column, using the mass spectral library.

<Fig. 3 here>

A well designed fluidized bed-tubular reactor with product collection trains was also developed to study secondary vapor phase reactions [10]. Compared with this, the present analytical pyrolysis (direct injection of the pyrolysis products) experiments offer a quicker and more comprehensive quantitative analysis of the products, which are gas chromatographically separable.

4.2. Product yields as a function of temperature

Fig. 4 shows the yields of alkynes and dienes as a function of pyrolysis temperature at an effective gas-phase residence time of 0.3 s. Although these compounds exhibit low yields of less than 1 %, these are important intermediates for aromatic hydrocarbons. However, the detailed characteristics of the formations of these compounds in the secondary gas phase reactions of cellulose are not well studied both experimentally and numerically.

<Fig. 4 here>

Even at around 500 °C, formations of the alkynes and dienes are observed. The formations of these highly unsaturated products at relatively low temperature and short residence time are of

interest since cellulose has no double and triple carbon-carbon bonds in its original chemical structure. The formation of propyne is observed from 500 °C, whereas that of its isomer propadiene is observed at temperature higher than 650 °C. This indicates that the propyne is a more preferable product at low temperature. This agrees well with the prediction of the reaction pathways in the cellulose secondary gas-phase cracking [13], which shows that the propyne is the most major precursor of the propadiene. The yields of the dienes such as propadiene, 1,3-butadiene, and cyclopentadiene show maximums at 800, 750, and 700 °C, respectively, whilst those of alkynes such as acetylene, propyne, and vinylacetylene increase monotonically with increasing temperature.

Fig. 5 shows the yields of the pyrolysates which were considered as important precursors for alkynes based on our previous kinetic modeling study on the cellulose vapor phase cracking [13]. As shown in Fig. 5, furan is detected even at 400 °C. Based on the kinetic model, furan can produce propyne and CO by the reaction:

The observation of the propyne formation at temperature as low as 500 °C is likely explained by the decomposition of furan, since furan is formed below 500 °C.

Fig. 5 also shows that yields of ethylene increases with increasing temperature and reaches a maximum value of 6 % at 800 °C. The yield of ethylene at 750 °C is $w_{\text{C}_2\text{H}_4} = 5 \%$, similar with the results by Funazukuri et al. [12] who reported that the C_2 hydrocarbons (ethylene+ethane) yield was 5 % when cellulose was fast pyrolyzed using a micro fluidized bed reactor at 750 °C.

The kinetic model suggested that acetylene is produced by the consecutive dehydrogenation of

ethylene through vinyl radical. Though the yields of acetylene are much lower than those of ethylene, the formation profile of acetylene along with the pyrolysis temperature is very similar with that of ethylene, indicating that ethylene is an important precursor of acetylene.

Propylene shown in Fig. 5 starts to form at 500 °C and its yield exhibits maximum at around 750 °C. Propylene provides the allyl radical which converts to cyclopentadiene through the reaction:

The coexistence of allyl with acetylene is a necessary condition for the cyclopentadiene formation and is likely realized in the cellulose pyrolysis. Acetylene is detected even at 500 °C, although the yield is very low, $w_{\text{C}_2\text{H}_2} = 0.005\%$. The rapid consumption of acetylene by allyl radical to produce cyclopentadiene is the possible explanation for the very low yield at 500 °C.

<Fig. 5 here>

Fig. 6 shows the yields of aromatic hydrocarbons. The yields of benzene and naphthalene increase with increasing temperature, while toluene yields shows maximum at around 600 °C. The formation of toluene is observed even at temperature lower than 550 °C, whereas little benzene is formed. This indicates that toluene is a major primary product than benzene at low temperature. Ipso substitution of toluene is suggested that one of the important reaction pathway leading to benzene. Naphthalene formation in the cellulose pyrolysis has been little dealt with so

far. This study revealed that naphthalene formation is observed even at 650 °C and its yield increases with increasing temperature.

<Fig. 6 here>

4.3. Detailed kinetic modeling and reaction pathways leading to benzene and naphthalene

Fig. 7 shows the yields of alkyne, dienes, and aromatic hydrocarbons as a function of residence time at 650, 750, and 850 °C in the secondary vapor phase cracking of cellulose. Besides the experimental results, numerically simulated curves obtained with the detailed chemical kinetic model are also shown for the critical evaluation of the kinetic model. As the comparison between experimental and numerical results for the products in the cellulose pyrolysis was exhaustively performed in the previous works [13], here the evaluations are limited to the alkynes and dienes which were not studied in the previous work. Considering that the low yields of these products and no adjustable parameters in the numerical simulation, it can be emphasized that the present kinetic model can capture the general trends for their formation and consumption profiles.

<Fig. 7 here>

Figs. 8 and 9 show reaction flux diagrams for the important pathways leading to benzene and naphthalene formations in cellulose pyrolysis at 650 and 850 °C, respectively. The arrows represent the formation flow of each species. The contribution of a reaction to the formation of a species is expressed by arrow thickness, which are graded into five different levels.

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<Fig. 8 here>

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Combination of cyclopentadienyl radicals is a dominant route to naphthalene at both temperature. Cyclopentadiene is mainly formed through combination of acetylene with propyne or allyl radical at 650 or 850 °C, respectively. Propargyl radical is an important precursor of toluene at both temperature, but its formation chemistry depends on temperature. Propargyl radical is formed by the decomposition of furan radical at 650 °C, while it is formed from propyne and propadiene at 850 °C since furan is no longer included in the primary pyrolysis products likely due to its high reactivity. Propyne and propadiene are produced from allyl radicals originated from propylene and butene at 850 °C. Propargyl radical and propadiene are the dominant precursors of benzene at 650 °C, while combination of ethylene with vinylacetylene produces benzene most dominantly at 850 °C. Acetylene is another important alkyne in aromatic hydrocarbon formation. The formation chemistry of acetylene at 650 °C is clearly different from that at 850 °C. As indicated in Figures 8 and 9, the kinetic model suggests that the acrolein and ethylene are dominant precursors of acetylene at 650 and 850 °C, respectively. Fig. 10 shows comparison of the numerically predicted and experimentally obtained product yields for acrolein (right) and ethylene (left). Acceptable agreements demonstrated in Fig. 10 supports the proposed mechanism for acetylene formation at two different temperatures.

<Fig.10 here>

Levoglucosan is an important constituent in the products from the primary pyrolysis of cellulose, in particular, at condition optimum to get maximum liquid product yield at around 773 K [35]. Such a low temperature, however, is unsuitable to study secondary gas phase pyrolysis kinetics because the significant changes in the composition in the gas phase are not expected at residence time up to several second. Nevertheless inclusion of the detailed chemical kinetic model for describing levoglucosan thermochemistry should be included in future challenges.

5. Conclusions

Analytical pyrolysis experiments with original configurations enabled us to find alkyne and diene compounds such as acetylene, propyne, propadiene, vinylacetylene, and cyclopentadiene were included in the products from the primary pyrolysis of cellulose even at temperature as low as 500–600 °C. These are important precursors for tarry constituents like aromatic hydrocarbons found in the vapor phase cracking of cellulose, which is originally free from aromatic structures. The reaction pathways leading to benzene and naphthalene via the alkyne and diene from primary pyrolysates of cellulose are discussed based on not only the experimental results but also numerical analysis of the reaction pathways using the detailed chemical kinetic model, which were validated and evaluated at 650, 750, and 850 °C, and residence time up to 4 s. Cyclopentadiene is a dominant precursor of naphthalene. Combination of acetylene with propyne or allyl radical can produce 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 temperature.

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Figure captions

Fig. 1.

A schematic representation of the experimental set-up for studying secondary gas-phase pyrolysis of the primary pyrolysis products of cellulose. A U-shaped two-stage tubular reactor (TS-TR), consisting of two sections divided by a quartz wool filter, is externally heated by an electric furnace which is movable vertically to adjust the effective reactor volume for the secondary pyrolysis. Fast pyrolysis of cellulose particles at the upstream of the TS-TR generates nascent volatiles which followed by secondary pyrolysis downstream. Products are directed to the online GCs or a GC/MS.

Fig. 2.

GC-FID chromatograms for products derived from cellulose fast pyrolysis with the TS-TR at 750 °C and an effective residence time for a secondary gas-phase reaction of 0.8 s. The left and right correspond to a chromatogram obtained by a packed column (Gaskuropak 54 GL Sciences Inc.) and that by a packed column (VZN-1, GL Sciences Inc.), respectively.

Fig. 3.

A GC-FID chromatogram for products derived from cellulose fast pyrolysis at 750 °C and an effective residence time for a secondary gas-phase reaction of 0.5 s. The chromatogram was obtained by using a capillary column (PoraBOND, GL Sciences Inc.).

Fig. 4.

Experimentally measured product yields of alkynes and dienes in the cellulose fast pyrolysis with the TS-TR at an effective residence time for a secondary gas-phase reaction of 0.3 s and varying temperatures.

Fig. 5.

Experimentally measured product yields in the cellulose fast pyrolysis with the TS-TR at an effective residence time for a secondary gas-phase reaction of 0.3 s and varying temperatures. Furan, ethylene, and propylene are considered as important precursors of alkynes and dienes in the vapor phase cracking of cellulose.

Fig. 6.

Experimentally measured product yields of aromatic hydrocarbons in the cellulose fast pyrolysis with the TS-TR at an effective residence time for a secondary gas-phase reaction of 0.3 s and varying temperatures.

491

492 Fig. 7.

493 Comparison of the numerically predicted and experimentally obtained product yields for alkynes, dienes,
494 and aromatic hydrocarbons found in the secondary pyrolysis of cellulose at three temperatures (650, 750,
495 and 850 °C) at varying residence times. Lines and symbols represent numerical predictions and
496 experimental data, respectively.

497

498 Fig. 8.

499 Reaction flux diagram for the formations of benzene and naphthalene in the secondary pyrolysis of
500 cellulose at 650 °C. Boxed compounds are the primary pyrolysis products.

501

502 Fig. 9.

503 Reaction flux diagram for the formations of benzene and naphthalene in the secondary pyrolysis of
504 cellulose at 850 °C. Boxed compounds are the primary pyrolysis products.

505

506 Fig. 10.

507 Comparison of the numerically predicted and experimentally obtained product yields for acrolein (right)
508 and ethylene (left), which are dominant precursors of acetylene at three temperatures (650, 750, and 850
509 °C) at varying residence times. Lines and symbols represent numerical predictions and experimental data,
510 respectively.

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514

Table 1

Gas chromatograph configuration and instrument conditions.

Instrument	Separation column	Detector	Analytes	Condition
Shimadzu GC-2014	Gaskuropack 54 (Packed column, GL Sciences)	TCD/FID serial	TCD	Injector ;200 °C
			Inorganic gases such as CO, CO ₂ , H ₂ , H ₂ O	Detector ;220 °C TCD current ;110 mA
Shimadzu GC-2014	VZN-1 (Packed column, Alltech)	FID	FID	Temperature program; 10 min hold at 40 °C, then heated at 5 K min ⁻¹ to 200 °C, and 60 min hold at 200 °C
			Organic products from methane to toluene	
Shimadzu GC-2010	PoraBOND (capillary column, Varian)	FID	Alkyne and diene compounds	Injector ;60 °C Detector ;60 °C Temperature ;isothermal at 30 °C
			Products larger than toluene and which cannot be well separated by the packed column	Injector ;345 °C Detector ;300 °C Temperature program ;13 min hold at 40 °C, then heated at 5 K min ⁻¹ to 300 °C
Shimadzu GCMS-QP5000	PoraBOND (capillary column, Varian)	Mass spectrometer	Used for peak assignment	Injector ;345 °C Detector ;300 °C Temperature program ;13 min hold at 40 °C, then heated at 5 K min ⁻¹ to 300 °C

Table 2

Volatile mass fraction (yield) distribution from cellulose used in the numerical simulation of the homogeneous gas phase reactions.

Products, %	Temperature, °C		
	650	750	850
H ₂	0.40	0.70	0.90
CO	43.1	52.0	58.0
CO ₂	3.82	4.00	4.00
H ₂ O	17.4	18.2	17.0
CH ₄	2.31	4.00	4.50
C ₂ H ₂	0.25	0.60	0.00
C ₂ H ₄	1.85	5.00	6.50
C ₂ H ₆	0.63	0.70	0.90
C ₃ H ₆	1.65	2.60	1.00
C ₃ H ₈	0.10	0.15	0.05
C ₃ H ₄ (propyne)	0.14	0.20	0.12
CH ₃ OH	0.89	1.40	0.70
CH ₃ CHO	3.96	2.50	0.50
C ₄ H ₈	0.81	1.60	0.60
C ₄ H ₁₀	0.19	0.17	0.02
C ₂ H ₅ OH	0.25	0.17	0.02
acrolein	1.80	0.50	0.00
furan	1.40	0.90	0.20
acetone	0.47	0.40	0.02
CH ₃ COOH	0.48	0.10	0.05
cyclopentadiene	0.20	0.30	0.30
2-propanol	0.10	0.01	0.01
methylfuran	0.54	0.10	0.02
2,3-butanedione	1.49	0.60	0.05
hydroxyacetone	0.43	0.50	0.50
benzene	0.18	0.50	1.20
dimethylfuran	0.10	0.01	0.00
toluene	0.25	0.30	0.35
furfural	1.40	0.40	0.10
propadiene	0.02	0.00	0.02
1-butyne	0.02	0.00	0.02
1,3-butadiene	0.40	0.00	0.00
1,2-butadiene	0.01	0.00	0.00
1-pentene	0.04	0.01	0.00
1,4-pentadiene	0.06	0.07	0.00
1,3-pentadiene	0.06	0.00	0.00
isoprene	0.03	0.00	0.00
2-butenal	0.08	0.02	0.00

vinylmethylketone	0.39	0.06	0.00
methylcyclopentadiene	0.08	0.06	0.00
ethylbenzene	0.02	0.00	0.01
phenol	0.09	0.10	0.08
styrene	0.05	0.00	0.00
levoglucosan	8.5	0.0	0.0
char *	3.5	1.1	2.3
total	100	100	100

* char is substituted with nitrogen in the simulation.

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Fig. 7. Norinaga et al.

Fig. 10. Norinaga et al.