Quantification of Cellulose Pyrolyzates via a Tube Reactor and a Pyrolyzer-Gas Chromatograph/Flame Ionization Detector-Based System

Shogo Kumagai,* Yusuke Takahashi, Tomohito Kameda, Yuko Saito, and Toshiaki Yoshioka

ABSTRACT: Pyrolysis of cellulose primarily produces 1,6-anhydro-β-D-glucopyranose (levoglucosan), which easily repolymerizes to form coke precursors in the heating zone of a pyrolysis reactor. This hinders the investigation of primary pyrolysis products as well as the elucidation of cellulose pyrolysis mechanisms, particularly because of the significant buildup of coke during slow pyrolysis. The present study discusses the applicability of a pyrolysis-gas chromatography/flame ionization detection (Py-GC/FID) system using naphthalene as the internal standard, with the aim of substantially improving the quantification of pyrolyzates during the slow pyrolysis of cellulose. This method achieved quantification of levoglucosan with a yield that was 14 times higher than that obtained from offline pyrolysis in a simple tube reactor. The high yield recovery of levoglucosan was attributed to the suppression of levoglucosan repolymerization in the Py-GC/FID system, owing to the rapid escape of levoglucosan from the heating zone, low concentration of levoglucosan in the gas phase, and rapid quenching of levoglucosan. Therefore, this method facilitated the improved quantification of primary pyrolysis products during the slow pyrolysis of cellulose, which can be beneficial for understanding the primary pyrolysis reaction mechanisms. This method can potentially be applied to other polymeric materials that produce reactive pyrolyzates.

INTRODUCTION

Pyrolysis is a relatively simple and robust thermochemical technology, which accomplishes the cleavage of multiple chemical bonds by heat alone; it is a promising method to convert biomass into chemical feedstock and fuels.1−3 The elucidation of pyrolysis mechanisms is necessary to control the reactions therein for maximizing the yield of the desired products or minimizing those of the undesired products.

Cellulose is a significant component of lignocellulosic biomass and accounts for 40−50 wt % of its total composition. Mechanisms of cellulose pyrolysis have been extensively investigated both experimentally4−6 and computationally.7−9 In their discussion on the advantages of cellulose pyrolysis, Itabaiana et al.10 concluded that 1,6-anhydro-β-D-glucopyranose (levoglucosan), a major product during the pyrolysis of cellulose, is a promising chemical platform. Therefore, there is a significant demand for the investigation and analysis of cellulose pyrolysis and pyrolyzates.

Levoglucosan is known to easily repolymerize to form coke precursors during the pyrolysis of cellulose,11,12 which hinders the elucidation of the primary pyrolysis reaction mechanism of cellulose. Several studies have reported significant coke deposits during cellulose pyrolysis in tube reactors.13,14 Coke deposition is substantial in slow pyrolysis (i.e., pyrolysis at a slow heating rate)15 because the long duration of heating accelerates the repolymerization of levoglucosan that is deposited in the heating zone.

Therefore, to prevent levoglucosan repolymerization, it is necessary to facilitate its rapid escape from the heating zone of the pyrolysis reactor; further, low concentrations of levoglucosan and its rapid quenching are necessitated. This can be achieved with micropyrolyzer-gas chromatography (Py-GC) systems, which are often applied in analytical and applied pyrolysis of plastics and biomass.16,17 Py-GC/mass spectrometry (Py-GC/MS) has also been actively applied for the investigation of cellulose pyrolysis mechanisms.18,19 Also, Py-GC analysis does not require a solvent for pyrolyzate recovery, which can limit issues such as pyrolyzate solubility and solvent overlap with the pyrolyzate peaks. However, most of the studies on Py-GC/MS have evaluated pyrolysis product distributions based on the percentage of the chromatogram area, which does not reflect the yield of the products. The focus of the present study was to analyze the advantages of Py-GC for the quantification of cellulose pyrolyzates by
performing offline pyrolysis in a simple tube (fixed-bed) reactor, which is often used for pyrolysis experiments.

Therefore, in the present study, slow pyrolysis of cellulose was conducted in a micropyrolyzer, and the pyrolyzates were directly quantified using a GC/flame ionization detector (GC/FID) (Figure 1a) with naphthalene as the internal standard.

The product yields were compared with those obtained from slow and fast offline pyrolysis experiments performed in a simple tube reactor (Figure 1b).13,14

■ RESULTS AND DISCUSSION

Weight Loss Behavior of Cellulose. Pyrolysis of the cellulose sample was first performed using thermogravimetric analysis (TGA) to confirm its weight loss behavior; the obtained TG and derivative thermogravimetric (DTG) curves are presented in Figure 2. The weight loss at ∼100 °C is attributed to the desorption of water. The maximum weight loss observed at 343 °C is attributed to the pyrolysis of cellulose. The gradual weight loss above 370 °C mainly corresponds to the charring process, and the weight loss is seen to be almost complete at 650 °C. The final weight, corresponding to char yield, was 8.9 wt %. These results are consistent with those obtained via cellulose pyrolysis at the same heating rate.20 Therefore, the selected heating protocol was confirmed to complete tar generation from cellulose, and the suitability of a tube reactor and Py-GC/FID systems for the analysis of tar was ensured.

Pyrolysis of Cellulose in a Tube Reactor. A 200 mg cellulose sample was pyrolyzed from ambient temperature to 650 °C at a heating rate of 10 °C/min in a tube reactor. The latter half of the reactor after pyrolysis is depicted in Figure 3. A significant amount of coke (i.e., the black deposit) is observed to be produced on the reactor wall in the heating zone. The deposited coke is produced via repolymerization of levoglucosan on the heated wall.21,22 The end of the reactor reaches ∼300 °C when the furnace is at 650 °C, which can promote the repolymerization of levoglucosan (i.e., the yellow deposit).23 The production of coke at the edge of the heating zone has been reported in our previous studies13−15 and is thus a known issue during cellulose pyrolysis. Moreover, the tube reactor test produced 8.6 wt % char, which is comparable with the TG results conducted using the same heating program (Figure 2).

The collected tar was identified and quantified by GC/MS and GC/FID, respectively. Only a small amount of tar could be identified and quantified (Table 1). The identified compounds are primarily anhydrosugars, such as levoglucosan (1.2 wt %), levoglucosenone (0.6 wt %), and 1,4:3,6-dianhydro-α-D-glucopyranose (0.6 wt %). This is a result of the consumption of levoglucosan for coke formation during slow pyrolysis. Previous studies have also revealed that slow pyrolysis is unfavorable for tar production.24−26 It should be noted that these yields are much lower than those obtained in the fast pyrolysis of cellulose at 650 °C using the same tube reactor, which results in a total of 15.3 wt % tar being identified, which includes 10.6 wt % anhydrosugars, 1.5 wt % C2−C3 compounds, and traces of other compounds.13 Although the pyrolysis temperature was different, the tar yields obtained via fast pyrolysis at 500 °C14 were also higher than those obtained under the present slow pyrolysis conditions. Therefore, these results support the fact that the analysis of tar, especially that of primary pyrolysis products obtained via slow pyrolysis of cellulose, in an offline pyrolysis reactor is difficult.
Pyrolyzates was next conducted in a Py-GC/FID system. Surprisingly, the total identified tar yield was significantly improved to 19.9 ± 1.0 wt %, which is 4.6 times higher than that from slow pyrolysis in the tube reactor (Table 1). Specifically, the levoglucosan yield (16.9 ± 1.0 wt %) is noted to be 14.1 times higher than that from the tube reactor. Additionally, traces of C₂−C₃ compounds such as acetaldehyde, glycolaldehyde, hydroxyacetone, and acrolein, and five-membered ring compounds such as furans, furfurs, and 5-hydroxymethylfurfural are also identified and quantified. The compounds identified in this study are consistent with those obtained from our previous studies using the same sample¹³,¹⁴ and other studies on cellulose pyrolysis.²⁶,²⁷ These results suggest that the Py-GC/FID system significantly inhibits the repolymerization of levoglucosan, which is known to progress via the acid-catalyzed ring opening of levoglucosan between 260 and 280 °C in its molten state by proton donation to the C₁-oxygen via intermolecular hydrogen bond formation.²³ The high-boiling-point levoglucosan is easily deposited on the reactor wall in the heating zone, where repolymerization is accelerated. The char yield obtained from the Py-GC test was 7.0 wt %, which was slightly lower than that obtained from the TGA (Figure 2) and the tube reactor test. This suggests that the lower cellulose loading in the Py-GC test inhibits levoglucosan polymerization in the sample holder.

A low concentration of levoglucosan, short residence time in the heating zone, and rapid quenching of levoglucosan are known to be effective for preventing the accumulation of levoglucosan. These conditions can be realized with the Py-GC/FID approach discussed in this study. To achieve this, the flow of levoglucosan is facilitated from the sample holder to the liquid N₂ trap and is depicted in Figure 4. Cellulose pyrolysis primarily produces levoglucosan, which is rapidly carried into the GC liner via He gas flow. The residence time in the pyrolyzer is <1 s, whereas that in the tube reactor in this study is ~18 s. The high injection split ratio (100:1) decreases the levoglucosan concentration in the gas phase. Subsequently, levoglucosan is rapidly quenched and trapped by liquid N₂ between the injection port and the separation column, where repolymerization is suppressed. Coke deposits are not observed inside the injection port because of the tiny amount of the sample (1 mg).

### Table 1. Identified Tar Compounds from the Tube Reactor and Py-GC/FID Experiments

| product name                      | tube reactor | slow pyrolysis up to 650 °C at 10 °C/min | fast pyrolysis at 500 °C at 10 °C/min | fast pyrolysis at 650 °C at 10 °C/min | Py-GC/FID up to 650 °C at 10 °C/min |
|-----------------------------------|--------------|-----------------------------------------|--------------------------------------|--------------------------------------|----------------------------------|
| anhydrosugars                    | 2.4          | 8.1                                     | 10.8                                 | 19.3 ± 1.0                           |
| levoglucosan                      | 1.2          | 7.1                                     | 10.6                                 | 16.9 ± 1.0                           |
| 1,6-anhydro-β-d-glucofuranose     | 0.6          | 0.6                                     | +                                    | 0.6 ± 0.0                            |
| levoglucosenone                   | 0.1          | 0.1                                     | +                                    | 1.0 ± 0.0                            |
| 1,4,5,6-dianhydro-α-d-glucopyranose| 0.6          | 0.3                                     | 0.2                                  | 0.8 ± 0.1                            |
| C₂−C₃ compounds                  |              |                                        |                                      |                                     |
| acetaldehyde                      |              | 1.4                                     | 1.5                                  | 0.1 ± 0.0                            |
| glycolaldehyde                    |              | 0.1                                     | 0.2                                  | +                                    |
| hydroxyacetone                    |              | 1.0                                     | 1.3                                  | +                                    |
| acrolein                          |              | 0.4                                     | +                                    | +                                    |
| furan                             |              |                                        |                                      |                                      |
| 2-methylfuran                     |              |                                        |                                      |                                      |
| 2,5-dihydrofuran                  |              |                                        |                                      |                                      |
| 2,5-dimethylfuran                 |              |                                        |                                      |                                      |
| furfural                          |              |                                        |                                      |                                      |
| 5-hydroxymethylfurfural           |              |                                        |                                      |                                      |
| others                            | 1.9          | 1.7                                     | 2.9                                  | 0.5 ± 0.0                            |
| identified tar total              | 4.3          | 11.2                                    | 15.3                                 | 19.9 ± 1.0                           |

*a* not detected. *b* less than 0.05 wt %. *c* less than ± 0.05 wt %.

**Figure 4.** Flow of levoglucosan from the pyrolyzer to the liquid N₂ trap.
The enhanced levoglucosan recovery through the Py-GC approach is supported by previous studies.12,25 Hosoya et al.12 tested the pyrolysis of levoglucosan with three different levoglucosan loadings (0.1, 1.0, and 10.0 mg) using a closed ampoule reactor. The high levoglucosan loading suppressed evaporation of levoglucosan, and levoglucosan polymerization was enhanced in the liquid/solid phase. Therefore, the tiny amount of levoglucosan in the Py-GC was suitable for preventing levoglucosan polymerization in the sample holder. Nomura et al.28 achieved almost complete inhibition of coke formation during cellulose pyrolysis by pyrolyzing it in benzophenone. This can be reasonably explained by the solvation of levoglucosan with benzophenone through CH/π and OH/π interactions. This solvation inhibits proton donation to the levoglucosan molecules through intermolecular hydrogen bonding, which can act as acid and base catalysts for levoglucosan thermal degradation. Therefore, this work revealed that reducing the contact between levoglucosan molecules in the liquid/solid phase is indispensable for promoting levoglucosan recovery.

Although complete inhibition of levoglucosan repolymerization was not achieved, the present study reveals the potential of Py-GC/FID as a method for studying the primary pyrolysis mechanism of cellulose.

**CONCLUSIONS**

A micropyrolyzer-gas chromatograph/flame ionization detector system (Py-GC/FID) with an internal standard was employed to achieve a short residence time in the heating zone, a low concentration of pyrolyzates, and their rapid quenching. These features facilitated significant inhibition of the repolymerization of levoglucosan during the slow pyrolysis of cellulose and resulted in yields of tar and levoglucosan that were 4.6 and 14.1 times higher than those obtained in an offline tube-reactor-based slow pyrolysis, respectively. Although the tar recovery can be further improved by modifying the gas flow rate, splitting ratio, and temperature of the furnace, our study has nevertheless revealed the significant potential of the approach presented herein for quantifying primary pyrolysis products obtained during the slow pyrolysis of cellulose. We believe that this methodology can contribute toward the elucidation of pyrolysis mechanisms of polymeric materials, including biomass components such as hemicellulose and lignin, which are known to produce highly reactive pyrolyzates.

**METHODS**

**Materials.** Commercial cellulose powder was sourced from Sigma-Aldrich. The elemental analysis (C, H, and N) of the commercial sample was conducted using a J-SCIENCE LAB JM-10 analyzer, which resulted in the following compositions—C: 43.6, H: 6.3, and O: 50.1 wt % (balance). The other chemicals used in this study were purchased from Kanto Chemical (Tokyo, Japan) and Tokyo Chemical Industry (Tokyo, Japan). TGA of the cellulose was performed using a STA7200RV (Hitachi High-tech Science Corporation, Tokyo, Japan) analyzer. A 10 mg sample of cellulose was loaded into a Pt pan, and a sapphire plate (10 mg) was placed in a separate Pt pan as the reference. The sample was heated from 50 to 650 °C at 10 °C/min under a N2 flow rate of 200 mL/min.

**Offline Slow Pyrolysis of Cellulose in a Tube Reactor.** The cellulose sample was pyrolyzed in a horizontal quartz tube reactor (16 mm ID) that was heated by an electric furnace (Figure 1a). The detailed experimental procedure is explained elsewhere.25 Briefly, a 200 mg sample was loaded into a ceramic sample holder, which was placed in the center of the heating zone in a quartz tube reactor. The furnace temperature was increased from ambient to 650 °C at a heating rate of 10 °C/min under He gas flow (100 mL/min). When the temperature reached 650 °C, heating was stopped and the tube reactor was cooled to ambient temperature under continuous He flow. The interior of the liquid N2 trap and reactor wall was subsequently washed with super dehydrated tetrahydrofuran (20 mL). Tar and coke were defined in the present study as tetrahydrofuran (THF)-soluble and THF-insoluble fractions, respectively.

The collected tar was identified using a GC/MS system (Agilent Technologies). The GC setup (model 6890N) included the following: an Ultra ALLOY UA-5 capillary column (30 m long, 0.25 mm ID, and a 0.25-μm-thick 95% poly(dimethylsiloxane) and 5% poly-(diphenyl(dimethyl)siloxane) stationary phase film (Frontier Laboratories)). The parameters of the MS setup (model 5975) were the following: column flow: 1 mL/min; split ratio: 20:1; inlet temperature: 300 °C; mass selective detector (MSD) source temperature: 230 °C; MS quadrupole temperature: 150 °C; acquisition mode: scan; scanning range: m/z = 10–600; MS library: NIST08; and MSD ChemStation E02.01.1177. The GC oven temperature program was set to 50 °C (5 min) → 5 °C/min → 320 °C (10 min).

The quantification of the collected tar was performed using a GC/FID system (GC390, GL Science, Japan) with naphthalene as the internal standard. GC conditions similar to those in the GC/MS analysis were selected. The areas of each product and naphthalene obtained from the FID response were calculated using Open Lab CDS EZChrom Edition software (Agilent Technologies). The intensity of the FID response depends on the effective carbon number and is influenced by the presence of partially oxidized carbon in the compounds. Therefore, the FID response factors of key compounds such as levoglucosan, glycolaldehyde, hydroxyacetone, and furan were determined with respect to naphthalene. FID response factors of the other minor compounds were predicted using Jorgensen’s method.20

**Pyrolysis of Cellulose and Online GC/FID Analysis.** Cellulose (1.0 mg) and naphthalene (0.2 mg, internal standard) were placed in a sample holder, which was subsequently inserted in the pyrolyzer (Figure 1b; EGA/PY-3030D, Frontier Laboratories Ltd.). The sample cup was heated using the same heating program as that in the tube reactor experiment under He flow (104 mL/min; 1 mL/min for the column, 3 mL/min for septum purge, and 100 mL/min for the split vent). Naphthalene evaporated from the sample cup and cellulose subsequently underwent pyrolysis. The evaporated naphthalene and cellulose pyrolyzates were directly introduced into the GC/FID system (split ratio: 100:1, with other conditions similar to those in the previous section on quantification of tar), and were captured by a liquid N2 trap placed between the GC injection port and separation column during pyrolysis. After termination of the pyrolysis, the cryotrap was removed and the GC temperature program was subsequently initiated (50 °C (5 min) → 5 °C/min → 320 °C (10 min)). The Py-GC/FID test was repeated three times to confirm the repeatability of this method.
Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c00622

Author Contributions
S.K. conceptualized this study, drafted the manuscript text, and devised all of the experimental setups. Y.T. and S.K. carried out all of the experiments and analyses. T.K., Y.S., and T.Y. contributed to the drafting of the introductory section. All authors have reviewed the manuscript.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This work was supported by the JSPS KAKENHI grant number 19H04306.

REFERENCES
(1) Dai, L.; Wang, Y.; Liu, Y.; He, C.; Ruan, R.; Yu, Z.; Jiang, L.; Zeng, Z.; Wu, Q. A review on selective production of value-added chemicals via catalytic pyrolysis of lignocellulosic biomass. Sci. Total Environ. 2020, 749, No. 142386.
(2) Dai, L.; Zhou, N.; Li, H.; Deng, W.; Cheng, Y.; Wang, Y.; Liu, Y.; Cui, Q.; Lei, H.; Chen, P.; Ruan, R. Recent advances in improving lignocellulosic biomass-based bio-oil production. J. Anal. Appl. Pyrol. 2020, 149, No. 104845.
(3) Wang, G.; Dai, Y.; Yang, H.; Xiong, Q.; Wang, K.; Zhou, J.; Li, Y.; Wang, S. A Review of Recent Advances in Biomass Pyrolysis. Energy Fuels 2020, 34, 15557–15578.
(4) Leng, E.; Ferreiro, A. I.; Liu, T.; Gong, X.; Costa, M.; Li, X.; Xu, M. Experimental and kinetic modelling investigation on the effects of crystallinity on cellulose pyrolysis. J. Anal. Appl. Pyrol. 2020, 152, No. 104863.
(5) Dai, G.; Wang, K.; Wang, G.; Wang, S. Initial pyrolysis mechanism of cellulose revealed by in-situ DRIFT analysis and theoretical calculation. Combust. Flame 2019, 208, 273–280.
(6) Fukutome, A.; Kawamoto, H.; Saka, S. Processes forming Gas, Tar, and Coke in Cellulose Gasification from Gas-Phase Reactions of Levoglucosan as Intermediate. ChemSusChem 2015, 8, 2240–2249.
(7) Malekian, V.; Daenhuemer, P. J.; Neurock, M. Glycosidic C–O Bond Activation in Cellulose Pyrolysis: Alpha Versus Beta and Condensed Phase Hydroxyl-Catalyzed Scission. ACS Catal. 2020, 10, 8454–8464.
(8) Wang, Q.; Song, H.; Pan, S.; Dong, N.; Wang, X.; Sun, S. Initial pyrolysis mechanism and product formation of cellulose: An Experimental and Density functional theory(DFT) study. Sci Rep 2020, 10, No. 3626.
(9) Lu, Q.; Wu, Y.-t.; Hu, B.; Liu, J.; Liu, D.-j.; Dong, C.-q.; Yang, Y.-p. Insight into the mechanism of secondary reactions in cellulose pyrolysis: interactions between levoglucosan and acetic acid. Cellulose 2019, 26, 8279–8290.
(10) Ibaiaiana, Junior, I.; Avelar do Nascimento, M.; de Souza, R. O. M. A.; Dufour, A.; Wojcieszak, R. Levoglucosan: a promising platform molecule? Green Chem. 2020, 22, 5859–5880.
(11) Kawamoto, H.; Murayama, M.; Saka, S. Pyrolysis behavior of levoglucosan as an intermediate in cellulose pyrolysis: polymerization into polyacetylene as a key reaction to carbonized product formation. J. Wood Sci. 2003, 49, 469–473.
(12) Hosoya, T.; Kawamoto, H.; Saka, S. Different pyrolytic pathways of levoglucosan in vapor- and liquid-solid-phases. J. Anal. Appl. Pyrolysis 2008, 83, 64–70.
(13) Kumagai, S.; Fujita, K.; Takahashi, Y.; Kameda, T.; Saito, Y.; Yoshioka, T. Impacts of Pyrolytic Interactions during the Co-pyrolysis of Biomass/Plastic: Synergies in Lignocellulose-Polyethylene System. J. Jpn. Inst. Energy 2019, 98, 202–219.
(14) Kumagai, S.; Yamamoto, M.; Takahashi, Y.; Kameda, T.; Saito, Y.; Yoshioka, T. Impact of Common Plastics on Cellulose Pyrolysis. Energy Fuels 2019, 33, 6837–6841.
(15) Kumagai, S.; Fujita, K.; Kameda, T.; Yoshioka, T. Interactions of beechn wood–polyethylene mixtures during co-pyrolysis. J. Anal. Appl. Pyrolysis 2016, 122, 531–540.
(16) Kumagai, S.; Yoshioka, T. Latest Trends in Pyrolysis Gas Chromatography for Analytical and Applied Pyrolysis of Plastics. Anal. Sci. 2021, 37, 145–157.
(17) Akahn, M. K.; Karagöz, S. Analytical pyrolysis of biomass using gas chromatography coupled to mass spectrometry. TrAC Trends Anal. Chem. 2014, 61, 11–16.
(18) Chen, L.; Liao, Y.; Guo, Z.; Cao, Y.; Ma, X. Products distribution and generation pathway of cellulose pyrolysis. J. Cleaner Prod. 2019, 232, 1309–1320.
(19) Kumagai, S.; Matsukami, A.; Kabashima, F.; Sakurai, M.; Kanai, M.; Kameda, T.; Saito, Y.; Yoshioka, T. Combining pyrolysis—two-dimensional gas chromatography—time-of-flight mass spectrometry with hierarchical cluster analysis for rapid identification of pyrolytic interactions: Case study of co-pyrolysis of PVC and biomass components. Process Saf. Environ. Prot. 2020, 143, 91–100.
(20) Yang, H.; Yan, R.; Chen, H.; Lee, D. H.; Zheng, C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel 2007, 86, 1781–1788.
(21) Kawamoto, H.; Morisaki, H.; Saka, S. Secondary decomposition of levoglucosan in pyrolytic production from cellulose biomass. J. Anal. Appl. Pyrolysis 2009, 85, 247–251.
(22) Hosoya, T.; Kawamoto, H.; Saka, S. Pyrolysis behaviors of wood and its constituent polymers at gasification temperature. J. Anal. Appl. Pyrolysis 2007, 78, 328–336.
(23) Kawamoto, H.; Hosoya, T.; Ueno, Y.; Shoji, T.; Saka, S. Thermal stabilization and decomposition of simple glycosides in the presence of aromatic substances in closed ampoules: The role of OH–···H hydrogen bonding. J. Anal. Appl. Pyrolysis 2014, 109, 41–46.
(24) Laird, D. A.; Brown, R. C.; Amonette, J. E.; Lehmann, J. Review of the pyrolysis platform for coproducing bio-oil and biochar. Biofuels, Bioprod. Biorefin. 2009, 3, 547–562.
(25) Brown, T. R.; Wright, M. M.; Brown, R. C. Estimating profitability of two biochar production scenarios: slow pyrolysis vs fast pyrolysis. Biofuels, Bioprod. Biorefin. 2011, 5, 54–68.
(26) Bridgewater, A. V. Review of fast pyrolysis of biomass and product upgrading. Biomass Bioenergy 2012, 38, 68–94.
(27) Fukutome, A.; Kawamoto, H.; Saka, S. Kinetics and molecular mechanisms for the gas-phase degradation of levoglucosan as a cellulose gasification intermediate. J. Anal. Appl. Pyrolysis 2017, 124, 666–676.
(28) Nomura, T.; Kawamoto, H.; Saka, S. Pyrolysis of cellulose in aromatic solvents: Reactivity, product yield, and char morphology. J. Anal. Appl. Pyrolysis 2017, 126, 209–217.
(29) Jørgensen, A. D.; Piel, K. C.; Stamoudis, V. C. Prediction of gas chromatography flame ionization detector response factors from molecular structures. Anal. Chem. 1990, 62, 683–689.