

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

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Cite This: *ACS Omega* 2021, 6, 12022–12026



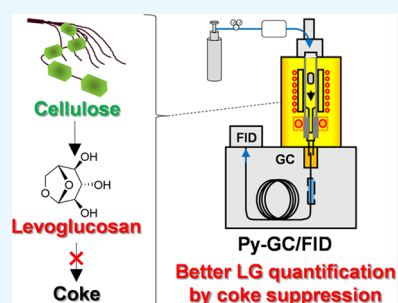
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ABSTRACT: Pyrolysis of cellulose primarily produces 1,6-anhydro- β -D-glucopyranose (levoglucosan), which easily repolymerizes to form coke precursors in the heating zone of a pyrolysis reactor. This hinders the investigation of primary pyrolysis products 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 experimentally^{4–6} 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

Received: February 3, 2021

Accepted: March 18, 2021

Published: April 26, 2021



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.

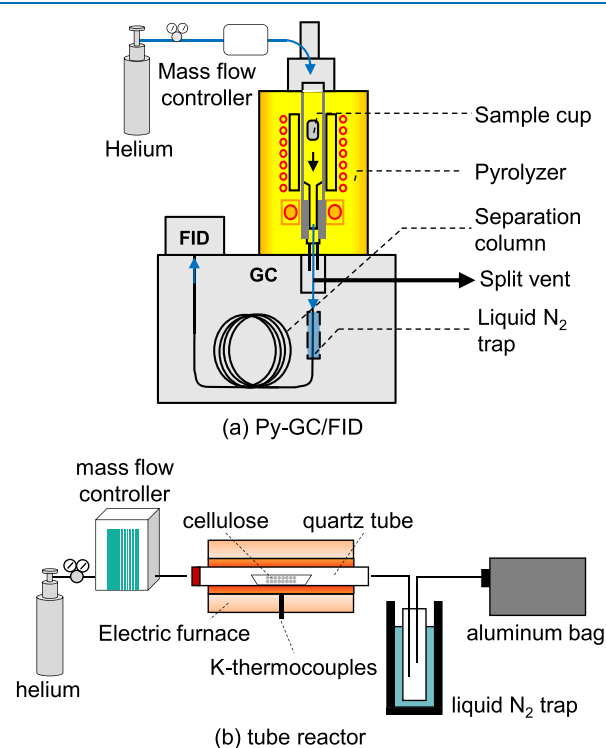


Figure 1. Schematics of (a) pyrolysis in a Py-GC/FID system and (b) offline pyrolysis in a tube reactor.

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

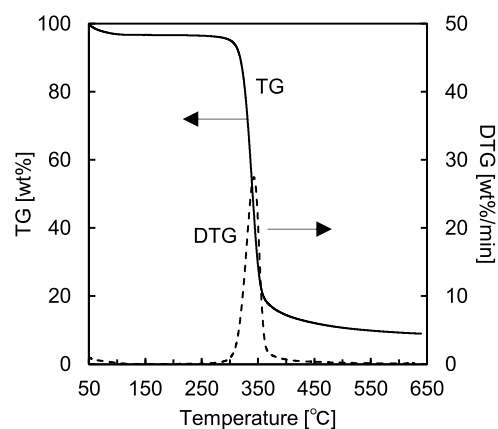


Figure 2. TG and DTG curves of cellulose pyrolysis at 10 °C/min.

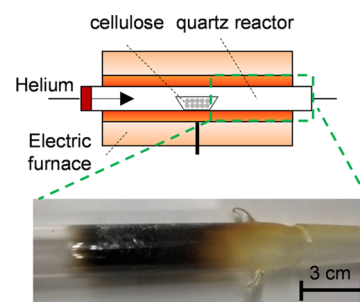


Figure 3. Image of the quartz reactor after slow pyrolysis of cellulose in a tube reactor.

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 studies,^{13–15} 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.

Pyrolysis of Cellulose in a Py-GC/FID System. The pyrolysis of cellulose and subsequent quantification of its

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

product name	tube reactor			Py-GC/FID up to 650 °C at 10 °C/min
	slow pyrolysis up to 650 °C at 10 °C/min	fast pyrolysis at 500 °C ¹⁴	fast pyrolysis at 650 °C ¹³	
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 ^c
levoglucosenone	0.1	0.1	+	1.0 ± 0.0
1,4:3,6-dianhydro-α-d-glucopyranose	0.6	0.3	0.2	0.8 ± 0.1
C ₂ -C ₃ compounds	–	1.4	1.5	0.1 ± 0.0
acetaldehyde	– ^a	0.1	0.2	+ ^b
glycolaldehyde	–	1.0	1.3	+
hydroxyacetone	–	0.4	+	+
acrolein	–	–	+	+
five-membered ring compounds	–	+	0.1	0.5 ± 0.1
furan	–	+	0.1	+
2-methylfuran	–	–	+	+
2,5-dihydrofuran	–	–	+	+
2,5-dimethylfuran	–	–	+	+
furfural	–	–	+	0.3 ± 0.0
5-hydroxymethylfurfural	–	–	+	0.1 ± 0.0
others	1.9	1.7	2.9	0.5 ± 0.0
identified tar total	4.3	11.2	15.3	19.9 ± 1.0

^anot detected. ^bless than 0.05 wt %. ^cless than ± 0.05 wt %.

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, furfurals, 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 sample^{13,14} and other studies on cellulose pyrolysis.^{6,27} 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

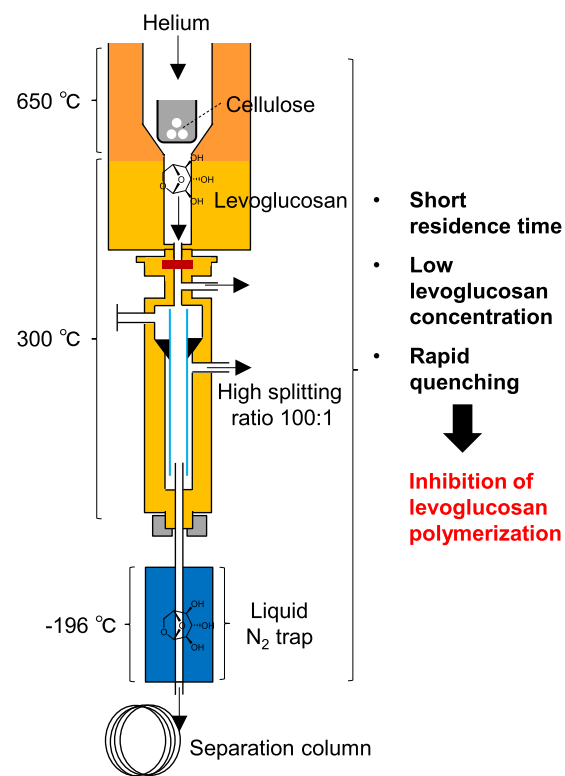


Figure 4. Flow of levoglucosan from the pyrolyzer to the liquid N₂ trap.

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).

The enhanced levoglucosan recovery through the Py-GC approach is supported by previous studies.^{12,28} 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.¹⁵ 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- μ m-thick 95% poly(dimethylsiloxane) and 5% poly(diphenyldimethylsiloxane) 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 E.02.01.1177. The GC oven temperature program was set to 50 °C (5 min) \rightarrow 5 °C/min \rightarrow 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.²⁹

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) \rightarrow 5 °C/min \rightarrow 320 °C (10 min)). The Py-GC/FID test was repeated three times to confirm the repeatability of this method.

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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.

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