Electronic supplementary information

Improving levoglucosan and hydrocarbon production through gas-phase synergy during cellulose and polyolefin co-pyrolysis

Shengyu Xie,[a] Chuan Ma,[a] Shogo Kumagai,[a,b,*] Yusuke Takahashi,[a] Tomohito Kameda,[a] Yuko Saito,[a] Toshiaki Yoshioka[a]

[a]*Graduate School of Environmental Studies, Tohoku University, 6-6-07 Aoba, Aramaki-aza, Aoba-ku, Sendai, Miyagi 980-8579, Japan*

[b]*Division for the Establishment of Frontier Sciences of Organization for Advanced Studies, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan*

[*]Corresponding author. E-mail address: kumagai@tohoku.ac.jp (S. Kumagai)

Product recovery and analysis

The pyrolysis products were collected in the following manner: the gases were collected in an aluminum bag; the liquid condensed in the cold end of the quartz tube, joint, and trap; and the solid (coke from cellulose and wax from polyolefin) was deposited in the cold zone of the quartz tube, with char remaining in the heated zone of the quartz tube. Therefore, the quartz tube is cut into two convenient sections for collecting each type of product, as shown in Fig. S1. One section contains the char, with the other containing the condensed liquid/solid. The liquid was collected by washing the cut tube, joint, and trap with super-dehydrated tetrahydrofuran (THF, 10 mL).

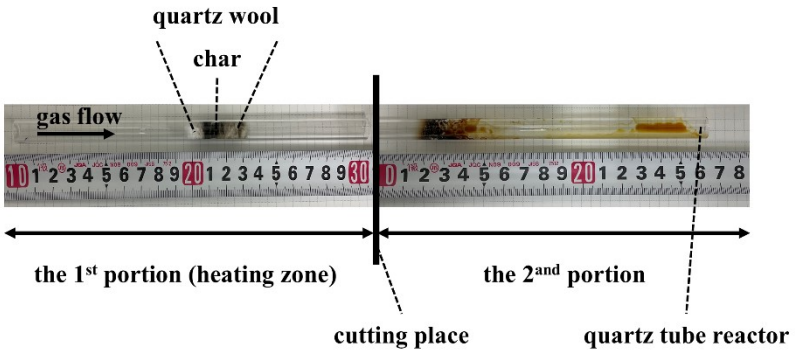

Fig. S1 Photograph of tube reactor, showing where it is cut after the pyrolysis experiment.

The gaseous products were identified by GC/MS (Agilent Technologies, Tokyo, Japan; GC:6890N; MS:5975C; column: CP-PORABOND) and quantified by GC/TCD (GL Science, Tokyo, Japan; GC323) and GC/FID (GL Science, Tokyo, Japan; GC4000; column: CP-PORABOND) using mixed standard gases of known concentration. The total gas yields comprised H_2, CO, CO_2, CH_4, and C_2–C_4 hydrocarbons. The liquid yield was calculated from the weight differences of the cut tube, joint, and trap before and after

THF rinsing, and the pyrolyzates were identified by GC/MS (Agilent Technologies, Tokyo, Japan; GC: HP6890; MS: HP5975; column: InertCap 5MS/Sil) and quantified by GC-FID (GL Science, Tokyo, Japan; GC390; column: InertCap 5MS/Sil) using naphthalene. Furthermore, part of the liquid was pretreated by the oxime-trimethylsilylation (oxime-TMS) method to quantify levoglucosan, glycolaldehyde, and hydroxyacetone.[1] The oxime-TMS derivatives were identified and quantified by GC/MS and GC/FID, respectively. Other than aliphatic hydrocarbons, the products were identified by using the NIST 17 library with >90 % of the degree of match. The solid yield was calculated from the weight differences of the THF-rinsed cut tubes before and after combustion at 900 °C. Moreover, the char yield was calculated from the weight difference of the cut tube before and after combustion at 900 °C.

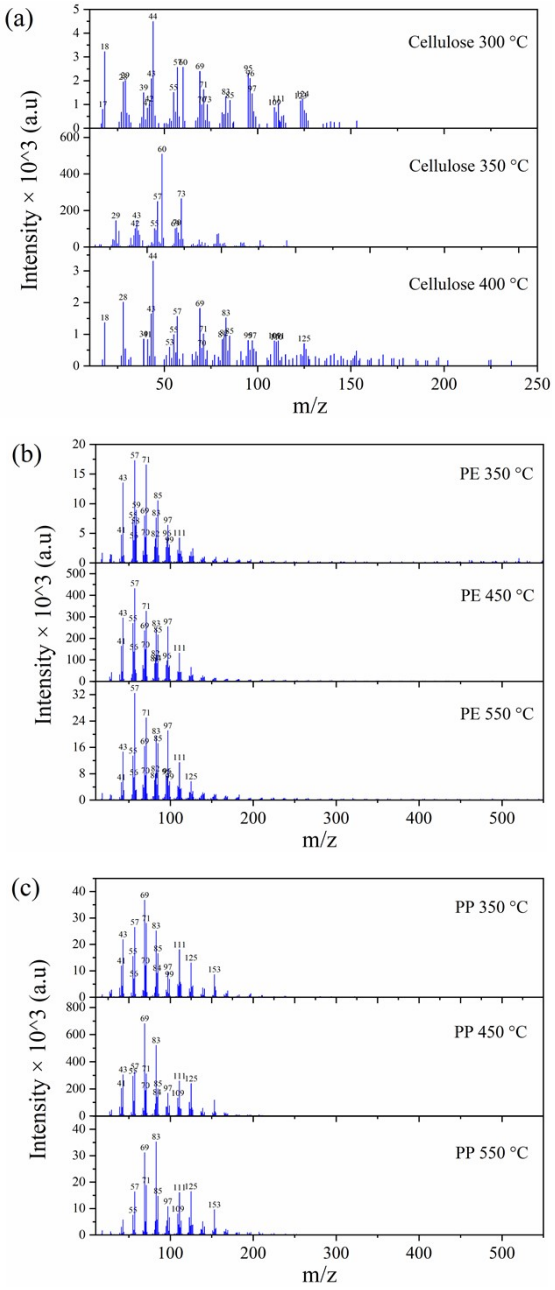

Fig. S2 Mass spectra of the evolving pyrolyzates during (a) cellulose, (b) PE, and (c) PP pyrolysis at various temperatures.

Table S1 Characteristics of the cellulose sample

Materials	Proximate analysis (wt%)			Ultimate analysis (wt%)		
	Ash	Volatile	Fixed carbon	C	H	O[b]
Cellulose	–[a]	96.3	3.7	43.3	6.3	50.4

[a] not detected; [b] balance

Table S2 Weight compositions of GC/MS-identified products obtained by the pyrolysis of cellulose, PE, and their mixtures

	Cellulose	Ce2PE1	Ce2PE1_gas	Ce2PE1_cal	Ce1PE2	Ce1PE2_gas	Ce1PE2_cal	PE
Gas (wt%)	**8.6**	**8.0**	**6.0**	**6.4**	**4.4**	**3.1**	**4.2**	**1.9**
CO	3.0	2.7	2.0	1.9	1.2	0.7	1.0	–
CO_2	5.2	4.3	3.3	3.4	2.0	1.3	1.7	–
CH_4	0.3	0.3	0.2	0.2	0.1	0.2	0.1	+
C_2H_4	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2
C_2H_6	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2
C_3H_6	+ [c]	0.1	0.1	0.1	0.2	0.2	0.2	0.3
C_3H_8	+	0.1	0.1	0.1	0.2	0.2	0.3	0.4
C_4H_8	+	0.1	0.1	0.1	0.2	0.2	0.3	0.4
C_4H_{10}	+	0.1	0.1	0.2	0.2	0.2	0.3	0.5
Tar [a] (wt%)	**13.1**	**10.6**	**13.0**	**8.6**	**6.6**	**10.2**	**4.3**	–
Anhydrosugars	*10.8*	*9.5*	*12.3*	*7.1*	*5.9*	*9.7*	*3.6*	–
Levoglucosan	8.6	7.8	10.3	5.7	4.8	8.8	2.8	–
1,6-anhydro-β-D-glucofuranose	0.4	0.3	0.6	0.3	0.2	0.5	0.1	–
Levoglucosenone	1.0	0.7	0.7	0.7	0.4	0.2	0.3	–
1,4:3,6-dianhydro-α-D-glucopyranose	0.8	0.7	0.7	0.5	0.5	0.3	0.3	–
C_2–C_3 carbonyl compounds	*2.1*	*1.0*	*0.7*	*1.4*	*0.6*	*0.5*	*0.7*	–
Acetaldehyde	0.2	0.1	0.1	0.2	0.1	0.0	0.1	–
Glycol aldehyde	1.4	0.6	0.5	0.9	0.2	0.3	0.4	–
Hydroxyacetone	0.5	0.3	0.1	0.4	0.2	0.2	0.2	–
Five-membered ring compounds	*0.2*	*0.1*	*0.1*	*0.1*	*0.1*	+	*0.1*	–
Furan	0.2	0.1	0.1	0.1	0.1	+	0.1	–
Oil [b] (wt%)	**– [d]**	**2.6**	**3.1**	**2.6**	**4.8**	**6.5**	**5.1**	**7.6**
C_5–C_{10} (Gasoline)	–	*0.4*	*0.4*	*0.9*	*0.5*	*1.0*	*1.7*	*2.6*
C_5	–	0.1	0.2	0.2	0.1	0.3	0.5	0.7
C_6	–	0.1	+	0.3	0.1	0.1	0.5	0.8
C_7	–	0.2	+	0.3	0.2	0.2	0.6	0.9
C_8	–	+	+	+	+	0.2	+	+
C_9	–	+	+	+	+	+	+	+
C_{10}	–	0.1	0.1	+	+	0.2	+	0.1
C_{11}–C_{13} (Kerosene)	–	*0.3*	*0.3*	*0.3*	*0.5*	*0.7*	*0.5*	*0.8*
C_{11}	–	0.1	0.1	0.1	0.1	0.3	0.2	0.3
C_{12}	–	0.1	0.1	0.1	0.1	0.1	0.1	0.2

C_{13}	–	0.1	0.1	0.1	0.3	0.3	0.2	0.3
C_{14}–C_{18} (Diesel)	–	*0.7*	*0.7*	*0.6*	*1.5*	*1.5*	*1.1*	*1.7*
C_{14}	–	0.1	0.1	0.1	0.3	0.3	0.3	0.4
C_{15}	–	0.2	0.1	0.1	0.3	0.3	0.2	0.3
C_{16}	–	0.1	0.1	0.1	0.3	0.3	0.2	0.3
C_{17}	–	0.1	0.1	0.1	0.3	0.3	0.2	0.3
C_{18}	–	0.2	0.2	0.1	0.3	0.3	0.2	0.3
C_{19}–C_{25} (Heavy gas oil)	–	*0.6*	*0.8*	*0.5*	*1.2*	*1.6*	*0.9*	*1.4*
C_{19}	–	0.1	0.1	0.1	0.2	0.2	0.2	0.3
C_{20}	–	0.1	0.1	0.1	0.2	0.2	0.1	0.2
C_{21}	–	0.1	0.1	0.1	0.2	0.2	0.1	0.2
C_{22}	–	0.1	0.1	0.1	0.2	0.2	0.1	0.2
C_{23}	–	0.1	0.1	0.1	0.2	0.2	0.1	0.2
C_{24}	–	0.1	0.1	0.1	0.1	0.2	0.1	0.2
C_{25}	–	0.1	0.1	0.1	0.1	0.2	0.1	0.2
C_{26}–C_{33} (Lubricating oil)	–	*0.5*	*1.0*	*0.4*	*1.1*	*1.7*	*0.8*	*1.2*
C_{26}	–	0.1	0.1	0.1	0.2	0.3	0.1	0.2
C_{27}	–	0.1	0.1	0.1	0.1	0.2	0.1	0.2
C_{28}	–	0.1	0.2	0.1	0.2	0.2	0.1	0.2
C_{29}	–	0.1	0.1	+	0.1	0.2	0.1	0.1
C_{30}	–	0.1	0.1	0.1	0.1	0.3	0.1	0.2
C_{31}	–	0.1	0.1	+	0.1	0.2	0.1	0.1
C_{32}	–	+	0.1	+	0.1	0.2	0.1	0.1
C_{33}	–	+	0.1	+	0.1	0.1	0.1	0.1

[a] Identified liquid pyrolyzates from cellulose. [b] Identified liquid pyrolyzates from polyolefin. [c] < 0.05 wt%. [d] Not detected.

Table S3 Weight compositions of GC/MS-identified products obtained by the pyrolysis of cellulose, PP, and their mixtures

	Cellulose	Ce2PP1	Ce2PP1_gas	Ce2PP1_cal	Ce1PP2	Ce1PP2_gas	Ce1PP2_cal	PP
Gas (wt%)	**8.6**	**7.0**	**5.9**	**6.6**	**4.9**	**3.1**	**4.6**	**2.6**
CO	3.0	2.3	1.8	2.0	1.2	0.5	1.0	–
CO_2	5.2	3.6	3.2	3.5	1.9	1.1	1.7	–
CH_4	0.3	0.3	0.2	0.2	0.1	0.1	0.1	+
C_2H_6	0.1	0.1	0.1	0.1	0.2	0.1	0.2	0.3
C_2H_4	0.1	+	0.1	0.1	0.1	+	0.1	0.1
C_3H_8	+ [c]	+	+	0.1	0.1	0.1	0.1	0.2
C_3H_6	+	0.5	0.5	0.6	1.1	1.0	1.2	1.7
C_4H_8	+	0.1	0.1	0.1	0.2	0.2	0.2	0.3
C_4H_{10}	+	+	+	+	+	+	+	+
Tar [a] (wt%)	**13.1**	**10.0**	**12.8**	**8.7**	**5.8**	**7.5**	**4.3**	–
Anhydrosugars	*10.8*	*9.1*	*11.2*	*7.2*	*5.0*	*6.8*	*3.5*	–
Levoglucosan	8.6	7.2	9.5	5.7	3.8	5.8	2.8	–
1,6-anhydro-β-D-glucofuranose	0.4	0.3	0.6	0.3	0.2	0.5	0.1	–
Levoglucosenone	1.0	0.9	0.5	0.7	0.5	0.2	0.3	–
1,4:3,6-dianhydro-α-D-glucopyranose	0.8	0.7	0.7	0.5	0.4	0.3	0.3	–
C_2–C_3 carbonyl compounds	*2.1*	*0.7*	*1.2*	*1.4*	*0.7*	*0.6*	*0.7*	–
Acetaldehyde	0.2	0.1	0.2	0.2	0.1	+	0.1	–
Glycol aldehyde	1.4	0.6	0.8	0.9	0.6	0.6	0.4	–
Hydroxyacetone	0.5	0.1	0.2	0.4	0.1	+	0.2	–
Five-membered ring compounds	*0.2*	*0.1*	*0.3*	*0.1*	*0.1*	+	*0.1*	–
Furan	0.2	0.1	0.3	0.1	0.1	+	0.1	–
Oil [b] (wt%)	**– [d]**	**7.1**	**11.4**	**8.2**	**16.4**	**18.8**	**16.5**	**24.6**
C_5–C_{10} (Gasoline)	–	*1.2*	*3.4*	*3.0*	*5.2*	*5.6*	*6.0*	*8.9*
C_5	–	0.5	1.0	0.8	1.6	1.4	1.6	2.3
C_6	–	+	+	+	+	+	+	+
C_7	–	+	+	+	+	+	+	+
C_8	–	+	0.1	+	0.1	+	+	+
C_9	–	0.7	2.2	2.1	3.4	4.2	4.3	6.4
C_{10}	–	0.1	0.1	0.1	0.1	+	0.1	0.2
C_{11}–C_{13} (Kerosene)	–	*0.6*	*1.1*	*0.8*	*1.7*	*1.9*	*1.5*	*2.3*
C_{11}	–	0.1	0.2	0.1	0.2	0.3	0.3	0.4
C_{12}	–	0.4	0.7	0.5	1.2	1.3	1.1	1.6

C_{13}	–	0.1	0.2	0.1	0.3	0.2	0.2	0.3
C_{14}–C_{18} (Diesel)	–	*2.2*	*3.1*	*2.1*	*4.6*	*4.8*	*4.2*	*6.2*
C_{14}	–	+	+	+	+	+	+	+
C_{15}	–	1.3	2.1	1.5	3.2	3.2	3.0	4.4
C_{16}	–	0.1	0.2	0.2	0.4	0.4	0.3	0.5
C_{17}	–	0.1	0.1	0.1	0.2	0.2	0.1	0.2
C_{18}	–	0.7	0.8	0.4	0.8	0.9	0.8	1.2
C_{19}–C_{25} (Heavy gas oil)	–	*1.6*	*1.8*	*1.2*	*2.5*	*3.0*	*2.5*	*3.7*
C_{19}	–	0.2	0.2	0.1	0.3	0.3	0.3	0.4
C_{20}	–	0.1	+	+	0.1	0.1	0.1	0.1
C_{21}	–	0.6	0.7	0.5	1.0	1.2	1.0	1.5
C_{22}	–	0.2	0.3	0.2	0.4	0.5	0.4	0.6
C_{23}	–	+	+	+	+	+	+	0.1
C_{24}	–	0.2	0.2	0.2	0.3	0.4	0.3	0.5
C_{25}	–	0.2	0.3	0.2	0.4	0.5	0.4	0.6
C_{26}–C_{40} (Lubricating oil)	–	*1.5*	*2.0*	*1.1*	*2.4*	*3.5*	*2.3*	*3.4*
C_{26}	–	+	+	+	+	+	+	0.1
C_{27}	–	0.2	0.2	0.1	0.3	0.4	0.3	0.4
C_{28}	–	0.2	0.3	0.2	0.4	0.5	0.4	0.6
C_{29}	–	+	+	+	+	+	+	+
C_{30}	–	0.1	0.1	0.1	0.2	0.2	0.1	0.2
C_{31}	–	0.1	0.2	0.1	0.3	0.3	0.2	0.3
C_{32}	–	+	+	+	+	+	+	+
C_{33}	–	0.1	0.1	0.1	0.1	0.2	0.1	0.2
C_{34}	–	0.2	0.2	0.1	0.3	0.4	0.2	0.4
$C_{\geq 35}$	–	0.5	0.8	0.4	0.9	1.5	0.8	1.2

[a] Identified liquid pyrolyzates from cellulose. [b] Identified liquid pyrolyzates from polyolefin. [c] < 0.05 wt%. [d] Not detected.

Reference

1. T. Hosoya, H. Kawamoto and S. Saka, *J. Anal. Appl. Pyrolysis*, 2006, **77**, 121-126.