

Hydrolysis of woody biomass by biomass-derived reusable heterogeneous catalyst

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Experimental details

***Eucalyptus*.** *Eucalyptus* powder (20 g, 150–355 μm) was boiled in 500 mL water for 0.5 h in an eggplant flask (2 L) to remove soluble ingredients. The resulting powder was filtered through filter paper (type 5A, 7 μm), transferred to an eggplant flask (100 mL), dried by a rotary evaporator (12 kPa) at 333 K, and further dried using a rotary pump (1 Pa) at 333 K with a trap (77 K). Composition of the washed *Eucalyptus* was determined by NREL/TP-510-42618,^{S1} NREL/TP-510-42622^{S2} and EDX (Shimadzu, EDX-720) on a dry basis. We determined the amount of xylan in hemicellulose, and other types of sugars were omitted. In this analysis, detected glucose was fully ascribed to cellulose, since hardwood hemicellulose contains almost no glucose.^{S3}

Air oxidation of *Eucalyptus*, reaction residue, and cellulose. Dried *Eucalyptus* or cellulose powder of 4.00 g was spread with a thickness of 3 mm on a Pyrex dish (ϕ 130) to uniformly prepare catalyst and avoid hot spots. The sample was calcined under air at atmospheric pressure in an electric furnace (Denken-Highdental, KDF S90) with the following program: 298 to 573 K by 5 K min^{-1} and 573 K for 1 h. In the case of reaction residue, the residue of 1.63 g (recovered in a large-scale experiment, see below) was calcined under the same conditions. Temperature inside the sample was monitored by a thermocouple (Chino; ϕ 0.5) equipped with a quartz tube (*ca.* ϕ 1).

Characterisation. Prepared catalysts were analysed by IR (JASCO, FT/IR 660Plus; deuterated L-alanine triglycine sulphate detector, transmission mode, KBr disk), ^{13}C CP/MAS NMR (Bruker, MSL-300; 75 MHz, MAS 8 kHz), XPS (JEOL, JPC-9010MC), N_2 adsorption (BEL Japan, Belsorp Mini; 77 K), water adsorption (BEL Japan, Belsorp Max; 298 K), Raman spectroscopy (Renishaw, inVia Reflex, 532 nm), and X-ray diffraction (Rigaku, Ultima IV). Acidity of 0.1 M NaCl solution ($I = 0.1$) of *E-Carbon* (50 mg / 40 mL) was measured by a glass electrode, which indicated pH 3.6. Therefore, the acidification of aqueous phase was limited even at the high ionic strength.

Pretreatment (mix-milling). *Eucalyptus* (5.0 g) and catalyst (0.77 g) were milled together in an Al_2O_3 pot (250 mL) with Al_2O_3 balls (99.9%, ϕ 15, 210 g) by Fritsch P-6 planetary ball mill. Milling conditions were 500 rpm for 2 h with a 10 min interval after every 10 min of milling.

Hydrolysis reaction. The hydrolysis of *Eucalyptus* was performed in a hastelloy C-22 high-pressure reactor (OM Lab-Tech, MMJ-100) equipped with an agitator operating at 600 rpm and a thermocouple. Mix-milled sample (374 mg) and 40 mL of 120 ppm HCl aq. were added into the reactor. The temperature of the reaction

mixture was elevated from 298 K to 488 K in *ca.* 17 min and then quickly lowered to 298 K. After finishing the reaction, the reaction solution was separated by centrifugation and decantation. The liquid phase was pale yellow due to dissolution of a small fraction of lignin and catalysts; however, this colouring was common in the hydrolysis of lignocellulose. In addition, we have confirmed that the dissolved part of the catalyst was inactive towards hydrolysis of lignocellulose. The remaining solid was washed twice with 40 mL of water, transferred to an eggplant flask (100 mL), dried by a rotary evaporator (12 kPa) at 333 K, and further dried using a rotary pump (1 Pa) at 333 K with a trap (77 K).

For the transformation of solid residue to fresh catalyst, we performed a large-scale experiment using 4.00 g of the mix-milled sample to accumulate the residue. A portion of the produced catalyst was used for the second-cycle reaction.

Products were analysed by high-performance liquid chromatography (Shimadzu; refractive index and ultraviolet detectors) with a SUGAR SH1011 (Shodex; $\varnothing 8 \times 300$ mm; eluent: water 0.5 mL min^{-1} ; 323 K) and a Rezex RPM-Monosaccharide Pb++ (Phenomenex; $\varnothing 7.8 \times 300$ mm; eluent: water 0.6 mL min^{-1} ; 343 K) columns.

Preparation of a typical conventional carbon catalyst

Production of 1 kg of an alkali-activated carbon (K26) requires 3.75 kg of KOH, since the weight ratio of KOH to carbon is 3 and the yield of activated carbon is 80%.^{S4} After the alkali-activation, KOH is neutralised with a 3.28 kg of H_2SO_4 , giving 5.83 kg of K_2SO_4 . As the solubility of K_2SO_4 in water at 293 K is $0.111 \text{ g g-water}^{-1}$, washing out it needs at least 52.5 kg of water. More water and HCl are necessary to completely remove salts from alkali-activated carbon.^{S4}

Comparison of *E*-Carbon with soluble acids

Sulphuric acid and organic acids have low activity at the pH (>3) given by weakly acidic carbons.^{S4,S5} It is known that the high-yielding production of glucose from lignocellulose requires more than 50 mM sulphuric acid,^{S6} which is significantly larger than the concentration of catalyst in our study (the concentration of carboxylic acid on *E*-Carbon corresponds to only 2.6 mM in the solution). Therefore, *E*-carbon is more active than sulphuric acid at such a low acid concentration.

Tables

Table S1 Weight percent of elements in *Eucalyptus* ash in EDX analysis^a

CaO	SiO ₂	MgO	Al ₂ O ₃	SO ₃	P ₂ O ₅	Fe ₂ O ₃	K ₂ O
54%	13%	9.3%	8.6%	7.3%	3.2%	1.8%	0.7%

^aContents of elements were determined as oxides (wt%).

Table S2 Effect of preparation temperature of *E-Carbon* on the formation amount of catalyst (recovery), and catalytic activity of the prepared catalysts in the hydrolysis of ball-milled cellulose^a

Entry	Preparation temp. /K	Recovery /wt%	Product yield in the hydrolysis reaction /%						
			Glucose	Fructose	Mannose	Oligomers	LG ^b	5-HMF ^c	Furfural
S1	523	86 ^d	–	–	–	–	–	–	–
S2	573	40 ^e	21	2.3	1.1	21	1.1	2.7	0.4
S3	623	23	21	n.d. ^f	0.8	21	1.1	2.8	0.5
S4	673	11	10	n.d. ^f	0.8	21	0.5	2.2	0.4

^a Ball-milled cellulose 324 mg, catalyst 50 mg, water 40 mL, 503 K. ^b Levoglucosan.

^c 5-Hydroxymethylfurfural. ^d The prepared material was not used for the hydrolysis of cellulose as the sample was almost lignocellulosic material. ^e Recovery based on carbon content was 49%. ^f Not determined due to overlap of peaks.

Table S3 Detailed results of hydrolysis of *Eucalyptus* at 488 K shown in Table 1

Entry	Solvent	Catalyst	Product yield /% (wt% based on whole <i>Eucalyptus</i>)								
			Glucose	Xylose	Sugar isomers ^a	Oligomers ^a	LG ^b	5-HMF ^c	Furfural		
1	Water	No catalyst	3 ^d (2)	30 ^e (3)	(1)	(7)	(<1)	(<1)	(<1)		
2	Water	<i>E-Carbon</i>	31 ^d (17)	83 ^e (9)	(3)	(21)	(<1)	(<1)	(1)		
3	0.012% HCl	No catalyst	32 ^d (17)	26 ^e (3)	(5)	(1)	(<1)	(3)	(3)		
4	0.012% HCl	<i>E-Carbon</i> (1st cycle)	78 ^d (40)	94 ^e (10)	(2)	(1)	(2)	(2)	(2)		
5	0.012% HCl	<i>E-Carbon</i> (2nd cycle)	82 ^d (42)	86 ^e (10)	(3)	(<1)	(2)	(3)	(3)		
6	0.012% HCl	N ₂ -treated <i>Eucalyptus</i>	28 ^d (14)	26 ^e (3)	(4)	(4)	(<1)	(2)	(2)		
7	0.012% HCl	Air-oxidised cellulose	77 ^d (40)	91 ^e (10)	(5)	(2)	(2)	(1)	(<1)		

^a Accuracy is not very high due to overlap of peaks. ^b Levoglucosan. ^c 5-Hydroxymethylfurfural. ^d Based on carbon of cellulose. ^e Based on carbon of xylan.

Table S4 Hydrolysis of *Eucalyptus* at a lower temperature of 473 K

Entry	Solvent	Catalyst	Product yield /% (wt% based on whole <i>Eucalyptus</i>)						
			Glucose	Xylose	Sugar isomers ^a	Oligomers ^a	LG ^b	5-HMF ^c	Furfural
S5	0.012% HCl	<i>E-Carbon</i> (1st cycle)	35 ^d (18)	91 ^e (10)	(4)	(6)	(<1)	(<1)	(<1)
S6	0.012% HCl	<i>E-Carbon</i> (2nd cycle)	54 ^d (28)	>95 ^e (11)	(3)	(8)	(1)	(<1)	(<1)

^a Accuracy is not very high due to overlap of peaks. ^b Levoglucosan. ^c 5-Hydroxymethylfurfural. ^d Based on carbon of cellulose. ^e Based on carbon of xylan.

Figures

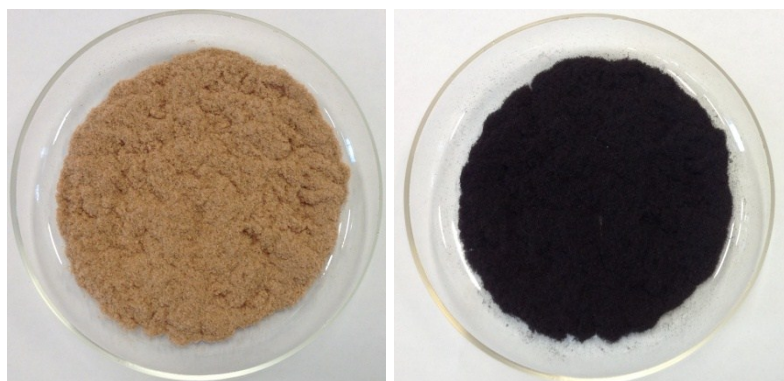
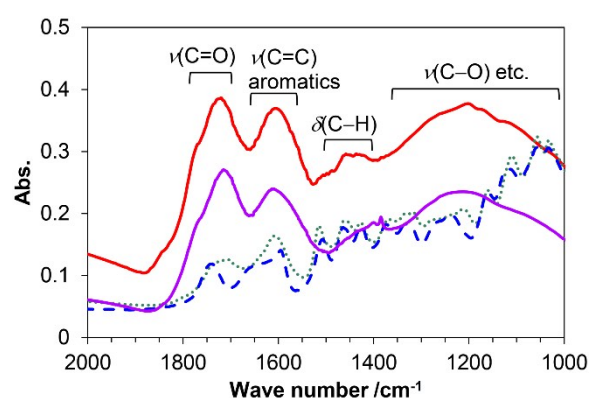
**Fig. S1** Photographs of *Eucalyptus* (left) and *E-Carbon* (right).

Fig. S2 FT-IR spectra of *E-Carbon* (red solid line), N₂-treated *Eucalyptus* (green dotted line), *Eucalyptus* (blue dashed line) and air-oxidised cellulose (violet solid line). Transmission mode, KBr pellet. Absorbance values have been normalised by concentration of sample for the quantitative comparison, but Abs. of raw data before the normalisation is similar (at most 20% difference).

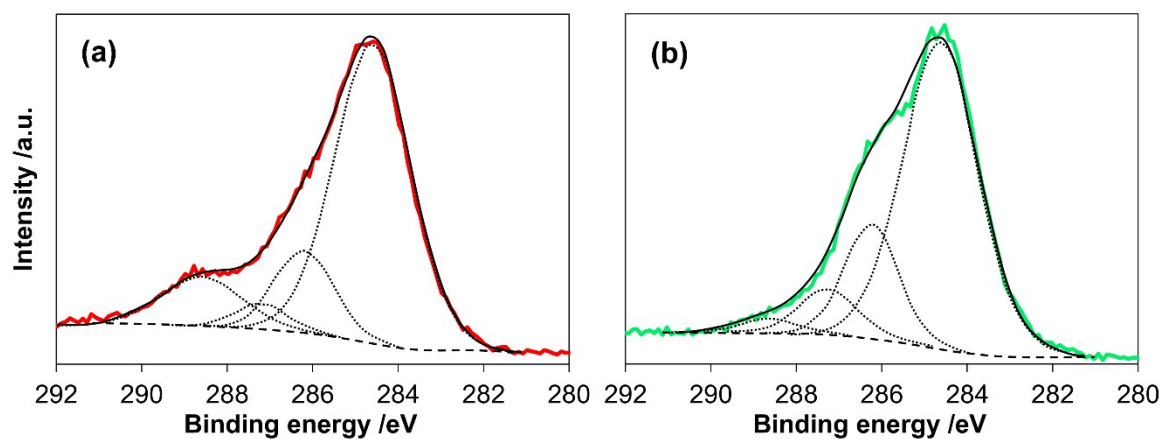


Fig. S3 XPS spectra of (a) *E-Carbon* and (b) N_2 -treated *Eucalyptus*. Peak positions of the curve fittings (black lines) were fixed at 284.6 eV for C–C and C=C, at 286.2 eV for C–C, at 287.2 for C=O and at 288.6 eV for $-\text{CO}_2\text{R}$.^{S7}

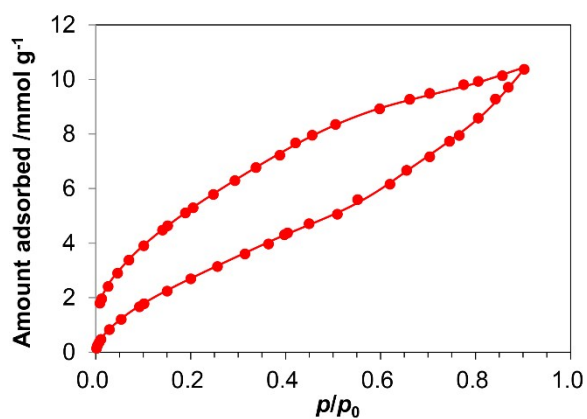


Fig. S4 Water adsorption isotherm for *E-Carbon* at 298 K.

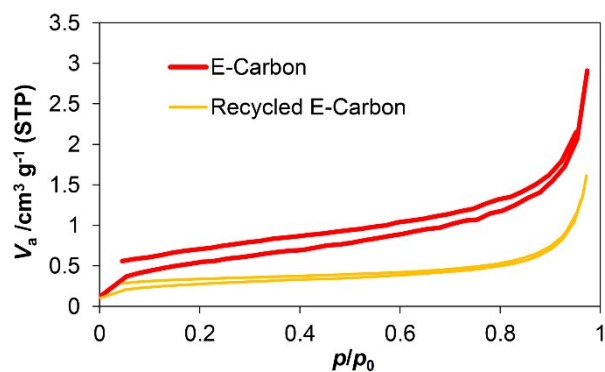


Fig. S5 N_2 adsorption isotherms for *E-Carbon* and recycled *E-Carbon*. The adsorption amounts were very low, and therefore the BET surfaces areas were not calculated accurately ($\leq 2 \text{ m}^2 \text{ g}^{-1}$).

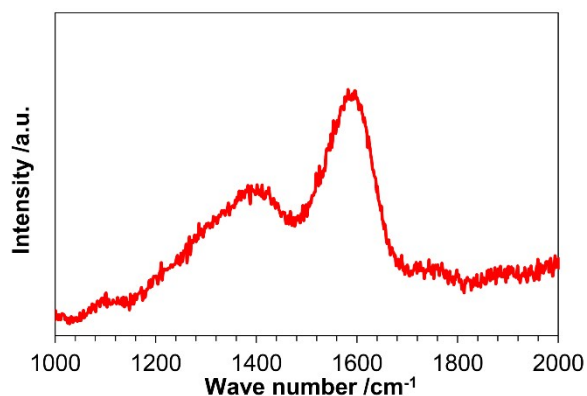


Fig. S6 Raman spectrum of *E-Carbon*.

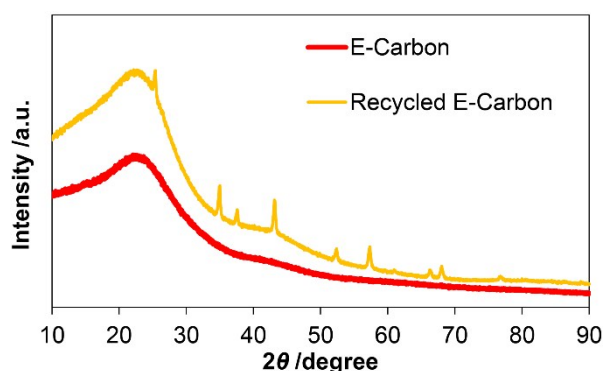


Fig. S7 XRD patterns of *E-Carbon* and recycled *E-Carbon*. The broad peak at 23° is a characteristic of amorphous carbon. Sharp peaks for the recycled catalyst are assigned to α -Al₂O₃ (derived from mix-milling instruments).

References

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