

## Supporting information

### Hydrolysis of Eucalyptus Lignocellulose using ECG-48 catalyst

#### Pretreatment process of eucalyptus lignocellulose

ECG-48 (0.5 g) and eucalyptus Lignocellulose (8.0 g) were milled together in a ceramic pot (1.5 L, with 0.5 Kg of alumina balls ( $\Phi = 1.5$  cm)) at 500 rpm for 1 h. Then, the milled powder was mixed with an aqueous solution of HCl (40 mL, 120 ppm) or H<sub>2</sub>O (40 mL) under ultrasonic treatment (frequency of 20 kHz and 200 W power) for 20 min. The same pretreatment process was used for ECG-24, ECG-36, and ECG-72 catalysts.

#### Hydrolysis process eucalyptus lignocellulose using ECG-48 catalyst

After sonication, the obtained mixture was charged in the reactor (Hastelloy C-22 high-pressure reactor equipped with an agitator operating at 500 rpm and thermocouple) followed by heating to 180 °C (10° C min<sup>-1</sup>) and promptly cooled down to the room temperature. Then, the reaction mixture was separated into solid and liquid by centrifugation and decantation. The aqueous phase was analyzed using high-performance liquid chromatography ((HPLC, Agilent 1260 series, USA) with an HPX-87H column (300×7.8mm, Bio-Rad, USA). The percentage (%) of glucose or xylose yield is calculated using the following equation  $\text{Glucose (Xylose) yield (\%)} = [(A/B) \times 100]$  Equation 1

Where A is the moles of glucose produced by hydrolysis, and B is the glucose in pure cellulose. The selectivity of glucose (xylose) (Si) was estimated using the following equation

$$S_i = [TC_{i,output} / TC_{input}] \times 100 \quad \text{Equation 2}$$

where  $TC_{i,output}$ , and  $TC_{input}$  are the total carbon in the products and input.

The selectivity of total sugars ( $S_{TS}$ ) was calculated using the following equation along with consideration carbon balance taking into account all the degradation products ( $C_{dp}$ )

$$S_{TS} = [TC_{input} - C_{dp} / TC_{input}] \times 100 \quad \text{Equation 3}$$

All the conversion yields of eucalyptus lignocellulose were calculated based on the carbon balance. The same hydrolysis process was used for ECG-24, ECG-36, and ECG-72 catalysts.

#### Hydrolysis Process using H<sub>2</sub>O or HCl

##### Pretreatment process

ECG-48 (0.5 g) was milled in a ceramic pot (1.5 L, with 0.5 Kg of alumina balls ( $\Phi = 1.5$  cm)) at 500 rpm for 1 h and then 0.5 g of the milled powder was dispersed in an aqueous solution of HCl (40 mL, 120 ppm) or H<sub>2</sub>O (40 mL) under ultrasonic (frequency of 20 kHz and 200 W power) treatment for 20 min. Then the hydrolysis process for cellulose and eucalyptus lignocellulose was carried out by the same method mentioned in the above.

#### Adsorption of glucose

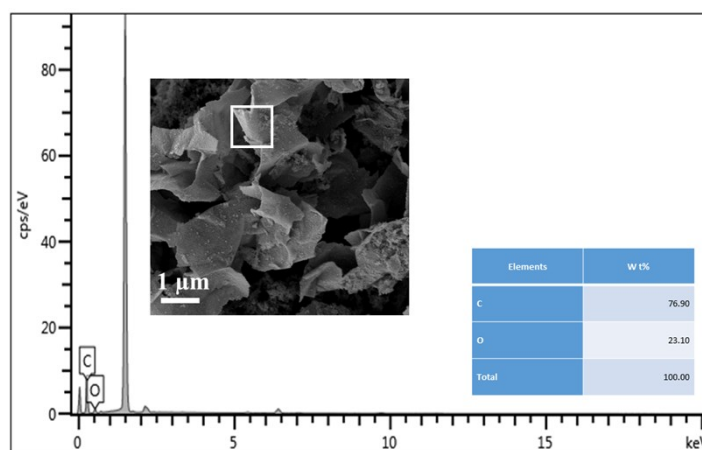
ECG -48 (75 mg) was added to an aqueous solution of glucose (10 mL, 0.5 mg/mL) under vigorous stirring at room temperature for 6 h. Then the obtained mixture was filtered through a polyvinylidene difluoride (PVDF) 0.20 mm mesh membrane, and the concentration of glucose in the solution was analyzed using HPLC (Shimadzu LC-20AD with a refractive index (RI) detector) with a Phenomenex Rezex RPM-Monosaccharide Pb<sup>2+</sup> column ( $\phi 7.8_{300}$  mm, mobile phase: water at 0.6 mL/min, 343 k. The adsorbed glucose concentration on ECG-48 catalyst was calculated via material balance from the measured decrease in liquid-phase compared to original concentration before adsorption using the following equation

$$Y = [C_0 - C_1 / C_0] \times 100$$

Where Y is the adsorption ratio of carbon-based solid acids,  $C_0$  and  $C_1$  are the glucose concentration before and after adsorption, respectively.

#### Durability Test for recovery of ECG-48 catalyst

After each hydrolysis cycle, the reaction mixture was separated into solid and liquid by centrifugation and decantation to recover the ECG-48 catalyst. The aqueous phase was analyzed by high-performance liquid chromatography, while the solid powder was rinsed 5 times in a hot water solution (200 mL, 60 °C) for 20 min under vigorous shaking at 500 rpm, followed by centrifugation at 6000 rpm and washing with hot water solution (60 °C) until pH reached 4. The obtained powder was dried at 70°C for 4 h under air before being used again.<sup>1</sup> The reaction conditions and reactants concentrations remain constant in each run. To this end, the additive amount of fresh cellulose (300 mg), eucalyptus lignocellulose (300 mg), ECG-48 h (75.0 mg), HCl (10 ml of 120 ppm), double deionized water (10 mL, resistivity ~18 M $\Omega$  cm), and heating from 25 °C to 180 °C (12°/ min) for 20 min and then quickly cooled down to 25°C).



**Figure S1.** The EDX of ECG. The table and SEM image are shown as insets. The EDX was carried out on the marked area in the SEM image.

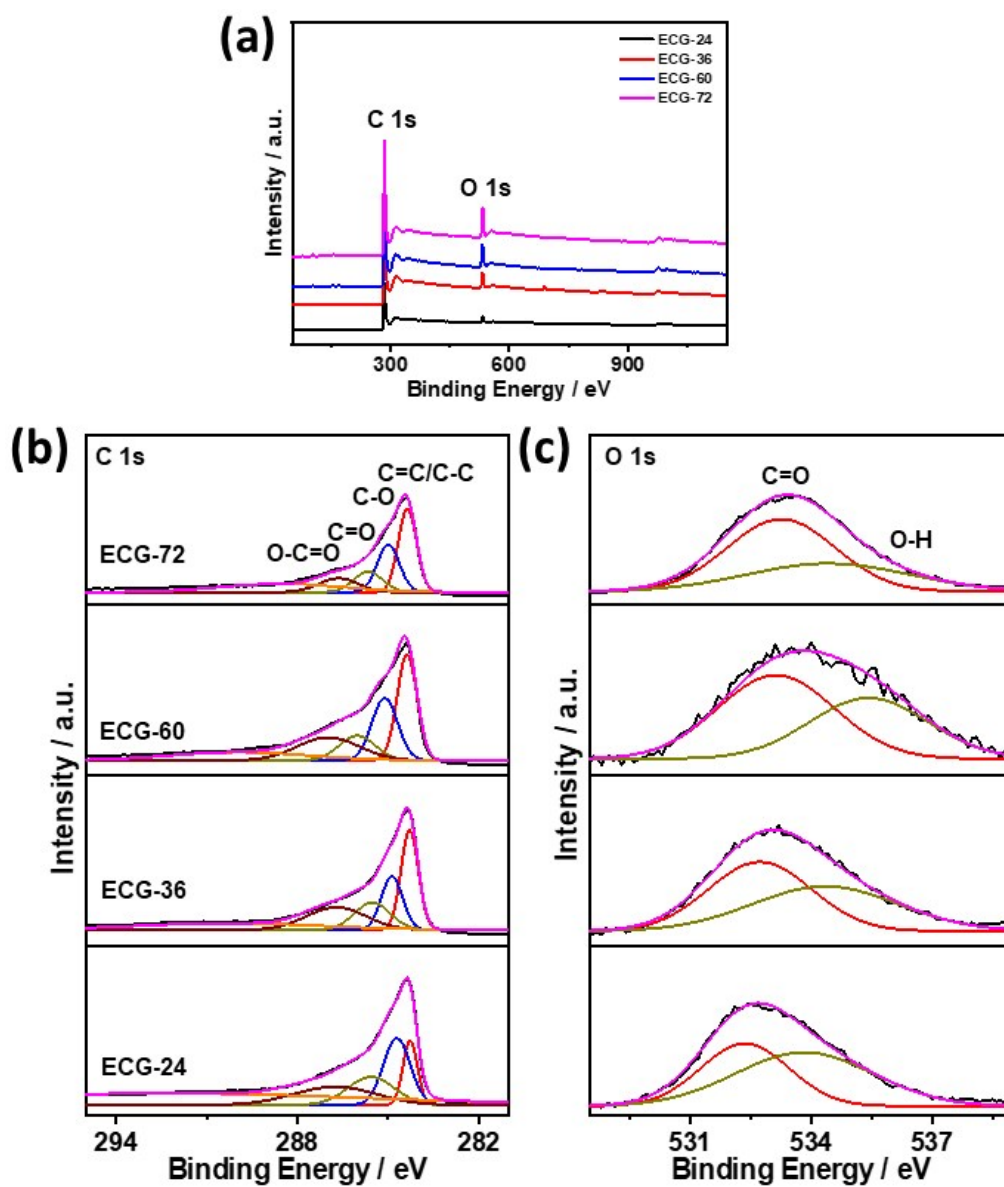
**Table S1** CHNOS elemental analysis of ECG catalyst

Catalyst	Milling time (h)	C (%)	H (%)	S (%)	N (%)	O (%)
Graphite	0	99.62	BDL <sup>a</sup>	BDL	BDL	0.15
ECG-24	24	97.65	0.31	1.51	BDL	2.00
ECG-36	36	91.82	0.76	1.04	BDL	4.03
ECG-48	48	72.03	1.02	0.01	BDL	26.45
ECG-60	60	72.65	1.03	BDL	BDL	26.31
ECG-72	72	71.61	1.09	BDL	BDL	26.65

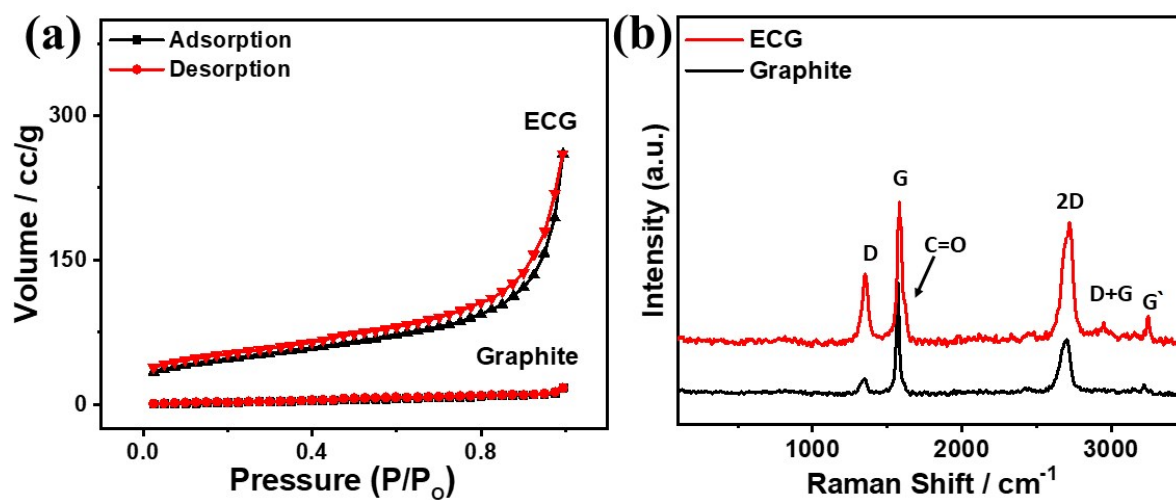
BDL = Below detection limit.

**Table S2** The COOH content as a function of milling time determined using the conductometric titration approach. The adsorption of cellulose as a function of COOH content.

Catalyst	Milling time (h)	ECG (Wt %)	COOH (mmol/g)	Glucose adsorption capacity (mg/g)
Graphite	0	2	0	40
ECG-24	24	2	1.58	120
ECG-36	36	2	2	210
ECG-48	48	2	2.9	380
ECG-60	60	2	3.1	200
ECG-72	72	2	3.	190



**Figure S2.** (a) XPS survey of ECG prepared under different milling times and (b and c) their high-resolution spectra of C 1s and O 1s, respectively. ECG-24, ECG-36, ECG-60, and ECG-72 catalysts prepared under milling times of 24, 36, 60, 72 h, respectively.



**Figure S3.** (a) N<sub>2</sub> isotherms physisorption spectra (b) Raman spectra of ECG compared to pure graphite.

**Table S3** The surface composition of ECG, prepared under different milling times determined by the XPS.

Catalyst	Milling time (h)	C (%)	O (%)
ECG-24	24	95.5	4.5
ECG-36	36	90.8	9.2
ECG-48	48	77.3	22.7
ECG-60	60	79.4	20.6
ECG-72	72	74.6	25.4

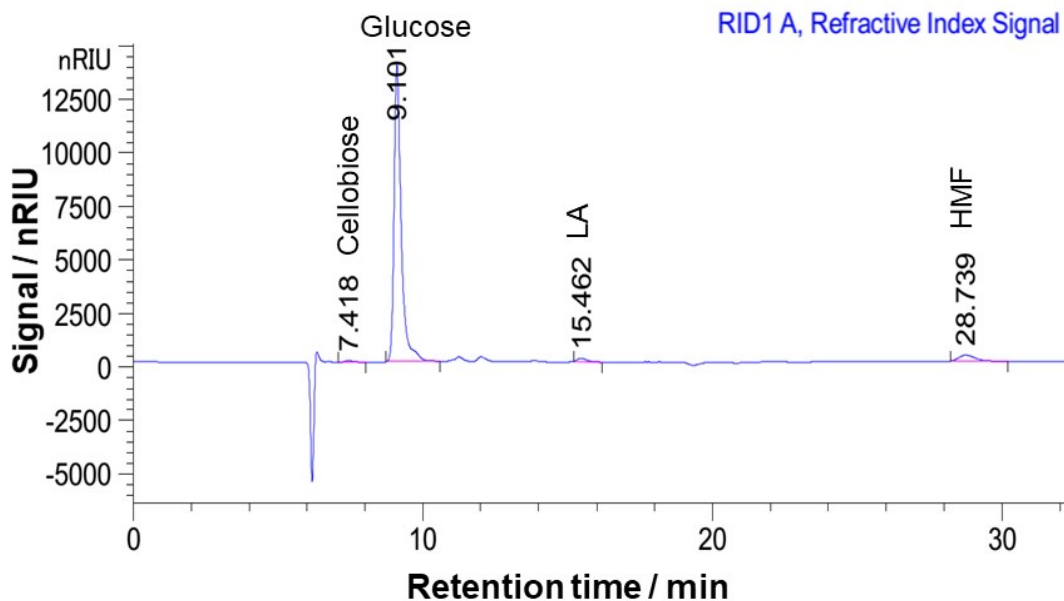


Figure S4 HPCL chromatogram of glucose, cellobiose, 5-hydroxymethylfurfural (HMF), and Levulinic acid (LA) produced on ECG-48 under typical conditions. Reaction conditions: cellulose (8 g), ECG-48 h (0.5 g), HCl (40 ml of 120 ppm), using ball-milling combined with sonication pretreatment. The reaction temperature was raised from 25 °C to 180 °C (10°/ min) for 20 min, then quickly cooled down to 25°C.

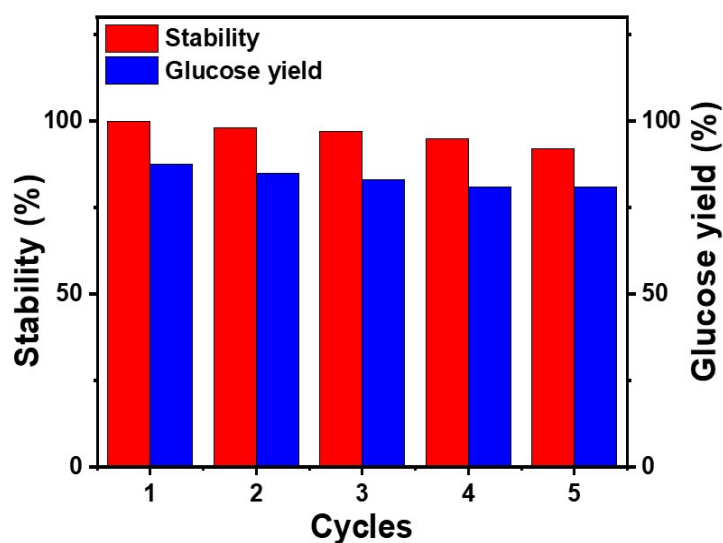
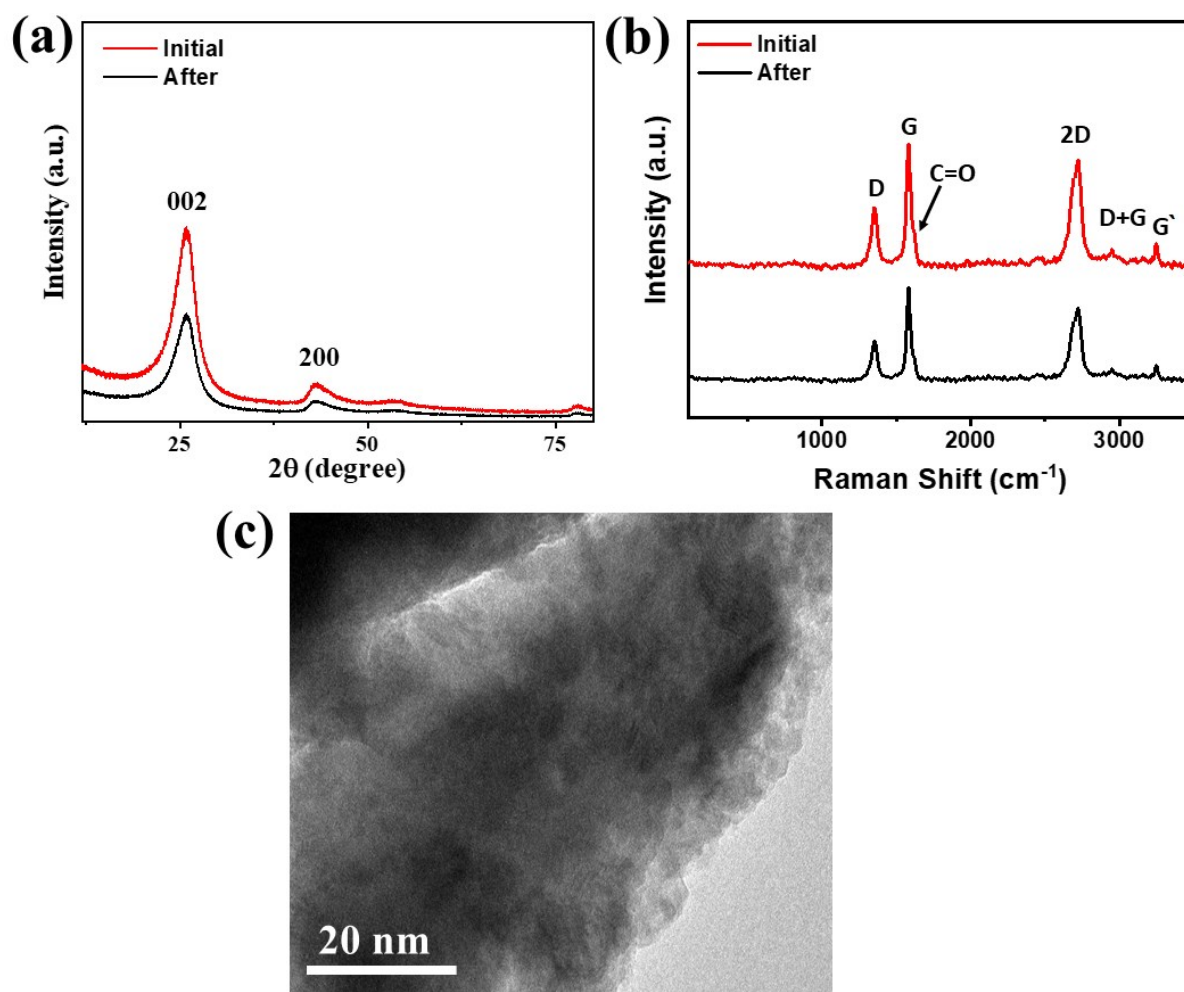


Figure S5. The durability testes for hydrolysis of cellulose and glucose yield measured at 180 °C on ECG-48 for 5 cycles under typical reaction conditions.



**Figure S6.** (a) PXRD, (b) Raman spectra, and (c) TEM image of ECG after the stability tests. Fresh prepared ECG-48 and ECG-48 after durability, showed the same (002) and (100) facet (a), same Raman modes (D, G, 2D, 2D+G, and G') (b), and 2D nanosheets with defective edges (c).

**Table S4** The glucose production on ECG-48 catalyst compared to previously reported carbon-based catalysts

Type of Catalyst	Materials	Glucose yield (%)	Time	Temperature (°C)	References
ECG-48+HCl	Cellulose	87	20 min	180 °C	Current work
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	Cellulose	50	2h	180	3
Ru/CMK-3	Cellulose	31.2	15 min	230	4
20% formic acid	Wheat straw pulp	40	7 min	220	5
Activated carbon (AC-SO <sub>3</sub> H)	Cellulose	40.5	24 h	150 °C	6
10 wt% Ru/CMK-3	Cellulose	34.2	24 h	230	7
	Cellulose	34.9	2 h	180	8

10 wt% Sn doped MgF <sub>2</sub>					
10 wt % Sn doped hydroxylated MgF <sub>2</sub>	Cellulose	34.9	2 h	180	8
Oxygenated E-carbon catalyst	Eucalyptus	77	1 h	215	9
Sulfonated CMK-3	Cellulose	74.5	24	150	10
Carbonated Graphen oxide bearing COOH and SO <sub>3</sub> H (10-SGOC)	Cellulose	17.76	5 h	160	11
Amberlyst-15	Cellulose	67.2	2 h	170	12
Sulfonated RGO/Gas-Liquid Interfacial Plasma	Cellulose	96.6	18 h	200	13
Sulfonated RGO/Hydrothermal	Cellulose	39.8	18 h	200	14
SO <sub>3</sub> H/RGO	Cellulose	95	2 h	130	15
silver mesoporous zeolite	Cellulose	77	90 min	180	16
SO <sub>4</sub> <sup>2-</sup> -TiO <sub>2</sub>	Cellulose	21.8	30 min	450	17
Sulfonated carbonaceous solid acid	Cellulose	30.9	12 h	170	19
Pretreated rice straw	Cellulose	52.1	60 min	200	18
bamboo-derived sulfonated catalyst	Cellulose	61.1	74 min	175	20
N-doped carbon materials	Cellulose	61.1	60 min	220	21

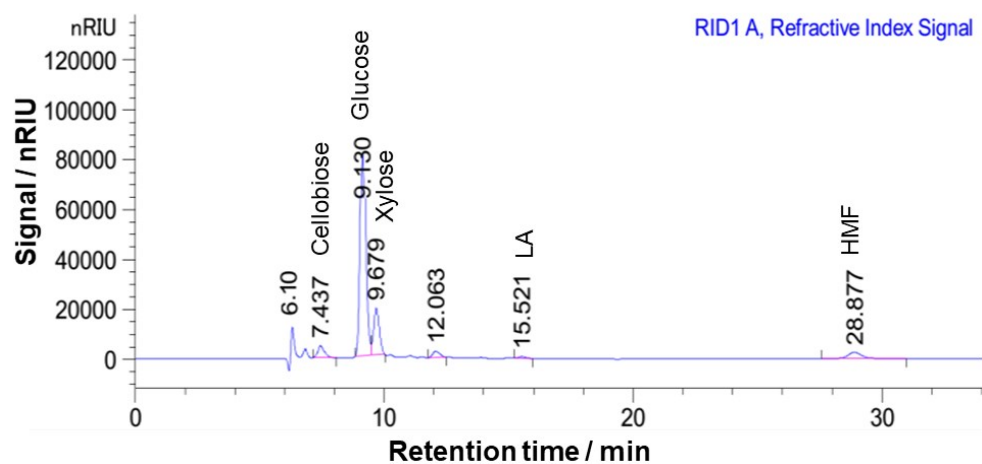


Figure S7 HPCL chromatogram of hydrolysis products of eucalyptus lignocellulose using ECG-48 under typical conditions. Reaction conditions: eucalyptus (8 g), ECG-48 h (0.5 g), HCl (40 ml of 120 ppm), using ball-milling combined with sonication

pretreatment. The reaction temperature was raised from 25 °C to 180 °C (10°/ min) for 20 min, then quickly cooled down to 25°C.

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