Supporting information

Advancing Biomass Utilization: Conversion of Solid Residues from Pretreatment and Enzymatic Hydrolysis into Porous Carbon Materials

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Table S-1: Elemental analysis showing the atomic mass percent of raw materials and biochars.

	COS				**COC**			
	R	**R-BC**	**OP-BC**	**OP-EH-BC**	**R**	**R-BC**	**OP-BC**	**OP-EH-BC**
C	**59.97**	**74.77**	**74.44**	**53.32**	**61.95**	**55.66**	**75.89**	**65.58**
O	**39.11**	**20.99**	**24.15**	**36.95**	**37.17**	**32.97**	**22.18**	**27.80**
S	0.04	0.08	0.05	0.07	0.06	0.49	0.11	0.14
P	0.08	0.10	0.05	0.04	0.09	1.46	0.30	0.16
Cl	0.06	0.07	0.01	0.05	0.02	0.07	0.02	0.02
Si	0.1	0.03	0.04	0.04	0.05	0.02	0.01	0.02
Na	0.26	0.05	0.03	7.71	0.19	0.04	0.05	4.61
K	0.04	2.88	0.72	0.88	0.12	6.31	0.70	0.67
Mg	0.16	0.17	0.06	0.02	0.18	1.49	0.16	0.05
Ca	0.02	0.57	0.44	0.83	0.02	0.63	0.43	0.80
Al	0.43	0.20	0.08	0.08	0.13	0.76	0.20	0.10
Mn	0	0.11	0.03	0.02	0.01	0.08	0.01	0.02
O/C	**0.65**	**0.28**	**0.32**	**0.69**	**0.60**	**0.59**	**0.29**	**0.42**

COS: *Camellia oleifera* shell (COS); COC: *C. oleifera* cake; R: raw; OP: oxalic acid pretreatment; EH: enzymatic hydrolysis; BC: biochar

Material balance

In this study, three biochar (BC) production routes were employed (Fig. 6a). In Route 1, the raw material (R) was directly converted into biochar (R-BC). In Route 2, the biomass underwent oxalic acidic pretreatment (OP) to produce fermentable sugars, and the resulting solid residues were used for BC fabrication (OP-BC). For Route 3, the biomass was pretreated, and the sugar-containing hydrolysate was preserved. The solid residue was then utilized in an enzymatic hydrolysis (EH) process to further produce sugars. Finally, the residual solids from the EH were subjected to pyrolysis for BC production (OP-EH-BC). Calculations of residual solid percentage, as well as sugar and biochar yields, are provided in the Eqs. S-1 and S-2.

$$Solid\ residue\ (\%) = \frac{solid\ residue\ (g)}{initial\ substare\ (g)} \times 100$$

S-1

$$Product\ yield\ = \frac{product\ content\ (g)}{initial\ substrate\ content\ (kg)}$$

S-2

Higher heating value

The fundamental thermal characteristic of biomass materials, specifically their higher heating value (HHV), is a decisive factor in evaluating their energy potential.[1] Prior to utilizing them as fuel sources, accurate determination of HHV is paramount. However, empirically measuring HHV through methods like bomb calorimetry can be expensive and time-consuming.[2] To streamline this process, alternative, cost-effective techniques for HHV estimation are often sought after. Various mathematical models exist, with HHV estimates based on different analyses, such as ultimate, proximate, structural, physical, and chemical [1]. HHV derived from ultimate analysis provides more detailed insights due to biomass fuel's elemental composition compared to proximate data.[1, 3]

This study evaluates eqs. S-3 to S-8 for an accurate fit, with a comparison of HHV results from previous works shown in Table S-2. Eq. S-3 emerged as the preferred method for the study. To estimate the HHV of biomass and BC materials, a series of equations were sourced from recent comprehensive review articles.[1] These equations take into account the elemental composition, particularly the percentage of carbon (C), oxygen (O), and sulfur (S), in order to provide a theoretically derived estimate of the energy content, a crucial step in optimizing their use as fuel alternatives. By leveraging the findings from these studies, the process of HHV determination becomes more accessible and less reliant on expensive experimental techniques. The results indicate that the BCs produced comparable or higher HHV values than reference materials (Table S-2). For instance, with HHVs of 26.49, 27.68, and 28.21 MJ/kg for COS-R-BC, COS-OP-BC, and COC-OP-BC respectively, they demonstrate potential as bioenergy resources. Chaturvedi's earlier study, which reported HHVs of 23─28 MJ/kg for BCs derived from eucalyptus, lantana, and pine needle, classified them as renewable solid fuels,[4] further highlighting their viability.

$$HHV = 0.4373C - 1.6701 \qquad \text{S-3}$$

$$HHV = -0.2413O + 28.9963 \qquad \text{S-4}$$

$$HHV = -3.3972S + 18.1625 \qquad \text{S-5}$$

$$HHV = -0.0769C - 0.3116O + 35.8357 \qquad \text{S-6}$$

$$HHV = 0.2425C + 0.6280S + 6.4386 \qquad \text{S-7}$$

$$HHV = -0.2523O + 0.7759S + 29.4066 \qquad \text{S-8}$$

Where HHV, C, O, and S represent higher heating value and elemental weight percent of carbon, oxygen, and sulfur, respectively. Equations were collected from recent review study.

Table S-2: Higher heating values (MJ/kg) of the raw materials and biochars from this research and previous literature studies.

Biomass/biochar	**Equations**						**Experimental**
	S-3	**S-4**	**S-5**	**S-6**	**S-7**	**S-8**	
COS-R	21.31	17.98	17.62	17.57	19.28	18.01	NA
COS-R-BC	**26.49**	23.19	17.55	23.38	22.17	23.47	NA
COS-OP-BC	**27.68**	22.00	17.75	21.64	22.79	22.19	NA
COS-OP-BC	17.17	19.40	17.69	20.13	16.97	19.48	NA
COC-R	22.18	18.45	17.62	18.02	19.76	18.50	NA
COC-R-BC	16.67	21.01	14.80	22.30	17.23	21.83	NA
COC-OP-BC	**28.21**	22.58	17.24	22.29	23.18	22.90	NA
COC-OP-BC	22.70	21.40	17.11	21.74	20.15	21.70	NA
COS-R[5]	**18.97**	17.72	17.58	17.64	17.99	17.75	**18.21**
COS-BC-Py[5]	**30.28**	23.32	17.35	22.88	24.31	23.65	**27.22**
COS-BC-Tor[5]	**28.00**	22.37	17.58	22.06	23.00	22.61	**25.51**
COS-R[6]	**21.11**	19.67	17.31	19.79	19.23	19.85	**18.16**
COS-BC[6]	**23.69**	24.95	17.72	26.15	20.58	25.27	**23.25**
Wood waste[2]	**19.21**	18.97	17.79	19.21	18.09	19.01	**19.26**
Paper waste[2]	**17.14**	19.10	17.48	19.75	16.99	19.22	**17.08**

COS: *Camellia oleifera* shell (COS); COC: *C. oleifera* cake; R: raw; OP: oxalic acid pretreatment; EH: enzymatic hydrolysis; BC: biochar; NA: not applicable; Py: pyrolysis; Tor: torrefaction

Table S-3: Assessment of the current study based on the 12 Principles of Green Chemistry.[7-9]

SN	Principles	Description	This study
1	Prevention of waste	Avoid waste generation rather than treating it at the end of the process	The solid residue resulting from biomass hydrolysis, often regarded as waste, was transformed into biochar.
2	Atom economy	Maximize incorporation of reactants into the targeted products	Routes 2 and 3 showed significantly higher product yields compared to Route 1 (refer to Section 3.3, Material Balance).
3	Less hazardous/toxic materials	Designs production processes with little or no toxicity to protect the environment and lower health risks	Biomass materials were employed, along with milder reaction conditions.
4	Safer products	Synthesize products with the same desired function, but with less toxicity	The fermentable sugar and the biochar are nontoxic.
5	Safer solvents and auxiliaries	Avoid or use less toxic solvents and purification agents should be avoided	A relatively small but eco-friendly solvent (oxalic acid) was used, derived from renewable sources and designed for efficient recovery/recycling during the process.
6	Energy efficiency	Minimize the energy expense of the process	Mild reaction conditions: pretreatment at 121°C for 30 min, enzymatic hydrolysis at 50°C for 24 h, and pyrolysis at 400°C for 3 h,
7	Renewable feedstocks	Prioritize the use of renewable or biomass-derived feedstock	Camellia oil refinery waste biomass was strategically employed as a sustainable feedstock in the process.
8	Derivatives reduction	Avoid generation of unnecessary derivatives	The process aimed to minimize generation of unnecessary byproducts, focusing on straightforward, targeted procedures that produced desired

			outcomes directly from biomass.
9	Catalytic better than stoichiometric reagents	Catalysis for more efficient, selective, and minimization of waste	Biocatalysis using enzymes produced through solid-state fermentation was employed, replacing the need for commercial enzymes or other catalysts.
10	Product design for degradation	Synthesize degradable products into nontoxic materials at the end-of-life	The fermentable sugars and biochars were designed with biodegradability in mind, ensuring that even their derived application products would contribute to a more environmentally friendly cycle.
11	Real-time analysis for pollution reduction	Instant, in situ monitoring and control of substances before the formation of hazardous materials	The analytical techniques employed in this research are carefully vetted, adhering to safety protocols and following established, standardized procedures, as detailed in the Materials and Methods section.
12	Safer process for accident prevention	Select inherently safer chemicals to prevent incidents	In this study, an emphasis on safety and environmental responsibility was evident, with the use of green alternatives like oxalic acid instead of harsh mineral acids or hazardous substances.

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