

Stage-Resolved Characterization of Wastewater Sludge Streams for Thermochemical Valorization: Moisture, Fuel Value, and Ash Mineralogy Constraints

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S1. Sample collection, handling, and preparation

Sludge samples were collected from the Ankara Central Wastewater Treatment Plant (Ankara, Turkey), with all five sludge streams collected on the same day. Each sludge type was taken directly from the outlet of its corresponding processing unit:

- primary clarification outlet for primary sludge
- secondary clarification outlet for WAS sludge
- thickening/mixing outlet for raw sludge
- digester outlet for anaerobic sludge
- dewatering unit outlet for sludge cake

All samples were collected in sealed plastic containers, transported to the laboratory, and stored refrigerated at 4 °C. Samples were oven-dried within the same week of collection, and all subsequent analyses were performed on the dried materials.

In addition to the residues, a set of reference solid fuels and biomass feedstocks was included to provide benchmarking context for proximate composition and calorific value. Commercially available materials were purchased and analyzed, including 11 lignite (brown coal) samples, 15 hard coal samples, and 6 coke samples, as well as 2 algal biomasses and 7 lignocellulosic/biomass materials. These reference samples were treated as purchased materials and were prepared and characterized using the same drying, homogenization, and analytical protocols applied to the sludge.

S2. Drying and storage conditions for dry-basis analyses

For dry-basis analyses, subsamples (approximately 5 g per replicate) were spread as a thin layer in pre-weighed, tared porcelain crucibles and dried at 105 °C for 6 h in a laboratory drying oven. After drying, crucibles were transferred to a desiccator containing silica gel and cooled for 40 min prior to weighing. Dried samples were stored in airtight containers until analysis. All measurements were performed in triplicate.

The results of the moisture determination are reported in Tables S1-S3. Table S1 summarizes the as-received moisture content and total solids of each Ankara sludge stream. Moisture content was calculated as

$$\text{Moisture content \%} = \frac{m_0 - m_{105}}{m_0} \times 100 \%$$

where m_0 is the initial mass and m_{105} is the mass after drying. Table S2 provides the underlying wet subsample masses and the corresponding dry residue masses used to calculate total solids according to:

$$\text{Total solids \%} = \frac{m_{\text{dry}}}{m_{\text{wet}}} \times 100 \%$$

Table S3 reports the residual moisture remaining after the standard pre-drying step (105 °C for 6 h), which was used to prepare samples for subsequent dry-basis analyses (e.g., TGA, HHV, and solid-phase characterization). As-received moisture contents for the benchmark fuels and biomass reference materials (lignite, hard coal, coke, and selected biomasses/algal materials) measured using the same drying protocol are reported in Table S4.

After drying, samples were homogenized and ground prior to subsampling for analytical measurements. Grinding was performed using Retsch ZM 200, equipped with a 0.5 mm ring sieve to obtain a uniform powder.

Table S1. As-received moisture content and total solids of sludge streams (triplicate measurements, mean $\pm$ SD, n = 3).

Sludge Type	Moisture content (%)			Mean $\pm$ SD (%)
	Rep 1	Rep 2	Rep 3	
Primary	96.2	98.3	97.6	97.4 $\pm$ 1.1
WAS	98.1	99.4	99.2	98.9 $\pm$ 0.7
Raw	96.4	98.9	97.5	97.6 $\pm$ 1.3
Anaerobic	97.1	99.3	98.4	98.4 $\pm$ 1.1
Cake	75.9	78.6	77.1	77.2 $\pm$ 1.4

Table S2. Wet subsample mass and corresponding dry residue mass after oven drying at 105 °C for 6 h for sludge streams (triplicate measurements, mean $\pm$ SD, n = 3).

Sludge Type	Wet subsamples (g)			Mean $\pm$ SD (g)	Dry mass after oven drying (g)			Mean $\pm$ SD (g)
	Rep 1	Rep 2	Rep 3		Rep 1	Rep 2	Rep 3	
Primary	4.9032	4.9178	5.0184	4.9465 $\pm$ 0.0627	0.1863	0.0836	0.1204	0.1301 $\pm$ 0.0520
WAS	4.9421	5.0329	4.9285	4.9678 $\pm$ 0.0568	0.0939	0.0302	0.0394	0.0545 $\pm$ 0.0344
Raw	5.0076	4.9953	4.9827	4.9952 $\pm$ 0.0125	0.1803	0.0549	0.1246	0.1199 $\pm$ 0.0628
Anaerobic	5.0825	4.9564	5.0471	5.0287 $\pm$ 0.0650	0.1474	0.0347	0.0808	0.0876 $\pm$ 0.0567
Cake	5.0638	4.9699	5.0973	5.0437 $\pm$ 0.0660	1.2204	1.0636	1.1673	1.1504 $\pm$ 0.0798

Table S3. Residual moisture content of sludge samples after drying at 105 °C for 6 h (triplicate measurements, mean $\pm$ SD, n = 3).

Sludge Type	Residual moisture content (%)			Mean $\pm$ SD (%)
	Rep 1	Rep 2	Rep 3	
Primary	2.7	3.2	2.3	2.7 $\pm$ 0.5
WAS	2.6	2.9	2.3	2.6 $\pm$ 0.3
Raw	3.5	4.8	3.0	3.8 $\pm$ 0.9
Anaerobic	3.8	3.3	3.6	3.6 $\pm$ 0.3
Cake	1.8	1.5	1.7	1.7 $\pm$ 0.2

Table S4. As-received moisture contents of benchmark fuels and biomass reference materials determined by oven drying (105 °C for 6 h, n = 2).

Sample	Moisture content (%)				Sample	Moisture content (%)			
	Rep 1	Rep 2	Mean	SD		Rep 1	Rep 2	Mean	SD
Lignite 1	8.8	8.8	8.8	0.0	Hard Coal 11	5.8	5.7	5.8	0.1
Lignite 2	9	9.3	9.2	0.2	Hard Coal 12	6.3	6.4	6.4	0.1
Lignite 3	9	8.7	8.9	0.2	Hard Coal 13	3.1	3.1	3.1	0.0
Lignite 4	8.5	8.5	8.5	0.0	Hard Coal 14	3.2	3.3	3.3	0.1
Lignite 5	9.3	9.2	9.3	0.1	Hard Coal 15	9.6	9.6	9.6	0.0
Lignite 6	11.7	11.4	11.6	0.2	Coke 1	0.2	0.3	0.3	0.1
Lignite 7	3.8	3.7	3.8	0.1	Coke 2	0.2	0.2	0.2	0.0
Lignite 8	12.7	12.7	12.7	0.0	Coke 3	0.4	0.5	0.5	0.1
Lignite 9	10.6	10.4	10.5	0.1	Coke 4	1.4	1.4	1.4	0.0
Lignite 10	9.8	9.7	9.8	0.1	Coke 5	0.7	0.6	0.7	0.1
Lignite 11	9	9	9.0	0.0	Coke 6	0.4	0.3	0.4	0.1
Hard Coal 1	3.6	3.5	3.6	0.1	Rice Hask	6.1	6.2	6.2	0.1
Hard Coal 2	4	4	4.0	0.0	Kenaf	6.1	6.3	6.2	0.1
Hard Coal 3	3.9	4	4.0	0.1	Miscanthus	5.0	4.9	5.0	0.1
Hard Coal 4	4.7	4.7	4.7	0.0	Wood Chips	6.5	6.6	6.6	0.1
Hard Coal 5	4.2	4.2	4.2	0.0	Hemp Straw	7.6	7.9	7.8	0.2
Hard Coal 6	4.4	4.5	4.5	0.1	Corn Straw	5.9	6	6.0	0.1
Hard Coal 7	3.9	3.9	3.9	0.0	Wood Pellets	6.3	6.3	6.3	0.0
Hard Coal 8	8.7	8.9	8.8	0.1	Spirulina	8.4	8.6	8.5	0.1
Hard Coal 9	5.3	5.3	5.3	0.0	Bladderwrack	8.9	8.8	8.9	0.1
Hard Coal 10	2.1	2.1	2.1	0.0					

S3. Thermogravimetric analysis (TGA) program and data reduction

Thermogravimetric analysis was performed using a LECO TGA-601 with porcelain crucibles. Prior to analysis, samples were oven-dried, homogenized, and ground as described in Section S1. Approximately 1.0 g of dried sample was analyzed per run (n = 3). Samples were first conditioned in the instrument at 150 °C for 1 h to remove residual moisture. Temperature was then increased from 150 to 950 °C at 10 °C/min under N₂ (10 L/min) and held at 950 °C for 7 min to quantify volatile matter by mass loss under inert atmosphere (Table S5). The purge gas was subsequently switched to air at 7 L/min, and the sample was heated to 550 °C at 10 °C/min and held for 1 h, with the remaining mass fraction reported as ash at 550 °C (Table S6). For preparation of high-temperature residues used in solid-phase characterization, the dried sludge samples were heated to 950 °C in a muffle oven under air and held for 30 minutes (Figure S1).

Volatile matter and ash values are reported on a dry basis. Proximate analysis results for the benchmark fuels and biomass reference materials analyzed under the same TGA program are provided in Table S9. Fixed carbon (Table S7) was calculated by difference as:

$$\text{Fixed Carbon \%} = 100 \% - (\text{Volatile matter \%} + \text{Ash}_{550^{\circ}\text{C}} \text{ content \%})$$

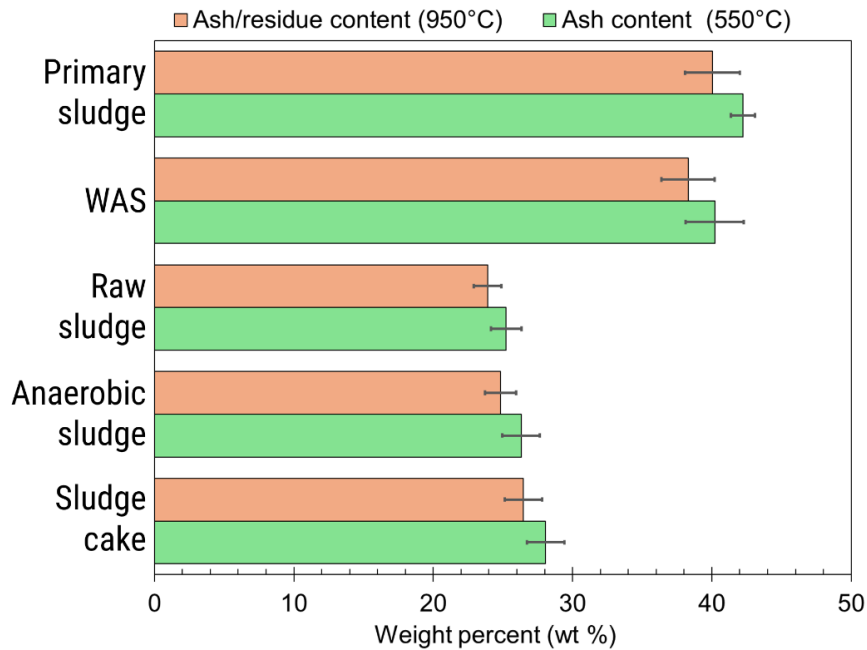


Figure S1. Comparison of ash content at 550 °C and high-temperature ash/residue at 950 °C for Ankara sludge streams (dry basis, mean $\pm$ SD, n = 3). Residue at 950 °C is reported after the oxidizing high-temperature hold used for residue generation and stability screening.

Table S5. Volatile matter content of Ankara sludge streams determined by TGA (dry basis, triplicate measurements, mean $\pm$ SD, n = 3).

Sludge Type	Volatile matter (wt %)			Mean $\pm$ SD (wt %)
	Rep 1	Rep 2	Rep 3	
Primary	64.8	68.9	66.8	66.8 $\pm$ 2.1
WAS	65.0	69.2	67.8	67.3 $\pm$ 2.1
Raw	64.6	69.0	67.6	67.1 $\pm$ 2.2
Anaerobic	51.8	55.6	54.2	53.9 $\pm$ 1.9
Cake	53.6	55.3	53.9	54.3 $\pm$ 0.9

Table S6. Ash content of Ankara sludge streams determined by TGA at 550 °C (dry basis, triplicate measurements, mean $\pm$ SD, n = 3).

Sludge Type	Ash content (wt %)			Mean $\pm$ SD (wt %)
	Rep 1	Rep 2	Rep 3	
Primary	26.7	29.4	28.1	28.1 $\pm$ 1.4
WAS	25.0	27.7	26.2	26.3 $\pm$ 1.4
Raw	24.0	26.1	25.6	25.2 $\pm$ 1.1
Anaerobic	38.1	42.3	40.2	40.2 $\pm$ 2.1
Cake	41.3	43.0	42.4	42.2 $\pm$ 0.9

Table S7. Fixed carbon content of Ankara sludge streams calculated by difference from volatile matter and ash at 550 °C (dry basis, triplicate measurements, mean $\pm$ SD, n = 3).

Sludge Type	Fixed Carbon (wt %)			Mean $\pm$ SD (wt %)
	Rep 1	Rep 2	Rep 3	
Primary	8.5	1.7	5.1	5.1 $\pm$ 3.4
WAS	10.0	3.1	6.0	6.4 $\pm$ 3.5
Raw	11.4	4.9	6.8	7.7 $\pm$ 3.3
Anaerobic	10.1	2.1	5.6	5.9 $\pm$ 4.0
Cake	5.1	1.7	3.7	3.5 $\pm$ 1.7

Table S8. High-temperature ash/residue of Ankara sludge streams after heating to 950 °C (dry basis, triplicate measurements, mean $\pm$ SD, n = 3).

Sludge Type	Ash content at 950 °C (wt %)			Mean $\pm$ SD (wt %)
	Rep 1	Rep 2	Rep 3	
Primary	25.1	27.8	26.5	26.5 $\pm$ 1.4
WAS	23.7	25.9	24.9	24.8 $\pm$ 1.1
Raw	22.8	24.7	24.2	23.9 $\pm$ 1.0
Anaerobic	36.3	40.1	38.5	38.3 $\pm$ 1.9
Cake	38.0	41.9	40.2	40.0 $\pm$ 2.0

Table S9. Proximate analysis of benchmark fuels and biomass reference materials by TGA (volatile matter, ash content, and fixed carbon by difference; dry basis; n = 2).

Sample	Volatile matter (wt %)				Ash content (wt %)				Fixed Carbon (wt %)			
	Rep 1	Rep 2	Mean	SD	Rep 1	Rep 2	Mean	SD	Rep 1	Rep 2	Mean	SD
Lignite 1	50.7	50.7	50.7	0.0	5.1	5.2	5.2	0.1	44.2	44.1	44.2	0.1
Lignite 2	47.3	47.8	47.6	0.4	5.2	5.2	5.2	0.0	47.5	47.0	47.3	0.4
Lignite 3	47.3	47.7	47.5	0.3	5.4	5.3	5.4	0.1	47.3	47.0	47.2	0.2
Lignite 4	47.7	47.6	47.7	0.1	5.3	5.5	5.4	0.1	47.0	46.9	47.0	0.1
Lignite 5	50.3	50.6	50.5	0.2	5.4	5.4	5.4	0.0	44.3	44.0	44.2	0.2
Lignite 6	46.3	46.5	46.4	0.1	16.5	16.3	16.4	0.1	37.2	37.2	37.2	0.0
Lignite 7	33.6	33.3	33.5	0.2	46.6	46.6	46.6	0.0	19.8	20.1	20.0	0.2
Lignite 8	51.1	51.3	51.2	0.1	7.2	7.3	7.3	0.1	41.7	41.4	41.6	0.2
Lignite 9	51.2	50.9	51.1	0.2	5.2	5.1	5.2	0.1	43.6	44.0	43.8	0.3
Lignite 10	51.5	51.2	51.4	0.2	5.3	5.3	5.3	0.0	43.2	43.5	43.4	0.2
Lignite 11	33.7	33.7	33.7	0.0	39.7	39.8	39.8	0.1	26.6	26.5	26.6	0.1
Hard Coal 1	34.1	34.4	34.3	0.2	6.2	6.2	6.2	0.0	59.7	59.4	59.6	0.2
Hard Coal 2	29.3	28.5	28.9	0.6	17.0	17.0	17.0	0.0	53.7	54.5	54.1	0.6
Hard Coal 3	27.4	27.9	27.7	0.4	21.3	21.2	21.3	0.1	51.3	50.9	51.1	0.3
Hard Coal 4	32.3	32.1	32.2	0.1	12.0	12.0	12.0	0.0	55.7	55.9	55.8	0.1
Hard Coal 5	31.4	32.0	31.7	0.4	9.9	10.0	10.0	0.1	58.7	58.0	58.4	0.5
Hard Coal 6	33.3	32.5	32.9	0.6	11.0	11.0	11.0	0.0	55.7	56.5	56.1	0.6
Hard Coal 7	33.0	32.8	32.9	0.1	6.4	6.4	6.4	0.0	60.6	60.8	60.7	0.1
Hard Coal 8	33.0	33.0	33.0	0.0	7.0	7.0	7.0	0.0	60.0	60.0	60.0	0.0
Hard Coal 9	31.6	31.5	31.6	0.1	13.2	13.3	13.3	0.1	55.2	55.2	55.2	0.0
Hard Coal 10	27.6	27.4	27.5	0.1	24.7	24.8	24.8	0.1	47.7	47.8	47.8	0.1
Hard Coal 11	30.5	30.6	30.6	0.1	13.0	13.1	13.1	0.1	56.5	56.3	56.4	0.1
Hard Coal 12	35.7	35.4	35.6	0.2	8.4	8.5	8.5	0.1	55.9	56.1	56.0	0.1
Hard Coal 13	29.7	29.3	29.5	0.3	17.6	17.6	17.6	0.0	52.7	53.1	52.9	0.3
Hard Coal 14	29.3	29.5	29.4	0.1	17.4	17.6	17.5	0.1	53.3	52.9	53.1	0.3
Hard Coal 15	34.3	34.4	34.4	0.1	7.1	7.1	7.1	0.0	58.6	58.5	58.6	0.1
Coke 1	0.9	0.9	0.9	0.0	9.9	9.9	9.9	0.0	89.2	89.2	89.2	0.0
Coke 2	1.1	1.2	1.2	0.1	9.0	9.3	9.2	0.2	89.9	89.5	89.7	0.3
Coke 3	1.3	1.1	1.2	0.1	10.6	10.3	10.5	0.2	88.1	88.6	88.4	0.4
Coke 4	1.5	1.7	1.6	0.1	7.8	7.9	7.9	0.1	90.7	90.4	90.6	0.2
Coke 5	1.4	1.4	1.4	0.0	8.1	8.3	8.2	0.1	90.5	90.3	90.4	0.1
Coke 6	1.1	1.3	1.2	0.1	9.6	9.6	9.6	0.0	89.3	89.1	89.2	0.1
Rice Hask	63.2	63.6	63.4	0.3	12.5	12.5	12.5	0.0	24.3	23.9	24.1	0.3
Kenaf	72.5	72.2	72.4	0.2	4.8	4.9	4.9	0.1	22.7	22.9	22.8	0.1
Miscanthus	76.9	76.8	76.9	0.1	2.0	1.8	1.9	0.1	21.1	21.4	21.3	0.2
Wood Chips	78.9	78.7	78.8	0.1	4.7	4.8	4.8	0.1	16.4	16.5	16.5	0.1
Hemp Straw	79.5	79.5	79.5	0.0	4.2	4.3	4.3	0.1	16.3	16.2	16.3	0.1
Corn Straw	77.3	77.4	77.4	0.1	7.6	7.4	7.5	0.1	15.1	15.2	15.2	0.1
Wood Pellets	84.5	84.8	84.7	0.2	0.2	0.4	0.3	0.1	15.3	14.8	15.1	0.4
Spirulina	79.2	79.6	79.4	0.3	7.3	7.3	7.3	0.0	13.5	13.1	13.3	0.3
Bladderwrack	69.9	70.1	70.0	0.1	21.8	21.7	21.8	0.1	8.3	8.2	8.3	0.1

S4. Bomb calorimetry

Higher Heating Value (HHV) was measured using an oxygen bomb calorimeter (LECO AC-350) at the Department of Geological Engineering of Hacettepe University. Dried, ground samples were analyzed as loose powder charges of approximately 0.90-1.00 g per run (n = 3). The bomb was charged with UHP grade oxygen to 30 atm, and the instrument was operated following the manufacturer's protocol. The calorimeter was calibrated using a certified benzoic acid

standard prior to measurements, and standard corrections were applied by the instrument software. HHV values are reported on a dry basis as mean $\pm$ SD in Table S10.

Table S10. Higher heating values (HHV) of Ankara sludge streams measured by bomb calorimetry after drying at 105 °C for 6 h (triplicate measurements; mean $\pm$ SD, n = 3).

Sludge Type	Higher Heating Value (MJ/kg)			Mean $\pm$ SD (MJ/kg)
	Rep 1	Rep 2	Rep 3	
Primary	19.3	20.4	19.9	19.9 $\pm$ 0.6
WAS	16.7	17.6	17.2	17.2 $\pm$ 0.5
Raw	17.7	18.8	18.3	18.3 $\pm$ 0.6
Anaerobic	13.1	13.8	13.5	13.5 $\pm$ 0.4
Cake	13.2	14.0	13.6	13.6 $\pm$ 0.4

Table S11. Higher heating values (HHV) of benchmark fuels and biomass reference materials measured by bomb calorimetry after drying at 105 °C for 6 h (mean $\pm$ SD, n = 2).

Sample	HHV (MJ/kg)				Sample	HHV (MJ/kg)			
	Rep 1	Rep 2	Mean	SD		Rep 1	Rep 2	Mean	SD
Lignite 1	22.5	21.5	22.0	0.7	Hard Coal 11	21.9	21.9	21.9	0.0
Lignite 2	21.0	20.8	20.9	0.1	Hard Coal 12	25.4	26.0	25.7	0.4
Lignite 3	23.1	22.6	22.8	0.4	Hard Coal 13	22.8	22.7	22.7	0.1
Lignite 4	22.4	22.0	22.2	0.3	Hard Coal 14	22.9	23.0	22.9	0.0
Lignite 5	21.0	21.2	21.1	0.1	Hard Coal 15	23.3	23.3	23.3	0.0
Lignite 6	17.5	17.5	17.5	0.0	Coke 1	27.7	26.6	27.2	0.8
Lignite 7	10.7	10.7	10.7	0.0	Coke 2	26.5	28.5	27.5	1.4
Lignite 8	20.0	20.0	20.0	0.1	Coke 3	26.7	28.0	27.3	0.9
Lignite 9	21.6	20.8	21.2	0.5	Coke 4	27.5	28.8	28.2	0.9
Lignite 10	21.1	20.6	20.9	0.4	Coke 5	27.2	27.9	27.6	0.5
Lignite 11	12.7	12.4	12.5	0.2	Coke 6	28.4	27.4	27.9	0.7
Hard Coal 1	25.7	25.8	25.7	0.1	Rice Hask	14.9	14.8	14.9	0.1
Hard Coal 2	22.4	22.3	22.4	0.1	Kenaf	15.7	15.4	15.6	0.2
Hard Coal 3	20.9	20.8	20.9	0.1	Miscanthus	15.5	15.5	15.5	0
Hard Coal 4	25.4	25.3	25.3	0.0	Wood Chips	16.1	16.4	16.3	0.2
Hard Coal 5	27.0	27.3	27.1	0.2	Hemp Straw	15.8	15.7	15.8	0.1
Hard Coal 6	24.1	24.1	24.1	0.0	Corn Straw	16.4	16.1	16.3	0.2
Hard Coal 7	28.7	28.5	28.6	0.2	Wood Pellets	19.3	19	19.2	0.2
Hard Coal 8	24.1	24.2	24.1	0.0	Spirulina	20.7	21.1	20.9	0.3
Hard Coal 9	21.7	21.7	21.7	0.0	Bladderwrack	13.1	13.3	13.2	0.1
Hard Coal 10	23.5	23.6	23.5	0.1					

S5. Ash/residue generation and handling for solid-phase characterization

Ash/residue for solid-phase characterization was generated using the muffle oven. Briefly, dried sludge samples were heated under air to 950 °C and held for 30 min to obtain high-temperature ash/residue. After completion of the program, crucibles were cooled to room temperature, and residues were transferred to clean, labeled containers. Prior to XRD and SEM/EDS, residues were gently homogenized to a uniform powder to minimize subsampling bias and were stored in airtight containers to limit moisture uptake.

S6. X-ray diffraction (XRD) acquisition and phase identification

XRD measurements were performed using a Rigaku D/MAX 2200 PC X-ray diffractometer. Data were collected using Cu K α radiation at 40 kV and 30 mA. Scans were acquired from 2° to 60° (2 θ) at a scanning speed of 2°/min. XRD was used to identify crystalline phases in oven-dried sludge samples, and their corresponding ash/residue after thermal treatment (950 °C). Phase identification was performed by matching peak positions and relative intensities against reference patterns.

S7. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) conditions

SEM imaging and EDS analysis were performed using a Carl Zeiss AG - EVO 50 scanning electron microscope. Samples were mounted on SEM stubs and coated with a thin carbon layer prior to analysis to minimize charging. Morphological imaging was conducted at an accelerating voltage of 15 kV using a backscattered electron (BSE) detector. EDS measurements were also acquired at 15 kV using the instrument's integrated X-ray energy spectrometer (detection range ⁴Be to ⁹⁴Pu). Elemental analysis was performed in mapping mode, with typical acquisition times of 30-60 s per point/location.