

From Agricultural Waste to Potential Radiation Shielding Materials: Linking Thermochemical Reactivity to Solid Residue Availability in Pyrolysis

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Abstract

The growing demand for sustainable and low-cost materials for radiation shielding has intensified interest in the valorization of agricultural waste. However, a critical limitation remains the lack of predictive frameworks linking intrinsic feedstock behavior to solid residue availability during thermochemical conversion. This study addresses this gap by investigating the relationship between thermochemical reactivity and product distribution in the pyrolysis of fourteen agricultural waste materials. A Thermal Reactivity Index (TRI) was developed to quantify feedstock behavior based on decomposition characteristics derived from temperature–time profiles. Controlled pyrolysis experiments were conducted to determine the yields of char, ash, liquid, and gas. The results show a strong inverse relationship between TRI and solid residue yield. Char yields ranged from 10.09 to 33.80 wt% while ash yields varied between 0 and 11.54 wt%, with mineral-rich residues obtained from tropical almond leaves and plantain leaves. Specific gas consumption ($0.29\text{--}1.22\text{ kg}\cdot\text{kg}^{-1}$) also exhibited an inverse relationship with TRI, indicating a trade-off between energy input and solid residue generation. Correlation analysis confirms a clear process–property relationship linking thermochemical reactivity to material output. Based on these findings, a predictive framework is proposed to guide the rational selection of agricultural feedstocks to maximize solid residue production. High-yield materials identified in this study are promising precursors for the development of radiation shielding and construction materials due to their enhanced solid retention characteristics. While shielding performance was not directly evaluated, this work establishes a foundation for future studies on the functional properties of waste-derived materials.

Highlights

- Agricultural waste feedstocks exhibit wide variation in thermochemical reactivity during pyrolysis.
- The Thermal Reactivity Index (TRI) reliably predicts solid material yield and energy demand.
- Low-reactivity feedstocks favor enhanced solid residue retention suitable for materials applications.
- Strong correlations link feedstock reactivity to char, oil, and gas formation pathways.
- Char and ash yields identify feedstocks suitable for material-oriented valorization.
- Pyrolysis enables conversion of agricultural residues into functional solids for sustainable radiation shielding.

1.0 Introduction

The development of sustainable radiation-shielding materials capable of replacing conventional, resource-intensive alternatives is a central challenge in modern materials science, nuclear science, and engineering [1, 2, 3]. Traditional shielding materials, including lead and dense cement-based composites, offer reliable functional performance but are associated with high embodied energy, environmental

toxicity, and limited recyclability [4, 5, 6]. Lead is toxic and difficult to manage at end-of-life, while concrete production contributes substantially to global carbon emissions [7–10]. These concerns have driven interest in sustainable, low-toxicity alternatives that can substitute conventional shielding constituents [11, 12].

Agricultural waste materials have emerged as promising candidates for sustainable shielding composites [13]. Their utilization diverts waste from landfills and reduces environmental footprint [14, 15, 16]. Studies demonstrate that waste-derived composites can enhance gamma attenuation while supporting circular economy goals [17–20]. Agricultural wastes are abundant lignocellulosic feedstocks (cellulose, hemicellulose, lignin) suitable for thermochemical conversion [21, 22]. Globally, millions of tonnes of agricultural residues are produced annually, representing a significant underutilized biomass resource [23, 24]. Biomass-derived materials, particularly biochar and ash, offer potential for functional solid production [11, 25–27].

Biochar, the solid carbonaceous residue from pyrolysis, exhibits a porous structure and high surface area dependent on feedstock and processing conditions [28–30]. Char yield is influenced by carbon content and lignocellulosic stability; high cellulose and lignin enhance char formation, while hemicellulose-rich biomass reduces yield [31]. Biomass ash contains mineral constituents such as silica, alumina, potassium, and calcium, which vary with feedstock type and combustion conditions, making them valuable for supplementary cementitious applications [32–34].

Pyrolysis provides a versatile pathway for transforming agricultural wastes into carbon-rich and mineral-rich solids [35, 36]. This oxygen-limited thermal decomposition produces biochar, condensable liquids, and gaseous products [37–39]. The solid fractions have attracted attention for use in construction materials and functional fillers due to their tunable properties [40, 41]. Biochar and biomass ash can be incorporated into cementitious systems and polymer composites, improving mechanical strength, thermal insulation, and durability while reducing environmental impact [42–47]. In radiation shielding, carbon-based and mineral-rich fillers show potential to improve attenuation performance [48, 49].

Despite these advances, waste-derived material development remains constrained by limited understanding of how intrinsic feedstock properties influence material yield and availability during thermochemical processing [50]. Many studies focus on post-production characterization without addressing which agricultural wastes are most suitable for producing consistent solid residues. Feedstock selection is often empirical, limiting scalability [50]. A critical underexplored factor is thermochemical reactivity, the rate at which a material responds to heating and undergoes decomposition [51, 52]. Agricultural wastes differ substantially in composition, structure, density, and mineral content, leading to wide variation in heating behavior, devolatilization rate, and solid residue formation. Highly reactive feedstocks devolatilize rapidly, favoring liquid and gas production, whereas less reactive materials retain mass and promote char and ash formation [29, 53–56]. These differences directly impact solid material availability for functional applications. Understanding and quantifying thermochemical reactivity is a key step toward rational design of sustainable materials. Linking reactivity

metrics to product yield distribution enables the prediction of feedstocks best suited for material-oriented valorization rather than energy recovery [34, 57]. Energy demand is another important sustainability factor; feedstocks requiring prolonged heating may undermine environmental benefits even with high solid yields [54, 58, 59]. Evaluating trade-offs between solid residue formation and process energy consumption is essential for identifying viable materials pathways.

Radiation shielding represents a high-value application benefiting from waste-derived solid materials. Shielding performance depends on composition, material availability, density control, and structural stability, attributes influenced by pyrolysis conditions and feedstock behavior [60–62]. Agricultural waste-derived char and ash can serve as fillers or supplementary components in shielding composites, reducing dependence on toxic or carbon-intensive materials [63]. Successful integration requires a systematic understanding of how feedstock properties, reactivity, and processing conditions determine solid residue yield and quality [50].

From a sustainable materials perspective, the challenge is not only whether agricultural wastes can be converted into char or ash, but whether such materials can be produced in sufficient quantity, stability, and consistency for use as functional fillers in advanced composites. Understanding feedstock-dependent solid availability is a prerequisite for scalable materials development. Despite growing interest in sustainable radiation shielding, few studies explicitly link the thermochemical reactivity of agricultural wastes to pyrolysis product distribution for shielding applications. Existing research emphasizes biochar for environmental remediation or energy recovery, with limited attention to radiation attenuation.

Despite extensive research on biomass pyrolysis, a critical limitation persists: the lack of a predictive framework linking intrinsic feedstock thermochemical behavior to solid material availability. Most studies emphasize post-production characterization of biochar and ash, with limited attention to how feedstock-dependent reactivity governs product distribution during conversion. Consequently, feedstock selection for material-oriented applications remains largely empirical, constraining scalability and process optimization. Furthermore, although biomass-derived materials have been proposed for radiation shielding, existing studies rarely address upstream determinants such as decomposition kinetics, heating behavior, and energy demand, which ultimately control material yield and consistency. This disconnect limits the practical translation of biomass pyrolysis into reliable material supply chains. This study addresses these gaps by systematically investigating the thermochemical reactivity of fourteen agricultural waste materials and their influence on pyrolysis product distribution. By introducing the Thermal Reactivity Index (TRI) as a comparative metric and integrating it with solid residue yield and energy demand, the study establishes a process–property framework for feedstock selection. The findings provide a predictive basis for identifying agricultural residues suitable for solid material for functional applications, with direct implications for sustainable radiation shielding and construction applications.

2.0 Materials and Methods

2.1 Scope of the Investigation

This study examines the thermochemical conversion behaviour of fourteen selected agricultural waste materials (AWMs) under controlled pyrolysis conditions using a locally fabricated system designed to operate under oxygen-limited conditions. The investigation characterizes feedstock thermal response and quantifies solid residue (char and ash) yields.

2.2 AWM Sourcing and Preparation

Fourteen agricultural waste materials were sourced from local farming communities, with cocoa bean husks obtained from a cocoa processing company to represent an industrially generated agrarian residue. All samples were sun-dried immediately after collection to reduce moisture content and preserve material integrity. A detailed summary of the collected materials is provided in Table 1. To ensure uniformity during reactor loading and reproducibility of the pyrolysis process, larger feedstock materials were manually cut into fragments of approximately 5–7 cm to facilitate efficient loading and heat transfer. All samples were thoroughly cleaned to remove extraneous materials such as soil particles, stones, and residual plant debris.

Table 1
Selected agricultural waste materials

S/N	Sample ID	Sample description	Mass (kg)
1	AWM1 (CBH)	Cocoa Bean Husk	6.448
2	AWM2 (DCS)	Dried Cocoa Stem	11.572
3	AWM3 (DRT)	Dried Rice Straw	12.448
4	AWM4 (DPL)	Dried Plantain Leaves	9.429
5	AWM5 (OPF)	Oil Palm Fronds	17.850
6	AWM6 (OPB)	Oil Palm Brooms	6.350
7	AWM7 (OPL)	Oil Palm Leaves	9.100
8	AWM8 (DCF)	Dried Coconut Fronds	10.530
9	AWM9 (DCB)	Dried Coconut Brooms	7.151
10	AWM10 (DCL)	Dried Coconut Leaves	10.150
11	AWM11 (DOP)	Dried Orange Peels	10.042
12	AWM12 (DFS)	Dried Fish Scale	3.405
13	AWM13 (TAL)	Tropical Almond Leaves	12.334
14	AWM14 (DCH)	Dried Cow Hooves	7.056

2.3 Pyrolysis System Description

Pyrolysis experiments were carried out using a locally fabricated system specifically designed for the thermochemical conversion of biomass into biochar and condensable liquid products (Fig. 1). The system consists of five principal components: a kiln, a sealed reactor chamber, a condenser unit, interconnecting transfer tubes, and a product collection vessel. The kiln, constructed with an insulating clay-based lining, encloses the reactor to minimize heat loss and promote uniform heat distribution. The reactor has an internal volume of approximately 5,369 cm³ and operates across a temperature range from ambient to > 800°C, depending on the targeted product properties. The system operates under oxygen-limited conditions to ensure pyrolytic conversion and suppress combustion. Volatile compounds generated during pyrolysis are conveyed through heat-resistant tubes to the condenser unit, where condensable vapours are recovered as bio-oil. Non-condensable gases are collected independently for subsequent analysis.

2.4 Pyrolysis and Combustion Protocol

Each experiment commenced with loading a predetermined mass of agricultural waste feedstock into the reactor chamber. The feedstock was gradually heated from ambient temperature (approximately 25°C) to induce thermal decomposition through pyrolysis. This process produced solid biochar alongside volatile and gaseous by-products. To obtain bio-ash, a portion of the produced biochar was subsequently subjected to controlled combustion in the presence of oxygen at temperatures ranging from 400°C to 700°C, facilitating the complete removal of residual organic matter and yielding mineral-rich ash. To ensure experimental reliability and prevent cross-contamination between successive runs, the pyrolysis system was thoroughly cleaned after each experiment using a sequential washing procedure with detergent, baking soda, and clean water to remove residual char, tar, and condensates.

2.5 Thermochemical Decomposition Parameters

For each pyrolysis run, the temperature at which the feedstock reached 300°C was defined as the onset temperature, corresponding to the initiation of rapid thermochemical decomposition, consistent with the primary devolatilization range of lignocellulosic biomass (280–320°C) [64, 65]. The residence time following attainment of 300°C was recorded as the active pyrolysis period. Temperature–time data were acquired for all feedstocks and used to quantify thermal reactivity. The Thermal Reactivity Index (TRI) was calculated according to Eq. (1):

$$TRI = \frac{T_f - T_o}{t_f - t_o} (1)$$

where T_o and T_f are the onset and final temperatures (°C), respectively, and t_o and t_f are the corresponding times (min). The TRI provides a normalized measure of the rate of thermal conversion under identical operating conditions.

2.6 Solid Residue Quantification

The initial mass of each feedstock was determined using a calibrated electronic balance before pyrolysis. After each experiment, biochar and biomass ash were recovered and quantified. Mass balance closure for the solid residue was calculated to assess experimental reliability and product recovery using Eq. (2):

$$\text{Mass Balance closure (\%)} = \frac{M_{\text{char}} + M_{\text{ash}}}{M_{\text{feedstock}}} \times 100 \quad (2)$$

where M_{char} and M_{ash} represent the masses of the solid pyrolysis products, and $M_{\text{feedstock}}$ denotes the initial biomass mass. Only solid residues (char and ash) are reported in the mass balance closure, consistent with the study's focus on material-oriented valorization.

2.7 Specific Gas Consumption (SGC)

The energy demand of the pyrolysis process for each experiment was evaluated using specific gas consumption (SGC), defined as the mass of fuel required to process a unit mass of feedstock. Liquefied petroleum gas (LPG) consumption was determined by weighing the fuel cylinder before and after each pyrolysis run. SGC was calculated using Eq. (3):

$$SGC = \frac{M_g}{M_f} \quad (3)$$

where M_g is the mass of LPG consumed (kg) and M_f is the mass of feedstock processed (kg). SGC values are reported in $\text{kg} \cdot \text{kg}^{-1}$ and serve as a comparative indicator of relative energy efficiency across different agricultural waste materials.

3.0 Results

3.1 Thermal Response and Decomposition Behaviour

3.1.1 Heating Rate Characteristics

Heating rates of the fourteen agricultural waste materials ranged from 2.7 to $8.3^\circ\text{C min}^{-1}$, indicating substantial variability in heat transfer behaviour in Fig. 3.

Lignocellulosic residues, dry cocoa stem (DCS), dry rice straw (DRS), and oil palm broom (OPB), exhibited the highest heating rates ($\geq 5.0^\circ\text{C min}^{-1}$). In contrast, tropical almond leaves (TAL), dried fish scales (DFS), and cow hooves (COH) showed the lowest heating rates ($\leq 3.0^\circ\text{C min}^{-1}$). The systematic variation in heating behaviour is summarized in Table 2.

Table 2
Thermal Behavior of AWMs during Pyrolysis

Feedstock Type	Heating Rate (°C/min)	Thermal Behavior/Heating Characteristics	Product Bias
DCS	≥ 7.0	Very Fast Heating: Very fast devolatilization and intense heat transfer, short vapour residence time, minimal secondary cracking.	High bio-oil and gas yield, low char formation
DRS, CCF, OPB, CCB	5.0 – 6.9	Fast Heating: Fast heat absorption, rapid devolatilization, enhanced primary pyrolysis reaction.	Moderate to high oil/gas yield, reduced char content
DOP, OPF, CCL, DPL	4.0–4.9	Moderate Heating: Controlled heating with steady temperature rise, balanced volatile and solid product formation.	Balanced oil, gas, and char yields
CBH, OPL	3.0–3.9	Slow Heating: Limited heat transfer rate, extended reaction time, dense matrix	High char yield, low oil yield
TAL, COH, DFS	< 3.0	Very Slow Heating: Low reactivity, protein-rich matrix, slow thermal diffusion, and volatilization	Higher carbon-rich char yield, lower oil/gas yield.

Higher heating rates ($\geq 5^{\circ}\text{C}/\text{min}$) observed in lignocellulosic biomass (e.g., DCS, DRS, OPB) favor volatile release and bio-oil production, whereas lower heating rates ($\leq 3^{\circ}\text{C}/\text{min}$) in dense or protein-rich feedstocks (TAL, COH, DFS) promote char formation and carbon stabilization

3.1.2 Temperature–Time Profiles

As illustrated in Fig. 4, all materials exhibited characteristic three-stage thermal progression: moisture removal ($< 150^{\circ}\text{C}$), active devolatilization ($200\text{--}450^{\circ}\text{C}$), and carbonization ($> 450^{\circ}\text{C}$) (Fig. 4).

Lignocellulosic feedstocks demonstrated steep temperature gradients during devolatilization, reaching 400°C within 45–60 min. Animal-based wastes (DFS, COH) and lignin-dense leaves (TAL) displayed extended lag phases, often requiring more than 60 min to reach active pyrolysis temperatures. Residence time above 300°C ranged from < 30 min for highly reactive materials to > 120 min for thermally stable feedstocks.

3.1.3 Thermal Reactivity Index (TRI)

The Thermal Reactivity Index (TRI), presented in Fig. 5, provides a quantitative measure of relative decomposition intensity by integrating heating rate and residence time. Thermal Reactivity Index values revealed a clear hierarchy of feedstock reactivity (Fig. 5). High TRI values ($\geq 3.0^{\circ}\text{C min}^{-1}$) were observed for DCS, OPB, and DRS. Low TRI values ($\leq 1.5^{\circ}\text{C min}^{-1}$) were recorded for DFS, COH, and TAL.

Intermediate TRI values ($2.0\text{--}3.0^{\circ}\text{C min}^{-1}$) characterized feedstocks such as cocoa bean husk (CBH), oil palm leaf (OPL), and coconut frond (CCF).

Based on TRI values, onset times, and residence durations, feedstocks were classified into three reactivity groups (Table 3):

Table 3
Thermal Reactivity Classes of the Selected Samples

Reactivity Class	Feedstock Samples	Typical Onset Time (min)	Residence Time (min)	Heating Rate / TRI Trend	Thermochemical Characteristics	Preferred Pyrolysis Regime / Product Potential
Highly Reactive	DCS, DRS, CCB, OPB	< 30	< 45	High (TRI $\approx$ 3–7°C/min)	Rapid temperature rise; high cellulose and hemicellulose; low ash; fast devolatilization	Fast pyrolysis - favors high bio-oil and syngas yields
Moderately Reactive	CBH, DPL, OPF, OPL, CCF, CCL, DOP	30–45	60–105	Moderate (TRI $\approx$ 2–3°C/min)	Balanced lignocellulosic matrix; moderate ash; controlled heat transfer and reactivity	Intermediate pyrolysis - co-production of bio-oil and biochar
Low Reactive**	TAL, DFS, COH	> 60	$\geq$ 120	Low (TRI < 1.5°C/min)	Dense, proteinaceous or lignin-rich structure; high mineral content; strong bonding	Slow pyrolysis - enhanced biochar yield and carbon stability

***Low-reactivity feedstocks are thermally stable*

3.1.5 Thermal Stability and Energy Demand

Thermal stability and relative energy demand were evaluated using TRI trends (Table 4). Feedstocks with high TRI values required less external energy input to sustain pyrolysis, reflecting efficient heat utilization. Conversely, low-TRI materials exhibited high thermal stability and significantly greater energy demand. Lignocellulosic residues generally require 20–40% less thermal input than animal-based wastes to achieve comparable decomposition.

Table 4
Thermal Stability and Energy Demand Classification of Samples

Sample Code	Description	TRI Trend (°C/min)	Thermal Stability	Relative Energy Demand	Thermal Behavior
DCS	Dry Cocoa Stem	High ($\approx 6-7$)	Low	Low	Rapid devolatilization; high cellulose; suitable for fast pyrolysis
DRS	Dry Rice Straw	High ($\approx 5-6$)	Low	Low	Quick heating; low ash; high volatile yield
CCB	Coconut Broom	High ($\approx 4-5$)	Low	Low	Fast-reacting fibrous structure; high bio-oil potential
OPB	Oil Palm Broom	Moderately High ($\approx 3.5-4.5$)	Low–Moderate	Low–Moderate	Efficient heating; suitable for energy recovery processes
CBH	Cocoa Bean Husk	Moderate ($\approx 2.5-3.0$)	Moderate	Moderate	Balanced decomposition; dual potential for oil and char
DPL	Dried Plantain Leaves	Moderate ($\approx 2.2-2.8$)	Moderate	Moderate	Gradual devolatilization; controlled heating response
OPF	Oil Palm Frond	Moderate ($\approx 2.0-2.5$)	Moderate	Moderate	Lignocellulosic; intermediate heating response
OPL	Oil Palm Leaf	Moderate ($\approx 2.0-2.3$)	Moderate	Moderate	Uniform heating; balanced reactivity and stability
CCF	Coconut Frond	Moderate ($\approx 1.8-2.3$)	Moderate	Moderate	Gradual temperature rise; steady heat utilization
CCL	Coconut Leaf	Moderate ($\approx 1.8-2.0$)	Moderate	Moderate	Stable heating; lignin-rich composition
DOP	Dried Oil Palm	Moderate ($\approx 1.8-2.2$)	Moderate	Moderate	Sustained heat absorption; medium thermal resistance
TAL	Tropical Almond Leaves	Low ($\approx 1.0-1.5$)	High	High	Lignin-rich; slow decomposition; high char formation
DFS	Dried Fish Scales	Very Low ($\approx 0.8-1.2$)	High	High	Proteinaceous (collagen); strong peptide bonds; slow pyrolysis

Sample Code	Description	TRI Trend (°C/min)	Thermal Stability	Relative Energy Demand	Thermal Behavior
COH	Cow Hooves	Very Low ($\approx 0.7\text{--}1.0$)	Very High	Very High	Keratin-rich; dense matrix; requires prolonged heating

Higher TRI values correspond to greater reactivity and lower energy input, while lower TRI values indicate enhanced thermal resistance and higher heating requirements

3.2 Pyrolysis Product Distribution

3.2.1 Absolute Product Masses

The absolute mass distribution of pyrolysis products is presented in Table 5. Char masses ranged from 0.93 kg (CCB) to 2.21 kg (DRS). Ash masses ranged from 0.13 kg (CCB) to 1.42 kg (TAL). Complete mass data for all feedstocks are provided in Table 5.

Table 5
Absolute Product Mass Data Obtained from the Pyrolysis

Feedstock Code	Feedstock Name	Mass of Char (kg)	Mass of Ash (kg)	Mass of Oil (kg)	Mass of Tar (kg)	Mass Loss (kg)
CBH	Cocoa Bean Husk	1.956	—	0.505	0.155	3.822
DCS	Dry Cocoa Stem	1.749	0.332	0.626	0.486	8.379
DRS	Dry Rice Straw	2.205	0.847	0.736	0.018	6.626
DPL	Dried Plantain Leaves	1.768	0.854	0.181	—	6.626
OPF	Oil Palm Frond	1.800	0.385	2.533	—	13.132
OPB	Oil Palm Broom	1.200	0.128	0.675	0.060	4.287
OPL	Oil Palm Leaf	1.762	0.579	1.630	0.078	5.051
CCF	Coconut Frond	1.425	0.320	0.728	0.361	7.516
CCB	Coconut Broom	0.930	0.130	0.723	0.063	5.305
CCL	Coconut Leaf	1.164	0.440	1.065	0.065	7.416
DOP	Dried Oil Palm	1.268	0.258	1.265	—	7.215
DFS	Dried Fish Scales	1.151	—	0.500	0.053	1.702
TAL	Tropical Almond Leaves	1.514	1.424	1.720	0.157	7.519
COH	Cow Hooves	1.516	—	0.672	1.375	3.493

***Variations in absolute product distribution indicate compositional differences among feedstocks, particularly in volatile, lignin, and protein contents, which influence the extent of devolatilization and solid residue formation.*

3.2.2 Normalized Solid Residue Yields

Normalized yields are presented in Table 6. Char yields ranged from 10.09 wt% (OPF) to 33.80 wt% (DFS). Ash yields ranged from 0 wt% (CBH, DFS, COH) to 11.54 wt% (TAL). Feedstocks with char yields exceeding 20 wt% included DFS (33.80%), CBH (30.33%), and COH (21.49%). Ash yields above 5 wt% were observed for TAL (11.54%), DPL (9.06%), and DRS (6.80%).

Table 6
Product Yield Distribution (wt%) from Pyrolysis

Feedstock Code	Char (%)	Ash (%)	Oil (%)	Tar (%)	Mass Loss (%)
CBH	30.33	—	7.83	2.40	59.27
DCS	15.11	2.87	5.41	4.20	72.41
DRS	17.71	6.80	5.91	0.14	53.21
DPL	18.75	9.06	1.92	—	70.29
OPF	10.09	2.16	14.19	—	73.56
OPB	18.90	2.02	10.63	0.94	67.52
OPL	19.37	6.36	17.91	0.86	55.51
CCF	13.77	3.09	7.04	3.49	72.61
CCB	13.01	1.82	10.11	0.88	74.18
CCL	11.47	4.34	10.50	0.64	73.05
DOP	12.63	2.57	12.60	—	71.90
DFS	33.80	—	14.68	1.56	49.96
TAL	12.28	11.54	13.94	1.27	60.97
COH	21.49	—	9.52	19.49	49.51

3.2.3 Mass Balance Closure

Mass balance closure values, based on solid residues (char and ash) only, ranged from 25.8% to 50.5% (Table 7, Fig. 6). Highly reactive lignocellulosic feedstocks exhibited lower closure (e.g., CCB at 25.8%), while animal-based wastes (DFS at 50.1%, COH at 50.5%) and ash-rich materials (OPL at 44.5%) showed higher closure.

Table 7
Mass Closure and Unaccounted Fraction of Pyrolysis Products

AWM Sample	Initial Mass (kg)	Char (kg)	Ash (kg)	Oil (kg)	Tar (kg)	Measured Total (kg)	Mass Closure (%)	Unaccounted (%)
CBHCocoa Bean Husk	6.448	1.956	—	0.505	0.155	2.616	40.6	59.4
DCSDry Cocoa Stem	11.572	1.749	0.332	0.626	0.486	3.193	27.6	72.4
DRSDry Rice Straw	12.448	2.205	0.847	0.736	0.018	3.806	30.6	69.4
DPLDried Plantain Leaves	9.429	1.768	0.854	0.181	—	2.803	29.7	70.3
OPFOil Palm Frond	17.850	1.800	0.385	2.533	—	4.718	26.4	73.6
OPBOil Palm Broom	6.350	1.200	0.128	0.675	0.060	2.063	32.5	67.5
OPLOil Palm Leaf	9.100	1.762	0.579	1.630	0.078	4.049	44.5	55.5
CCFCoconut Frond	10.350	1.425	0.320	0.728	0.361	2.834	27.4	72.6
CCBCoconut Broom	7.151	0.930	0.130	0.723	0.063	1.846	25.8	74.2
CCLCoconut Leaf	10.150	1.164	0.440	1.065	0.065	2.734	26.9	73.1
DOPDried Oil Palm	10.042	1.268	0.258	1.265	—	2.791	27.8	72.2
DFSDried Fish Scales	3.405	1.151	—	0.500	0.053	1.704	50.1	49.9
TALTropical Almond Leaves	12.334	1.514	1.424	1.720	0.157	4.815	39.0	61.0
COHCow Hooves	7.056	1.516	—	0.672	1.375	3.563	50.5	49.5

3.3 Relationship Between Thermal Reactivity and Solid Residue Yield

Correlation coefficients between TRI and product yields are presented in Table 8 and Figs. 7–8. Char yield exhibited a moderate negative correlation with TRI ($r = -0.45$). Ash yield showed a weak negative

correlation with TRI ($r = -0.21$). Gas yield, calculated as the unaccounted fraction, showed a moderate positive correlation with TRI ($r = +0.58$).

Table 8
Correlation Coefficients Between TRI and Product Yields

Product Type	Correlation Coefficient (r)	Trend Direction	Relationship Strength	Interpretation
Char Yield (%)	-0.45	↓ Negative	Moderate	Higher TRI reduces char formation as faster heating promotes devolatilization and limits carbonization.
Oil Yield (%)	-0.50	↓ Negative	Moderate	Increased reactivity enhances secondary cracking, reducing condensable oil formation and favoring gas evolution.
Tar Yield (%)	-0.36	↓ Negative	Weak	Slight decrease in tar yield with higher TRI, reflecting sensitivity to vapor residence time and condensation behavior.
Gas Yield (%)	+0.58	↑ Positive	Moderate to Strong	Gas yield increases with TRI, indicating enhanced volatile release and decomposition at higher reactivity levels.

Pearson correlation coefficients showing the strength and direction of relationships between TRI (°C/min) and pyrolysis product yields. Negative correlations indicate a decline in solid and condensable products with higher thermal reactivity, while positive correlations correspond to increased gaseous evolution.

3.4 Specific Gas Consumption

Specific gas consumption (SGC) values ranged from 0.29 to 1.22 kg gas kg⁻¹ feed (Table 9). The lowest SGC was observed for DCS (0.29 kg kg⁻¹) and OPB (0.39 kg kg⁻¹). The highest SGC was recorded for DFS (1.22 kg kg⁻¹), followed by COH (0.82 kg kg⁻¹) and TAL (0.80 kg kg⁻¹).

Table 9
Specific Gas Consumption of Feedstocks During Pyrolysis

Sample	Mass of Feed (kg)	Mass of Gas Used (kg)	SGC (kg gas/kg feed)
CBHCocoa Bean Husk	6.45	3.73	0.58
DCSDry Cocoa Stem	11.57	3.32	0.29
DRSDry Rice Straw	12.45	9.53	0.77
DPLDried Plantain Leaves	9.43	9.12	0.97
OPFOil Palm Frond	17.85	8.70	0.49
OPBOil Palm Broom	6.35	2.49	0.39
OPLOil Palm Leaf	9.10	7.46	0.82
CCFCoconut Frond	10.35	4.56	0.44
CCBCoconut Broom	7.15	2.90	0.41
CCLCoconut Leaf	10.15	7.04	0.69
DOPDried Oil Palm	10.04	7.15	0.71
DFSDried Fish Scales	3.41	4.14	1.22
TALTropical Almond Leaves	12.33	9.85	0.80
COHCow Hooves	7.06	5.80	0.82

Calculated as the ratio of the mass of gas used to the mass of feedstock processed (kg gas kg⁻¹ feed). The values indicate the relative fuel requirement for each feedstock during pyrolysis, serving as an index of thermal energy demand and process efficiency.

4.0 Discussion

4.1 Thermochemical Reactivity as a Determinant of Solid Material Availability

The results demonstrate that thermochemical reactivity is not merely a descriptive parameter but a governing factor that dictates the partitioning of biomass into solid, liquid, and gaseous fractions during pyrolysis. The observed inverse relationship between TRI and char yield confirms that rapid heating and high reactivity enhance primary devolatilization pathways, thereby limiting secondary solid-phase reactions responsible for carbon stabilization. Highly reactive lignocellulosic feedstocks exhibited accelerated heat transfer and short residence times within the active pyrolysis regime, resulting in incomplete structural rearrangement and reduced char formation [29, 53]. In contrast, low-reactivity materials, particularly proteinaceous and lignin-rich feedstocks, underwent prolonged thermal exposure,

facilitating cross-linking, aromatization, and carbon matrix stabilization. These mechanisms promote the formation of carbon-rich residues with higher structural integrity and mass retention. Importantly, the findings extend beyond conventional biomass pyrolysis studies by quantitatively linking reactivity to material availability [31, 55]. The TRI-based classification provides a predictive tool for identifying feedstocks that inherently favor solid-phase retention, thereby reducing reliance on post-process optimization. This represents a shift from process-driven to feedstock-informed design in sustainable materials development.

4.2 Solid Residue Yields and Material Potential

The distribution of solid residues (char and ash) provides direct insight into the suitability of agricultural waste feedstocks for material-oriented valorization. Char yields varied substantially among feedstocks, ranging from 10 to 34 wt%, with the highest values observed in DFS, CBH, and COH. These feedstocks share common characteristics: high thermal stability, dense matrices, and compositions that promote secondary solid-phase reactions during prolonged heating. DFS, composed primarily of collagen and hydroxyapatite, exhibited the highest char yield (33.8 wt%). The mineral fraction (calcium phosphate) likely contributed to thermal stabilization and reduced volatile release. Similarly, COH, rich in keratin, produced a char yield of 21.5 wt%, reflecting the thermal resistance of disulfide-bonded protein structures. These findings suggest that animal-derived agricultural wastes, often overlooked in biomass conversion studies, may represent valuable feedstocks for char production. Among lignocellulosic residues, CBH produced a char yield of 30.3 wt%, attributable to its balanced composition and moderate reactivity. In contrast, OPF (10.1 wt%) and CCL (11.5 wt%) produced the lowest char yields, reflecting their rapid devolatilization and limited carbonization under identical processing conditions. These results confirm that feedstock selection based solely on availability or cellulose content is insufficient; reactivity must be considered to predict solid yield. Ash yields ranged from 0 to 11.5 wt%, with TAL exhibiting the highest value (11.5 wt%), followed by DPL (9.1 wt%) and DRS (6.8 wt%). High ash content is associated with elevated mineral constituents, particularly silica, potassium, and calcium, which have been investigated for use as supplementary cementitious materials in construction [33, 34]. The variability in ash yield underscores the importance of feedstock-specific characterization for applications requiring mineral-rich fractions.

4.3 Energy Demand and Sustainability Implications

Energy demand during pyrolysis, as reflected by specific gas consumption (SGC), varied substantially among feedstocks and was closely linked to thermochemical reactivity. Highly reactive materials (DCS, OPB) required lower external energy input (SGC: 0.29–0.39 kg kg⁻¹) due to rapid heating and short residence times. Low-reactivity feedstocks (DFS, COH, TAL) exhibited higher energy demand (SGC: 0.80–1.22 kg kg⁻¹), reflecting slower heating kinetics and extended processing durations. This introduces an important sustainability consideration: maximizing solid yield may incur higher processing energy, potentially offsetting environmental gains if not carefully managed. However, when viewed through a materials substitution perspective, the increased availability of durable, carbon-rich solids may justify higher energy input, especially when these materials replace energy-intensive or toxic traditional

alternatives like lead or Portland cement [9, 10]. The inverse relationship between SGC and TRI ($r \approx -0.6$) confirms that energy efficiency is inherently tied to feedstock reactivity. Optimizing pyrolysis for sustainable materials, therefore, requires balancing solid yield against energy demand. The present results provide quantitative insight into this balance and enable informed selection of feedstocks that align with both performance and sustainability objectives.

4.4 Implications for Radiation Shielding and Construction Materials

The solid residues generated from low- and intermediate-reactivity feedstocks exhibit characteristics relevant to functional material applications, including high mass retention, carbon stability, and mineral enrichment. These attributes are particularly important for radiation shielding materials, where density, elemental composition, and structural integrity govern attenuation performance [60, 61]. Although shielding performance was not directly evaluated in this study, the upstream identification of feedstocks that preferentially produce stable solid residues represents a critical enabling step. Char and ash fractions derived from such feedstocks can serve as fillers or supplementary components in shielding composites, reducing reliance on lead-based or high-carbon materials [62, 63]. The high ash content of TAL and DPL, rich in silica and calcium oxides, aligns with the composition of conventional cementitious binders, suggesting potential for use in lightweight shielding concrete [46, 47]. Beyond radiation shielding, these residues are equally relevant to construction materials, where biochar and biomass ash have been shown to enhance mechanical performance, thermal insulation, and durability while reducing environmental impact [45, 70]. The high char yields from animal-derived wastes (DFS, COH) present opportunities for carbon-sequestering construction materials, contributing to circular economy objectives [28, 48].

4.5 Framework for Feedstock Selection

The results establish a process–property framework linking feedstock reactivity to solid residue availability. By integrating TRI, solid yield data, and energy demand, feedstocks can be classified according to their suitability for material-oriented valorization:

- **Preferred for solid residue production (char and ash):** Low-to-moderate reactivity feedstocks, TAL, DFS, COH, CBH, OPL, characterized by char yields > 20 wt%, ash yields > 5 wt%, and extended residence times.
- **Preferred for energy recovery:** Highly reactive feedstocks (DCS, DRS, OPB), characterized by rapid devolatilization, low char yields, and low energy demand.
- **Balanced candidates:** Moderately reactive feedstocks with intermediate char yields, including OPF, CCF, and DOP, are appropriate for co-producing biochar and bio-oil depending on process optimization.

This framework supports rational feedstock selection, reducing reliance on trial-and-error processing and enabling more efficient design of waste-derived materials for sustainable applications.

4.6 Contribution to Sustainable Materials Development

This study advances sustainable materials research by moving beyond post-production characterization and addressing the upstream determinants of material availability. Unlike conventional pyrolysis studies that emphasize yield optimization in isolation, the present approach integrates reactivity, energy demand, and solid retention into a unified process–property perspective. This enables more efficient design of waste-derived materials and reduces uncertainty in material supply chains. By linking intrinsic feedstock behaviour to material availability, this study provides a rational basis for selecting agricultural residues for construction and radiation shielding applications. The findings contribute to the broader transition towards circular, low-impact material systems, demonstrating that agricultural waste valorization via pyrolysis can produce functional solids that could replace conventional, resource-intensive materials.

4.7 Limitations of the Study

While this study establishes a clear relationship between thermochemical reactivity and solid residue yield, several limitations should be acknowledged. First, the analysis of gaseous products was not conducted, resulting in incomplete mass balance closure and limiting detailed insight into gas-phase reaction pathways. Second, the Thermal Reactivity Index (TRI), although effective as a comparative metric, was not directly validated against conventional kinetic parameters such as activation energy derived from thermogravimetric analysis (TGA). Third, the radiation shielding performance of the derived materials was not experimentally evaluated, and conclusions regarding applicability remain inferential. Future work should incorporate gas composition analysis, kinetic modeling, and experimental validation of shielding performance to strengthen the applicability of the proposed framework.

5.0 Conclusion

This study investigated the relationship between thermochemical reactivity and pyrolysis product distribution in fourteen agricultural waste materials to identify feedstocks suitable for material-oriented valorization, particularly for sustainable radiation shielding and construction applications. The findings demonstrate that feedstock reactivity is a key determinant of solid material availability, with significant implications for process efficiency and material yield.

- **Feedstock classification:** The Thermal Reactivity Index (TRI) enabled classification based on heating behavior and decomposition kinetics. Highly reactive feedstocks favored volatile production; low-reactivity materials promoted carbon stabilization and solid retention.
- **Solid residue yields:** Char yields ranged from 10 to 34 wt%, highest in dried fish scales (33.8 wt%), cocoa bean husk (30.3 wt%), and cow hooves (21.5 wt%). Ash yields ranged from 0 to 12 wt%, highest in tropical almond leaves (11.5 wt%), dried plantain leaves (9.1 wt%), and dry rice straw (6.8 wt%).
- **Energy demand:** Specific gas consumption ranged from 0.29 to 1.22 kg kg⁻¹ and was inversely related to TRI, revealing a trade-off between solid yield and process efficiency.

- **Implications:** Low-to-moderate reactivity feedstocks are best suited for solid residue production, providing a practical framework for selecting agricultural wastes for sustainable radiation shielding and construction applications.
- **Future work:** Further research should evaluate the radiation attenuation performance of derived char and ash in composite formulations, assess long-term durability under service conditions, and conduct life-cycle analysis to quantify environmental benefits relative to conventional shielding materials.

This study shifts biomass valorization from empirical feedstock selection toward a predictive, reactivity-driven approach for sustainable material production.

Declarations

Author Contribution

Emmanuel Amponsah: Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Writing – original draft, Visualization. Eric Clement Kotei Addison: Validation, Supervision, Review & editing. Martin Owusu-Mensah: Validation, Supervision, review & editing. Michael Commeh: Conceptualization, Resources, Laboratory support, Data collection. Stanley Kukubor:** Investigation, Resources, Writing – review & editing.

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Figures



Figure 1

A) Pyrolysis reactor with connecting tube and two condenser units; B) Temperature measurement during pyrolysis; C) Pyrolysis plant schematic diagram

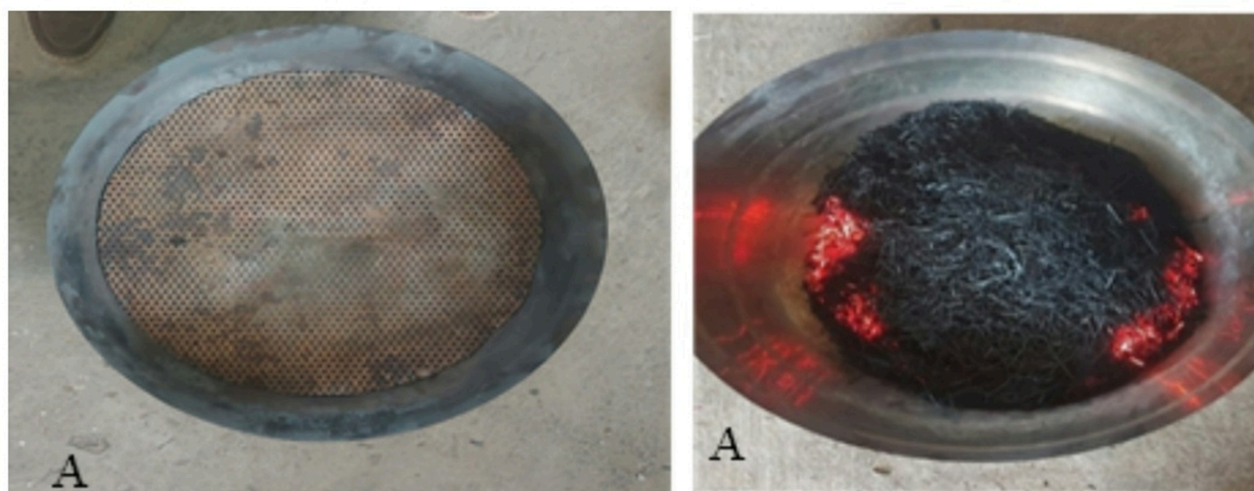


Figure 2

A) Setup for combustion and B) combustion of remaining biochar into bio-ashes

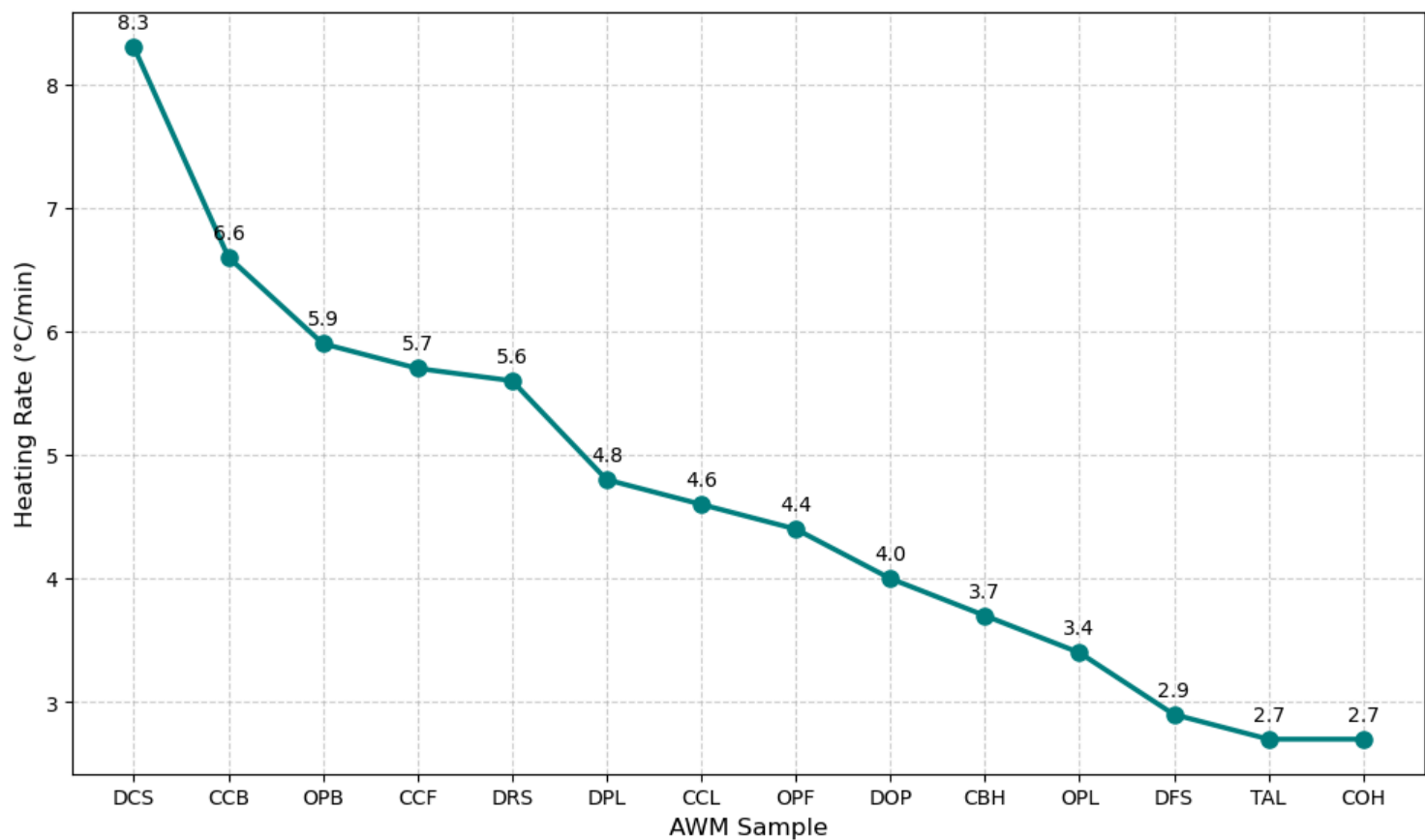


Figure 3

Heating Rate Comparison of Agricultural Waste Samples

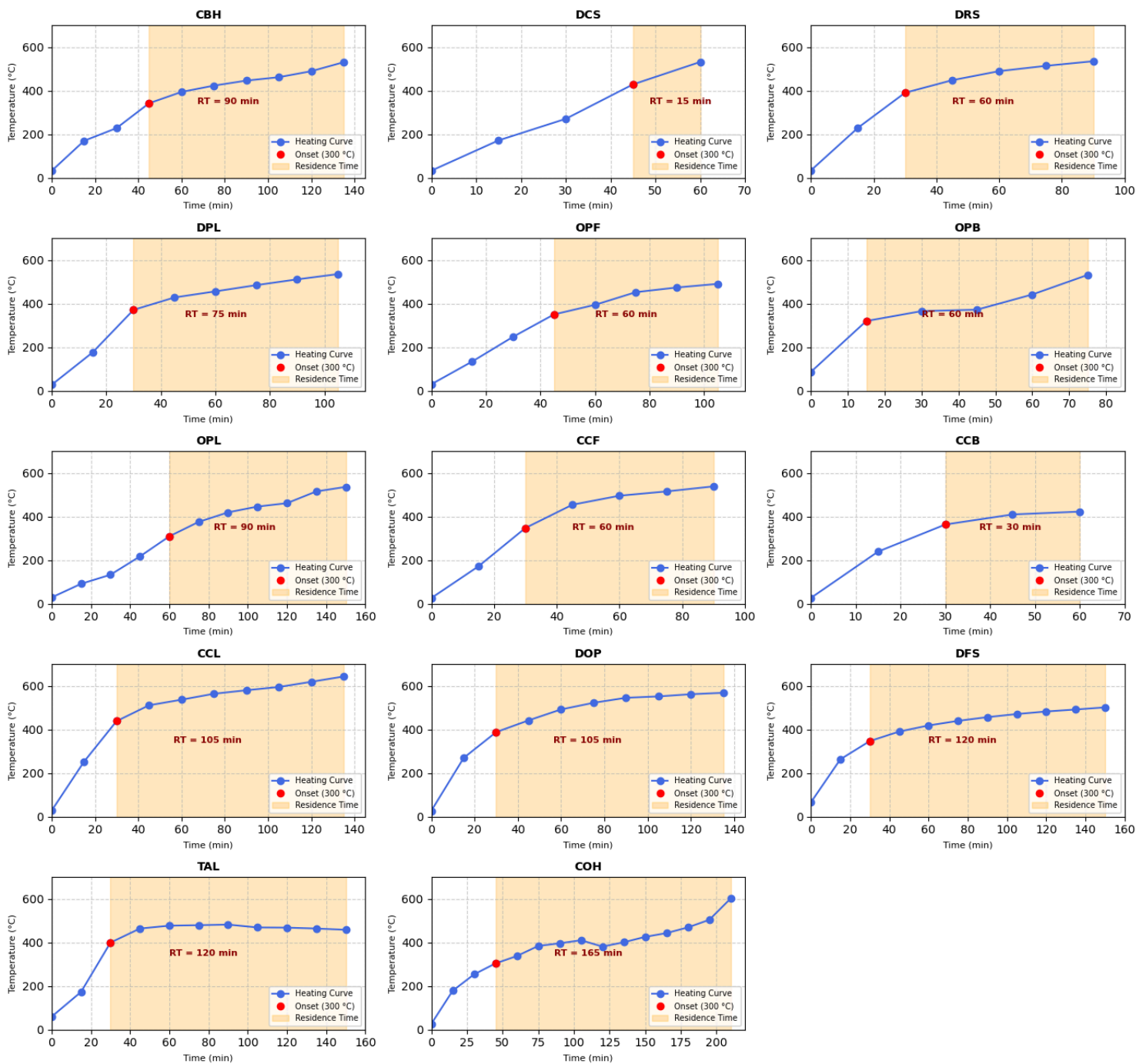


Figure 4

Temperature–Time Profiles and Heating Characteristics of Samples: *Temperature profile, onset, and residence time behaviors of feedstocks during pyrolysis, showing contrasting thermal reactivity between lignocellulosic and proteinaceous materials.*

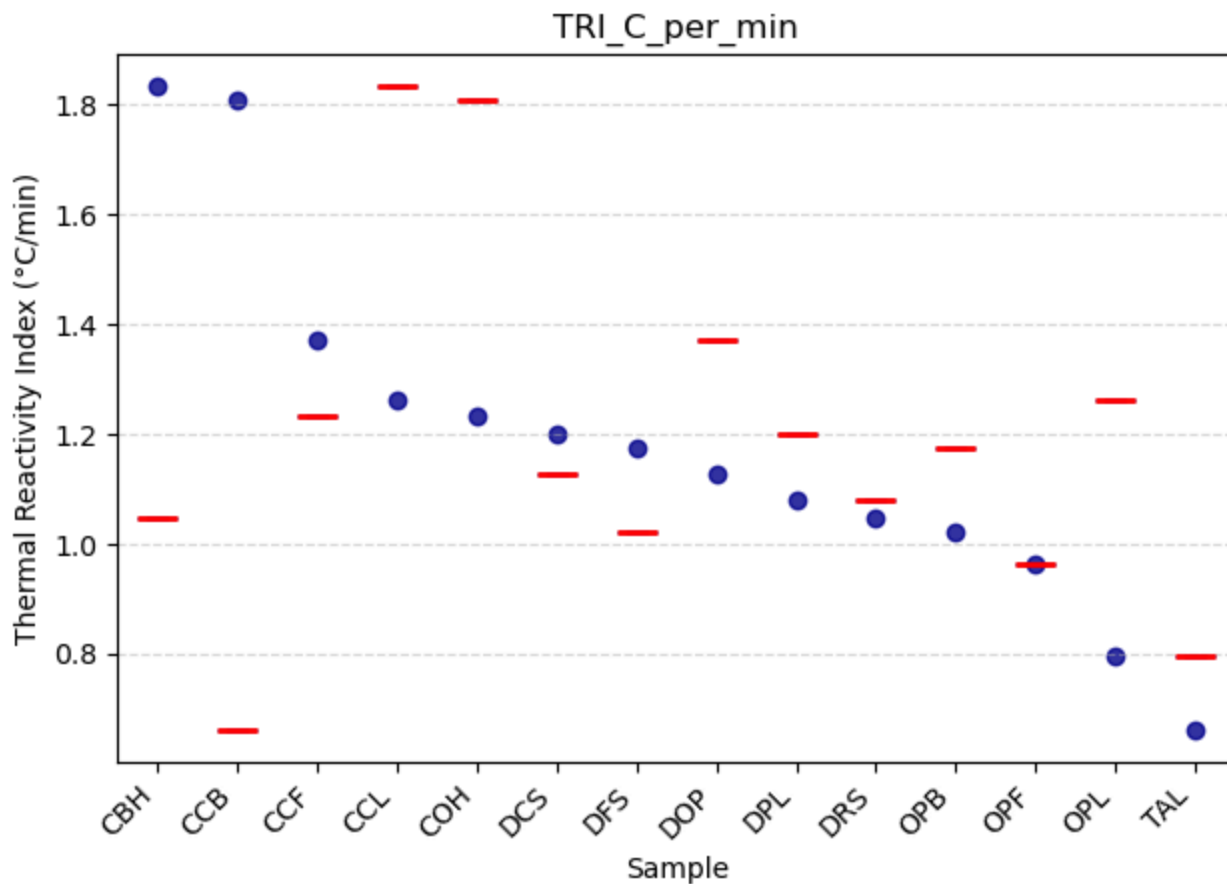


Figure 5

Thermal Reactivity Index (in °C/min) of the Feedstocks during Pyrolysis: *Showing higher reactivity in lignocellulosic residues and lower values in protein- and mineral-rich materials*

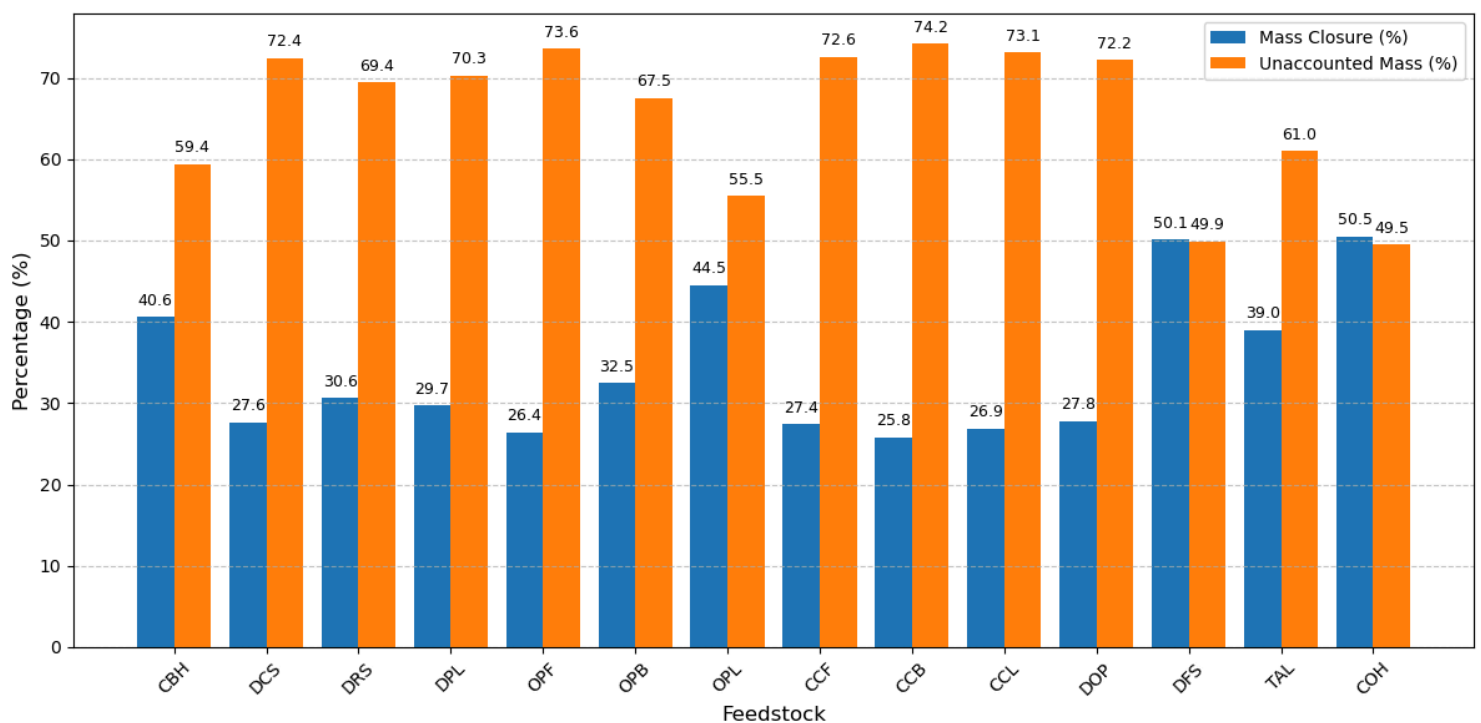


Figure 6

Mass Closure and Unaccounted Fraction of Pyrolysis Products: *The closure values represent the proportion of measurable products (char, ash, oil, and tar) recovered relative to initial feed mass. Unaccounted fractions correspond to unmeasured gaseous and light volatile losses.*

Supplementary Files

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