

Article

Pilot-Scale Slow Pyrolysis, Post-Heat Treatment, and Self-Heating Performance of Biochar Fuels Derived from Construction, Renovation, and Demolition (CRD) Wood Waste

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Abstract

The accumulation of non-recyclable construction, renovation, and demolition (CRD) wood waste necessitates sustainable management strategies, for which thermochemical valorization is a promising option. Slow pyrolysis is particularly suitable due to its high biochar yields and potential to partially replace fossil coal in energy, metallurgical, construction, and environmental applications. In this study, end-of-life CRD wood was converted into biochar using a pilot-scale vertical retort–kiln system at furnace set-point temperatures of 600 °C and 800 °C for 4 h. The biochar produced at 800 °C, which exhibited superior characteristics, was subsequently subjected to post-heat treatment at 600 °C for 30–90 min in the presence of nitrogen within a tightly sealed rotary retort–kiln assembly. Self-heating behavior was evaluated using adiabatic oven tests at 120–140 °C. Biochar properties were characterized by proximate and elemental analysis, TGA/DTG, R50, FTIR, and SEM–EDX. Increasing the pyrolysis temperature to 800 °C increased carbon content from 49.88% in the raw feedstock to 85.11% in biochar, while oxygen and hydrogen contents decreased to 5.91% and 1.52%, respectively. Van Krevelen ratios ($H/C = 0.21$; $O/C = 0.05$) indicated enhanced carbon stability, with the higher heating value reaching 30.81 MJ/kg. The thermostable fraction reached 75.18%, R50 recalcitrance index 0.57, fixed carbon 70.59%, volatile carbon 23.31%, pH 8.9, and surface area 188.33 m²/g. Post-heat treatment further enhanced aromaticity ($H/C = 0.18$; $O/C = 0.02$) of this higher pyrolysis temperature biochar, increasing its fixed carbon and stability, and reducing volatile content. Extending treatment time from 30 min to 90 min raised fixed carbon to 77–78% and thermostability to 84–85%, while volatile carbon decreased to 13–15%. Microporosity peaked at 350–380 m²/g by 75 min before declining due to pore widening. SEM and EDX analyses confirmed this structural evolution, increased carbon content, reduced oxygen, suppressed alkali metals, and enrichment of alkaline earth metals. Yield loss was highest at 90 min (20–21%), highlighting the need to balance treatment severity and biochar product yield. Both the 800 °C biochar and its post-heat-treated forms passed self-heating tests, confirming improved oxidative stability for energy and environmental applications.



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1. Introduction

Construction, renovation, and demolition (CRD) activities generate large volumes of waste, of which only 20% is recycled, with the rest ending up in landfills, including non-recyclable wood fractions such as treated, tinted, and adhesive laden wood, and drywall containing gypsum [1–3]. Furniture waste further contributes to contaminated CRD wood, which when improperly disposed of, harms the environment through greenhouse gas (GHGs) emissions, land, and water pollution [4]. Leachate from such landfills poses environmental and public health risks, yet CRD wood's heterogeneous composition has hindered both its classification and valorization.

Pyrolysis converts CRD wood into valuable products such as bio-oil, biochar, pyrolysis gas, and wood vinegar. Pyrolysis can also stabilize heavy metals into mineral complexes within the biochar matrix, reducing their mobility relative to the raw feedstock [5]. This study focuses exclusively on slow pyrolysis, which maximizes solid biochar yield relative to gasification or combustion while operating at moderate temperatures compatible with pilot-scale sealed retort systems [6,7]. As per [8], the feasibility of producing biochar from furniture wood waste was demonstrated, suggesting applicability to other CRD wood streams. Pyrolysis decomposes organic matter in an oxygen deficient environment, offering an environmentally responsible alternative to incineration [9,10]. The stable aromatic matrix derived in pyrolysis products like biochar, reduces atmospheric carbon return relative to incineration. Incineration, by contrast, offers no solid carbon product and generates metal-laden fly ash requiring separate hazardous waste management. The relative merits of pyrolysis versus incineration for feedstock like CRD wood are, therefore, application-dependent. In pyrolysis, parameters such as temperature, heating rate, particle size, and biomass residence time (BRT) influence biochar's carbon content and reactivity [11]. These, alongside secondary treatments like activation, can enhance biochar quality and physico-chemical properties [12]. CRD wood requires pre-sorting and size reduction to improve heat transfer, while upstream washing can further reduce ash and impurities [13,14]. Also, woody biomass from forestry wastes and organic municipal wastes such as furniture waste, paper, and cardboard could fall under the category of low ash biomass (<5%), whereas agricultural residues like rice husk and straw are considered high ash feedstock (>10%) [15].

Biochar must be stable and resistant to chemical and microbial degradation, assessable through incubation experiments [16]. These methods are time- and resource-intensive and may yield unreliable long-term predictions due to inaccuracies or unrealistic assumptions about biochar's behavior under open environmental conditions [17]. Carbon in biochar exists in two pools. (a) persistent and (b) semi-persistent, depending upon molecular stability, degradation resistance, and half-life under environmental conditions [18,19]. The Van Krevelen indices (H/C and O/C) from elemental analysis predict pyrolysis efficiency, biochar's organic oxygen, and stability [20]. Biochars with H/C < 0.7 and O/C < 0.6 have a half-life of at least 100 years, while O/C < 0.2 extends this to over 1000 years [21]. Both indices are influenced by pyrolysis conditions and feedstock properties [22].

Biochar reactivity poses challenges for large-scale production, affecting storage, handling, and operational risks [23]. It results from surface oxidation, internal heat buildup, and eventual thermal runaway. Key contributors include volatiles, surface functionalities, porosity, and secondary modifications like air oxidation or steam/CO₂ activation, which create exothermic zones leading to smoldering [24]. Condensed hydrocarbons or tar further catalyze oxidation, forming reactive secondary char [25]. Paint contaminants in CRD wood heighten oxidation risks [26,27]. Pre-treatments such as washing or torrefaction help reduce volatiles. Low-temperature biochars have poor oxidative stability due to high volatiles, while high temperatures improve stability but may increase oxygen adsorption and exothermicity due to enhanced microporosity [23,28]. Aromaticity improves stability,

while amorphous structures at low temperatures promote oxidation. Clay and silica in ash could reduce reactivity, while alkaline and alkaline earth metals (AAEM) and metal oxides could accelerate oxygen uptake due to their catalytic characteristics. Post-pyrolysis treatment minimizes reactive volatiles, though chemical treatments may introduce disposal challenges pertinent to salts or solvents used for activation [29]. High reactivity could lead to self-heating and limit biochar's usability.

Biochar self-heating, also known as self-ignition, auto-ignition, or self-combustion, occurs when internal heat from exothermic reactions surpasses dissipation, leading to flammability [30,31]. Contributing factors include oxygen diffusion forming reactive functional groups, oxidation of condensed volatiles generating free radicals and heat, low pyrolysis temperatures, fine particles, large stockpile volumes, increased microporosity, and very low moisture content [32–38]. Industrial-scale stockpiles face additional risks from environmental exposure, where heat loss varies across pile regions, potentially leading to smoldering and combustion. Three theoretical frameworks describe ignition in reactive solids: the Semenov model (uniform temperature, negligible reactant consumption), the Frank-Kamenetskii model (temperature gradients, non-linear thermal behavior), and the Thomas model, which extends Frank-Kamenetskii by adding convective heat exchange with ambient air [39–43]. None fully captures changes in biochar volume, moisture, and particle size within real stockpile geometries; this study therefore relies on established theory without developing new predictive models [39–43].

A promising method to enhance biochar stability and control reactivity is secondary thermal activation at 600–800 °C [44]. Unlike physical activation using air, CO₂, or steam at even higher temperatures, thermal activation focuses on eliminating residual volatiles from biochar surfaces and pores [45]. Oxygen-rich functional groups such as phenols, hydroxyls, carbonyls, and carboxylic acids, if retained, increase self-ignition risks, especially in biochars with high surface area and porosity. This is particularly relevant for CRD wood biochar, where extractives and organic residues contribute significantly to volatile content. Heat treatment reduces volatile carbon (VC), increases fixed Carbon (FC), porosity, surface area, and oxidative stability [46]. Established activation routes include CO₂, air-nitrogen, and chemical agents (KOH, NaOH, ZnCl₂) [44,47,48]; however, moderate-temperature thermal-only activation avoiding reactive gases, chemicals, and water remains underexplored and is the focus of this work. Since moderate temperature thermal activation remains largely underexplored, this work investigates biochar heat treatment post-pyrolysis, under varying time intervals, avoiding reactive atmospheres, chemicals, and water with an intention to prevent “excessive” carbon loss and eliminate downstream waste generation.

CRD wood biochar offers significant economic and environmental benefits. It stabilizes organic carbon otherwise released as CO₂ or CH₄ in landfills, functioning as a GHG reduction tool, and may also serve as landfill covers to adsorb pollutant gases like H₂S [49]. Its high pH, due to concentrated inorganics and metal salts, increases cation exchange capacity (CEC), improving nutrient, mineral, and water retention for soil fertility and remediation, especially in dry and arid regions [50]. CRD wood biochar can also adsorb heavy metals and pollutants from wastewater, with greater porosity and higher hydrophobicity proving more effective for larger molecules due to size constraints [51]. CRD wood biochar produced at high temperatures exhibits properties approaching metallurgical coal, supporting use as a carbon reductant substitute [52]. Integrated pyrolysis gas recycling also offers an energy co-product, reducing reliance on external fuel input.

Building on the pilot-scale methodology established in [53], to our knowledge no study has simultaneously characterized pilot-scale CRD wood pyrolysis across multiple temperatures, applied thermal-only post-heat treatment without chemical or reactive gas activation, and assessed self-heating behavior of the resulting biochars, accompanied by

relevant characterizations. This study tests four specific hypotheses: (1) CRD wood's heterogeneous composition necessitates upstream size segregation to ensure consistent pyrolysis performance; (2) pyrolysis temperature is the primary determinant of biochar quality at pilot scale, irrespective of feedstock variability; (3) moderate-temperature thermal activation without reactive gases, chemicals, or water can meaningfully improve biochar's fixed carbon, surface area, and oxidative stability; and (4) self-heating propensity is jointly governed by biochar physicochemical properties, particle size, packed volume, and moisture content, with pyrolysis conditions as the overriding factor. To test these, CRD wood was size-separated, pyrolyzed at 600 °C and 800 °C in a pilot retort-kiln, subjected to post-heat treatment at 600 °C for 30–90 min, and assessed for oxidative self-heating behavior across particle sizes, volumes, and moisture conditions. The findings are directly relevant to CRD waste managers evaluating valorisation pathways, biochar producers establishing fuel-grade specifications, and engineers designing safe storage and handling protocols for carbonaceous solid fuels. Future work should incorporate calibrated gas flow metering and calorimetry to quantify energy recovery, cross-validation against standardised self-heating test methods, and leaching studies to assess soil amendment and environmental suitability.

2. Materials and Methods

2.1. Preparation of CRD Wood Biomass Samples for Pyrolysis and Characterization

Non-recyclable CRD wood collected from “BRQ Fibre et Broyure”, Trois-Rivières, QC, Canada, was transported to Innofibre's factory in pails. As shown in Supplementary Figure S1, the CRD wood was mechanically sieved (Labtech vibrational sieving unit) into particle sizes of >4.5 cm, >0.7 cm, >0.5 cm, and >0.3 cm after contaminant screening and removal, offering a simple upstream conditioning approach without resource intensive procedures. Washing was avoided to prevent the leaching of contaminated wastewater from CRD wood. Chips of >0.7 cm and <4.5 cm were selected for pyrolysis based on their role in heat transfer and efficient conversion, with sieving alone sufficient to achieve the target particle size without milling or shredding. The desired biomass fraction was dried overnight at 105 °C prior to pyrolysis. A Retsch SM300 mill with a high-speed tungsten carbide rotor and screens as fine as 500 µm, or a Thomas Wiley mill with a screen of similar pore size, was used to produce fines from biomass and biochar for further characterization.

2.2. Physicochemical Characterization

Characterizations of biochars were carried out based on analysis metrics in different categories: 1, 2, and 3, each highlighting a unique objective related to physicochemical composition, stability, and permeance. These methods were followed exactly for biomass as well, whenever applicable.

2.2.1. Category 1: Chemical Makeup and Aromaticity

Proximate and elemental analysis were used to characterize chemical composition and aromaticity [54,55].

Proximate Analysis

This characterization measured ash, VC, and FC in biochar. For ash, 1 g of dry biochar fines in a crucible was heated in a muffle furnace per an adapted ISO 1171 [56] procedure: from room temperature to 105 °C at 5 °C/min for 1 h, then to 550 °C at the same rate for 6–8 h. The crucible was cooled in a desiccator and the remaining ash was weighed. For VC, 1 g of dry biochar fines was heated to 900 °C for 7 min in a sealed crucible, cooled, and weighed to measure lost carbon. VC differentiates labile carbon from other volatiles in relevant discussions. FC was calculated as $100 - (\text{VC} + \text{ash})$ on a wt%DB basis. For this

expression, the following foundational Equation (1) is adapted from [57]. However, if not represented on %DB, the humidity factor is to be considered in the equation.

$$VC + FC + \text{ash} = 100 \text{ wt\%DB} \quad (1)$$

Using this, a stability index called thermostable fraction (TSF) was calculated for biochar. The equation was adapted from [58] and [59], and it can be expressed as shown in Equation (2):

$$\text{TSF(\%)} = \left(\frac{FC}{VC + FC} \right) \times 100 \quad (2)$$

Elemental Analysis

An Elementar Vario Macro Cube analyzed 1–200 mg of dry biochar fines and biomass for elements such as carbon, hydrogen, nitrogen, and sulfur, using helium (purity > 99.996%) as a carrier gas and oxygen (purity > 99.996%) for combustion up to 1200 °C. The oxygen content was estimated by difference using the percentages of all individual elements and ash from 100%, as followed in [60]. The expression is given in Equation (3).

$$\text{oxygen} = 100 - (\text{carbon} + \text{hydrogen} + \text{nitrogen} + \text{sulfur} + \text{ash}) \quad (3)$$

2.2.2. Category 2: Oxidative and Thermal Resistance

TGA, DTG, and TGA R50 were used to quantify oxidative and thermal resistance; incubation-based methods, as described in [61], were outside the scope of this study.

TGA/DTG

To investigate weight loss of biochar or biomass as a function of temperature, a PerkinElmer TGA 8000 analyzer was employed. This device also measured proximate analysis parameters including moisture, VC, FC, and ash, requiring only 8 mg of biochar or biomass fines per vial in non-dried form. Compressed air with purity exceeding 99.996% served as the process gas. The system achieved temperatures up to 1200 °C with adjustable heating rates, and a rate of 10 °C/min up to 900 °C was applied to analyze oxidation behavior. DTG curves were obtained via first-order differentiation of the residual weight versus temperature curve (i.e., TGA curve), yielding peaks that indicate the temperature of maximum weight loss or melting, and providing insights into chemical composition and hydrocarbon framework.

TGA R50

According to [62], the oxidation resistance of biochar can be evaluated through a cost-effective method called TGA R50, a quantitative screening tool that predicts thermal stability, where a higher R50 value indicates appreciable recalcitrance. Factors such as pyrolysis temperature, heat treatment duration, and feedstock type are directly correlated with R50 values [63]. Based on R50 values, biochars are classified into three categories: Class A ($R50 \geq 0.7$) with the least degradation potential; Class B ($0.5 \leq R50 < 0.7$) with moderate degradation; and Class C ($R50 < 0.5$) representing the highest sensitivity towards degradation [64]. The R50 value was calculated from biochar's thermogram corrected for ash and moisture, using the formula and procedure in [63]. It can be expressed as in Equation (4).

$$R50 = \left(\frac{T_{50\% \text{ weight loss for biochar}}}{T_{50\% \text{ weight loss for graphite}}} \right) \quad (4)$$

Here, $T_{50\% \text{ weight loss for biochar}}$ is the temperature in (°C) of a biochar sample where it experienced exactly 50% of its weight loss from the corrected thermogram. Likewise,

$T_{50\%}$ weight loss for graphite is the theoretical temperature in ($^{\circ}\text{C}$) obtained for 50% weight loss of the reference graphite material's corrected thermogram (886°C). The same procedure was followed for the CRD wood biomass as well to establish a base value for R50 and compare it with that of biochars.

2.2.3. Category 3: Permeance

FTIR spectroscopy was used to identify surface functional groups and assess their evolution with pyrolysis temperature and PHT.

Fourier Transform Infrared Spectroscopy (FTIR)

The surface functional group distribution of biochar was analyzed using an Agilent Technologies Cary 630 spectroscope, operated with Microlab PC software version 5.8. Approximately 1 g of dry biochar fines was applied to a diamond crystal surface which was periodically cleaned with ethanol. The analysis was conducted in transmittance mode across a spectral range of $500\text{--}4000\text{ cm}^{-1}$ to identify the chemical bonds constituting the material. Baseline and peak correction were performed on the derived spectra, followed by smoothing the signals.

2.2.4. Other Characterizations

Brunauer–Emmett–Teller (BET)

The Micromeritics Tristar II, equipped with a deaerator system to eliminate impurities, measured the specific surface area and pore volume of dry biochar fines using nitrogen or helium gas physisorption. It detected pore sizes ranging from 0.35 to 100 nm and surface areas starting from $0.01\text{ m}^2/\text{g}$. If micropore volume was to be specifically computed, the t-plot method was applied to the BET data.

Metals

Metal concentrations in biomass and biochars were determined using an Agilent Technologies 4210 Microwave Plasma Atomic Emission Spectrometer (MP-AES), equipped with a nitrogen fuel source and an SPS 4 autosampler, enabling simultaneous multi-element analysis. Prior to analysis, samples ($\sim 0.25\text{ g}$) were digested using aqua regia ($3:1\text{ HCl:HNO}_3$) in a microwave digestion system at 180°C for 30 min, followed by dilution to a fixed volume with ultrapure water. All measurements were performed in analytical triplicate per sample. Relative standard deviations were within $\pm 10\%$ for AAEM elements and $\pm 15\%$ for trace heavy metals. Spike recovery tests using a certified multi-element standard solution were performed at two concentration levels. The recovery rates fell within 90–115% for all reported elements, confirming acceptable analytical accuracy.

Higher Heating Value (HHV)

The HHV of CRD wood biomass and biochars was calculated using the method described in [65,66]. This method links calorific value to the elemental composition of the samples derived via elemental analysis.

pH

The method in [67] was adapted to measure the pH of biochars. Dry biochar fines and demineralized water (DMW) at a 1:10 weight ratio, were mixed with a magnetic stirring plate for 60 min. Post-shaking, a bench-top pH analyser was used to measure the pH of the biochar suspension.

Scanning Electron Microscopy—Energy Dispersive X-Ray Spectroscopy (SEM-EDX)

The development of porous channels, surface roughness or smoothness, pore clogging, and surface concentration of metallic and non-metallic elements in biochar were analyzed using SEM-EDX. All biochars were tested internally at the microscopy laboratory at I²E³, UQTR, using a Hitachi electron microscope SU-70 attached to an X-ray analyzer. Magnifications of 50X, 100X, 250X, 500X, and 1000X, with a 15 kV acceleration voltage under vacuum, were adopted for this characterization.

2.3. Slow Pyrolysis at Pilot-Scale

In the pilot-scale retort-kiln assembly, CRD wood with particle sizes ranging from >0.7 cm to <4.5 cm was subjected to pyrolysis. The process was conducted with a BRT of 4 h at furnace set-point temperatures of 600 °C and 800 °C, respectively. Each batch operation accommodated 20 kg of biomass feedstock to produce biochar. Due to equipment availability and feedstock supply constraints at the pilot facility, each pyrolysis condition (600 °C and 800 °C) was conducted as a single production batch. Full production-batch replication is recommended as a priority in future pilot-scale validation studies of this system.

Pyrolysis Experimental Setup

The experimental set-up is depicted in Figure 1. A total of 20 kg of prepared CRD wood with a particle size range of <4.5 cm and > 0.7 cm was loaded into a cylindrical retort.

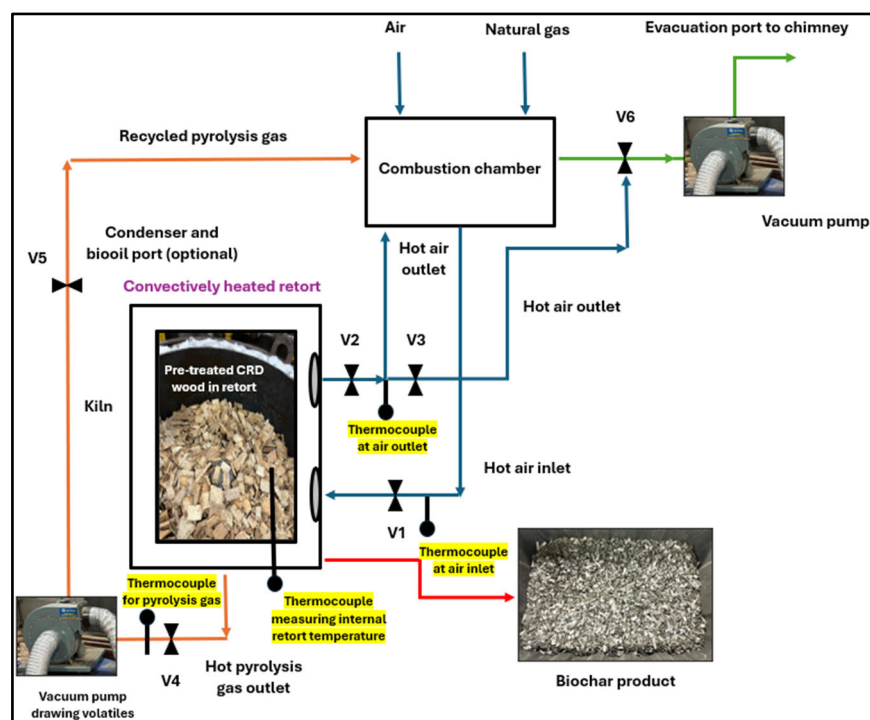


Figure 1. Pilot retort-kiln process flow diagram for CRD wood pyrolysis, an integrated method. The hot air circulates externally around the sealed retort and does not enter the retort's interior. Thermocouples positioned at V1, V2, V4, and inside the feedstock bed monitor the temperature at each stage of the process.

The feedstock was manually mixed on a tarpaulin using rakes prior to loading, then transferred into the retort. The retort was sealed as tightly as possible using screws to reduce infiltration of atmospheric air and mechanically placed inside the kiln in a fixed vertical configuration. Throughout pyrolysis and cooling, the retort always remained stationary and did not rotate. Also, no internal agitation or mixing device was used inside

the retort. It remained sealed throughout the heating and holding stages and was only opened once it reached ambient temperature.

Hot air from the combustion chamber circulated through the clearance space between the retort exterior and the kiln wall via valve V1, providing indirect convective heating to the sealed retort. The retort interior was not exposed to this air stream at any point during the run. The heating air exited via valve V2 and returned to the combustion chamber, closing the external heating loop. A suction pump continuously withdrew pyrolytic volatiles from inside the retort via valve V4, maintaining the retort interior under negative pressure throughout the run. Internal retort pressure was monitored continuously. The extracted pyrolysis gas was recycled to the combustion chamber as supplementary fuel before the resulting hot air re-entered the external heating loop via V1. Continuous suction was followed based on an aim of reducing the settling of tarry volatiles on the biochar surface, and limiting their residence time inside the retort for avoiding secondary reactions aiding the formation of PAHs. The system was designed so that recycled pyrolysis gas automatically reduced the natural gas demand of the furnace.

Four thermocouples were used to monitor temperature during each run. One thermocouple, lodged into the tubing near valve V1, measured the temperature of incoming hot air entering the kiln clearance space. A second thermocouple, lodged into the tubing near valve V2, measured the temperature of hot air exiting the clearance space back to the combustion chamber. A third thermocouple, lodged into the tubing near valve V4, measured the temperature of pyrolysis gas extracted from the retort. A fourth thermocouple was suspended directly within the feedstock bed inside the retort, measuring the internal retort temperature within the reaction zone. The pyrolysis gas phase temperature recorded near V4 is consistently lower than the reaction zone temperature recorded inside the initial feedstock bed. This difference reflects the distinct heat transfer paths to each sensor. The gas phase thermocouple sits downstream in the extraction tubing, where volatiles have already lost sensible heat to the tubing walls before reaching the sensor. The two readings, therefore, represent different points in the heat transfer pathway, not a single uniform retort temperature.

Continuous extraction of hot pyrolysis volatiles under negative pressure represents an active heat removal pathway from the retort interior, since each unit of gas leaving the retort carries sensible heat with it. This continuous loss of thermal energy, together with the endothermic nature of primary pyrolysis reactions, contributes to the retort interior lagging behind the furnace set-point temperature throughout the run. Where bio-oil characterization was required, pyrolysis gas could be diverted through a portable condensation setup at valve V5. In emergency conditions, all valves were closed and valve V6 opened to a suction pump that displaced hot air to a dedicated evacuation chamber. As pyrolysis approached completion and gas evolution declined, natural gas input to the furnace was increased to sustain kiln temperature until shutdown. The retort was then mechanically removed from the kiln to cool overnight to ambient temperature, after which it was opened the following day to recover the biochar.

2.4. Secondary or Post-Heat Treatment (PHT): Experimental Set-Up

As depicted in Figure 2, the reactor setup for biochar PHT consisted of a horizontal rotary retort-furnace assembly with an internal diameter of 32 cm, a length of 160 cm, and a total volume of approximately 129 L, capable of processing up to 5 kg (or in volume terms, 30% of the void volume) of biochar per batch normally.

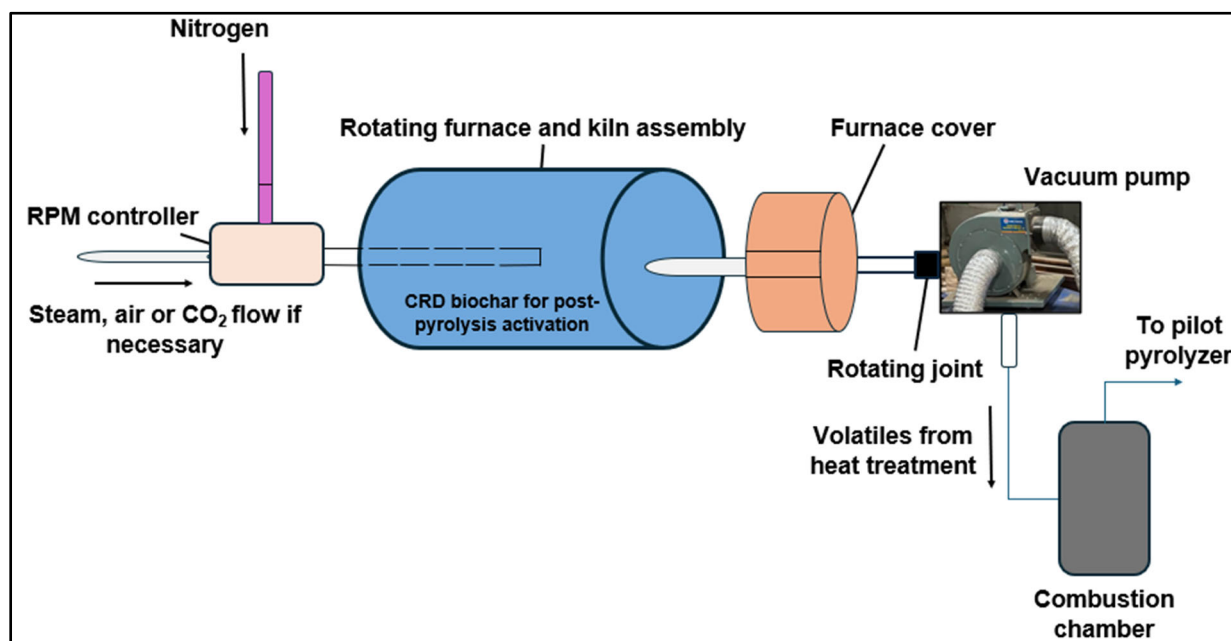


Figure 2. Instrumentation setup for biochar PHT. The vacuum unit operates as a forced-exhaust system for the removal of pyrolytic volatiles at near-atmospheric pressure.

The system had three temperature controllers connected to K type thermocouples monitoring furnace set-point temperatures at three distinct zones (T1, T2, T3) of the retort. To prevent volatiles settling on biochar during PHT, a forced-exhaust vacuum pump at the exit gas zone withdrew volatiles and redirected them to the combustion chamber to supply process energy, with operating pressure within the retort remaining near-atmospheric throughout. Rotary motion ensured uniform heat distribution throughout the biochar framework and its internal pores, reducing surface heating effects. A rotational speed of <10 rpm was found to be optimal, as higher speeds caused excessive shearing, fines release, and entrainment by the vacuum suction unit, making lower rpm preferable to maximize passivated biochar yield. For PHT, 2 kg of biochar from pilot pyrolysis was loaded into the rotary retort, sealed, and flushed with nitrogen gas to eliminate reactive atmospheres. Then the furnace was switched on with the set-point temperature logged into the control panel. The retort design aimed to prevent air penetration upon proper sealing, minimizing interference from ambient oxygen. After PHT, the furnace was switched off and biochar was naturally cooled to room temperature inside the retort, with rotation continued for faster heat dissipation. The vacuum suction unit remained active until biochar was fully recovered for analysis.

A PHT trial at 600 °C for 30 min was first conducted on B800 to verify VC reduction and FC increase. Higher PHT temperatures were avoided to limit yield loss and because high-temperature activation via chemical or physical means has been widely demonstrated. Self-heating tests were conducted post-PHT to assess oxidative stability.

Only if the aforementioned hypothesis was validated would subsequent longer residence times be tested at the same temperature, with the necessary characterizations to correlate heat treatment duration with biochar properties.

2.5. Preparation of Biochar Derived from Slow Pyrolysis and PHT for Self-Heating Tests

Biochar lumps and fines (<500 µm) were compared to assess particle-size effects on self-heating behavior. Lumps were collected from the cooled retort, while fines were produced by vibrational sieving (Supplementary Figure S2). When very dry material (<1%

moisture) was required, lumps were oven-dried at 105 °C before sieving; dry lumps were used directly. The same procedure was applied to PHT biochar.

Self-heating propensity was evaluated using basket heating tests in thermostatically controlled adiabatic ovens, following the UN 33.4.6 method with a minor adjustment to test duration (Supplementary Figure S3). Square steel mesh baskets (0.5 mm mesh, 10.16 cm side length) containing biochar samples were enclosed in steel cages, suspended in oven racks [30]. The samples were held at either 140 °C (short-moderate exposure duration) or 120 °C (long exposure duration). A central K-type thermocouple connected to a 200 °C alarm monitored temperature spikes, while a second central thermocouple logged temperature profiles of biochar samples. Tests were performed on pilot-scale and PHT biochars across variations in particle size (lumps or fines), basket fill volume (half or full), and moisture content (as is, dry, wet).

Typically, a test is designated as passed when the central thermocouple reading remains within 10 °C of the oven set-point temperature and shows no sustained exponential rise. It is considered failed when the temperature increases continuously and exponentially beyond the set-point, trending toward or exceeding 200 °C, indicating the onset of smoldering or fire. Each test was done as triplicates and the mean/average readings are reported.

3. Results and Discussion

3.1. Characterization of CRD Slow Pyrolysis Biochars from Pilot-Scale and PHT Trial Run

CRD wood biochar properties, covering chemical composition, surface structure, stability, metals, and thermal/structural analyses, are summarized before and after the PHT run. Comparisons to untreated CRD wood are included only when needed.

3.1.1. Physicochemical Properties

As shown in Table 1, the proximate and elemental analysis parameters of biochar varied with increasing pyrolysis temperature and BRT.

Table 1. Physicochemical, stability, and calorific characteristics of CRD wood biomass and biochars. Proximate analysis values for biomass and biochars (B600, B800, HTB800) are expressed as wt%DB, while coal and coke values are reported on an as-received basis (wt%) from [68]. Elemental analysis results are expressed as wt%DB for all samples. B600 denotes biochar produced at a furnace set-point temperature of 600 °C, and B800 denotes biochar produced at a set-point of 800 °C. After 30 min of PHT, the improved B800 is termed HTB800. “B” and “HTB” represent biochar and heat-treated biochar, respectively.

Metrics	CRD Wood Biomass	B600	B800	HTB800	Coal	Coke
Proximate analysis (wt%) for coal and coke, (wt%DB) for CRD wood, B600, B800, and HTB800						
Moisture	-	-	-	-	6	1.34
VC	82.35	27.74	23.31	16.19	41.50	10.30
FC	16.48	67.78	70.59	76.33	39.60	88.00
Ash	1.17	4.48	6.10	7.48	12.90	0.40
Elemental analysis (wt%DB)						
C	49.88	80.16	85.11	87.00	80.70	87.00
H	6.12	1.83	1.52	1.27	5.80	3.50
S	0.10	0.65	0.56	0.62	3.60	7.90
N	0.99	0.97	0.80	1.05	1.20	1.10

Table 1. *Cont.*

Metrics	CRD Wood Biomass	B600	B800	HTB800	Coal	Coke
O	41.74	11.91	5.91	2.58	8.70	0.50
Stability indices: Van Krevelen parameters (no units), TSF (%), and R50 (no units)						
H/C	1.47	0.27	0.21	0.18	0.86	0.48
O/C	0.63	0.11	0.05	0.02	0.08	0.004
TSF	16.68	70.96	75.18	82.50	48.83	89.52
R50	0.52	0.57	0.58	0.58	N.A. *	N.A. *
Calorific value (MJ/kg)						
HHV	20.28	28.86	30.81	31.49	20.60	27.20
BET surface area (m²/g) and micropore volume (cm³/g)						
BET surface area	N.A. *	71.35	188.33	202.09	4.13	4.40
Micropore volume	N.A. *	0.08981	0.09570	0.09652	N.A. *	N.A. *
Reference	Present study	Present study	Present study	Present study	[68]	[68]

* N.A.— Not assessed.

A consistent 250–300 °C gap between the furnace set-point and the internal retort thermocouple was observed across both pyrolysis runs (Supplementary Figure S4). As the biomass bed contracts during carbonization, the thermocouple may lose contact with the solid matrix and become suspended freely in the headspace, recording headspace gas temperature rather than solid-phase temperature. Pyrolysis is conduction-dominated. Heat conducts from the retort wall directly into the solid bed through physical contact. Headspace gas, by contrast, is heated indirectly through convection and radiation from the wall and solid surfaces. The solid in direct wall contact, therefore, approaches wall temperature more readily than the suspended headspace gas. Solid-phase temperature exceeding headspace gas temperature is a direct consequence of this differential. This interpretation is independently confirmed by AAEM volatilization data where >80% reduction in B800 may have required higher solid-phase temperatures than observed. The biochar designations B600 and B800 are, therefore, retained as furnace set-point identifiers, where sustained measurement of internal retort temperature is not practical in the above situation. Readers comparing these results with studies using directly embedded probes should account for this systematic difference, acknowledged as a limitation of the current pilot-scale configuration.

For a larger mass of feedstock, both biochars exhibited a carbon content of >80%. CRD wood's dyes and resins may have introduced heteroatoms upon pyrolysis, consistent with the elevated sulfur and nitrogen in B600. Progressive decomposition of VC likely exposed previously bound organometallics (e.g., Ca-O-C, Na-O-C), concentrating ash and shifting pH to 8.1, and reflecting a probable loss of protonic surface functionalities. At 600 °C, FC stabilized alongside early aromatic structure formation, with a TSF of 70.96% confirming meaningful thermal conversion.

Increasing pyrolysis temperature to 800 °C via B800 drove further deoxygenation and dehydrogenation, with Van Krevelen parameters (H/C = 0.21; O/C = 0.05) confirming heightened aromaticity and carbon enrichment [69,70]. These values satisfy IBI guidelines for different biochar applications (H/C < 0.7; O/C < 0.4) [71]. However, for carbon sequestration, long-term incubation studies are needed to substantially validate biochar stability. The higher HHV relative to CRD wood reflects concentration of energy-dense C–C and C–H bonds, supporting its use as a fuel substitute [71]. The surface area of

188.33 m²/g may have arisen from gradual volatilization of holocellulose and lignin at the same 4 h BRT, favoring enhanced porosity [72]. Biochar yields were 30% (B600) and 25% (B800), respectively.

Further, PHT at 600 °C for 30 min (HTB800) induced a second phase of dehydration, dehydrogenation, and deoxygenation, further concentrating aromatic carbon and reducing chemical instability [73–77]. This is evidenced by improved Van Krevelen parameters (H/C 0.18; O/C 0.02) and a 9.7% TSF gain, confirming well-ordered, thermally stable aromatic structures. The resulting FC of 76.33% aligns with woody biomass-derived biochars, consistent with the known VC-FC-H/C interdependence, where H/C_{organic} serves as a carbon-centric stability predictor [74–77]. The elevated pH of 9.3 reflects progressive loss of acidic surface functionalities, while the HHV of 31.49 MJ/kg and surface area gain to 202.09 m²/g (+7.3%) reinforce suitability for energy and metallurgical applications [74–77]. The ~15% yield loss at 30 min underscores the need to optimize activation severity against yield retention.

Benchmarking Against Metallurgical Coal and Coke: Industrial Application Potential

From Table 1, B600, with slightly higher oxygen content and O/C ratio, exhibits properties comparable to metallurgical coal, while B800 surpasses all key characteristics of metallurgical coal, making it a stronger, sustainable substitute. Lower ash content of CRD wood biochars can also conserve product quality from the metallurgical sector, with fewer impurities in the final metal. HTB800 closely matches specific metallurgical coke grades, sharing similar elemental analysis properties including equivalent carbon, lower hydrogen (H/C), nitrogen, and sulfur, which helps reduce NO_x and SO_x emissions. However, HTB800 contains more oxygen and a higher O/C than coke. Coke also remains superior in terms of lower volatile content, higher FC, and thermal stability (via TSF). Biochars B600, B800, and HTB800 all exhibit higher HHV than coal and coke, indicating enhanced fuel efficiency [68]. Bulk density of B600, B800, and HTB800 was between 200 and 600 kg/m³ due to decomposition of moisture, combustible volatiles, and concentration of carbon-rich, dense compact structures [78]. Higher bulk density could reduce biochar friability, making it denser and more resistant to weathering due to ordered crystallite formation [79]. Increased heat treatment severity and devolatilization led to more micropore formation with reduced meso- and macropores, alongside shrinkage and volume reduction [79]. Overall, these results validate that thermal-only PHT, without chemical reagents or reactive gases, is sufficient to advance B800 to near-coke grade properties, demonstrating a resource-lean activation pathway with direct industrial relevance.

3.1.2. Metals

Inherent AAEM in CRD Wood Biomass

As part of the physicochemical characterization, the metal content in CRD wood biomass, B600, B800, and HTB800 was analyzed as shown in Supplementary Table S1. CRD wood biomass ash contains a significant metal fraction, primarily AAEM (Na, K, Ca, Mg, Ba) and heavy metals (Pb, Ni, Cu, Cd, Cr). These metals interact with biomass carbon and under prolonged BRT could alter reaction pathways, increase gas production, and induce secondary char formation during pyrolysis [80]. While secondary char formation can enhance biochar yield, it is rich in volatiles originating from cracking tarry compounds or condensed volatiles, contributing to oxidative instability and self-heating risks. AAEM salts such as carbonates, sulfates, and nitrates concentrate in biochar, influencing chemical properties including pH increase from 8.1 (B600) to 8.9 (B800), as AAEM in ash substitutes biomass protons in phenolic, acidic, or carbonyl groups, leading to salt formation [15]. The role of ash in biochar self-heating remains an important area for further study.

AAEM dominated CRD wood metal content (87%), with alkaline earth metals (Ca, Mg, Ba) accounting for ~60% and alkali metals (K, Na) ~27%. AAEM concentration dropped sharply with increasing pyrolysis temperature. There was a 78% reduction in AAEM in B600 and 85% in B800; consistent with volatilization at high temperatures. In HTB800, divalent Ca, Mg, and Ba dominated residual AAEM, suggesting PHT selectively volatilised the more mobile monovalent alkalis. Heavy metals (Cd, Ni, Cu) showed increasing persistence with pyrolysis temperature, probably stabilizing into mineral complexes that could reduce their leaching risk. However, no leaching tests were conducted in this study, and future validation is required.

Cr and Cu concentrations have direct consequences for energy use. Both metals partially volatilize above 800 °C, entering the flue gas as particulate and vapor-phase species. These biochars are therefore suitable for energy applications only with emission-control systems (fabric filters or electrostatic precipitators for particulates; wet scrubbers for vapor-phase metals). At low co-firing ratios (<20% with coal), metal emissions scale proportionally with blend level. For metallurgical reductant use, Cr and Cu partition into the slag phase during smelting (>1400 °C), where they are already accommodated in existing waste-handling streams. Open disposal or landfilling is not recommended. Appropriate end-of-life pathways are energy recovery, metallurgical use, or controlled/engineered soil-amendment systems, contingent on leaching and risk-assessment regulations.

Effect of Inherent AAEM in CRD Wood Biomass on Pyrolysis Equipment

The presence of AAEM in CRD wood can lead to reactor slagging, fouling, and bed agglomeration as illustrated in Supplementary Figure S6. These phenomena share a common origin in AAEM composition and thermal behavior during pyrolysis. Slagging occurs when elevated temperatures melt ash constituents into glassy, clinker-like residues that are difficult to remove [81]. K and Na bring down ash melting temperatures, promoting clinker formation, while Ca, Ba, and Mg counteract this by elevating melting points [82]. CRD wood's AAEM is reportedly ~60% Ca, Mg, and Ba, suggesting some inherent slagging resistance. However, Ba is typically a trace constituent in biomass ash, and its meaningful contribution to melting-point elevation at realistic concentrations is not well established. The absence of substantial Si further limits ash stabilization. Unlike herbaceous feedstocks where Si delays thermal degradation, CRD wood is better classified as “Ca, K-rich, Si-lean” rather than “Si, Ca-rich, K-lean” [83]. Fouling, driven by K and Na volatilization and subsequent alkali chloride/sulphide/phosphide condensation on reactor surfaces, is partly mitigated by CRD wood's low S, N, and P content, which reduces the formation of corrosive acidic species above 700 °C [84–87]. Bed agglomeration, typically initiated by alkali-silicate interactions [84,88], was not encountered in these experiments, which is unsurprising given that no bed material or heat carriers were employed.

3.1.3. TGA/DTG/TGA R50

To analyze the TGA results, weight loss curves of biomass and biochars were examined as a function of temperature during thermal degradation. Four samples—CRD wood biomass, B600, B800, and HTB800, were tested under an air atmosphere with a heating rate of 10 °C/min. The characterization aimed to evaluate the decomposition of residual organic matter, the stability of biochar carbon against thermal degradation, and the influence of ash content on biochar behavior. These are collectively shown in Figure 3.

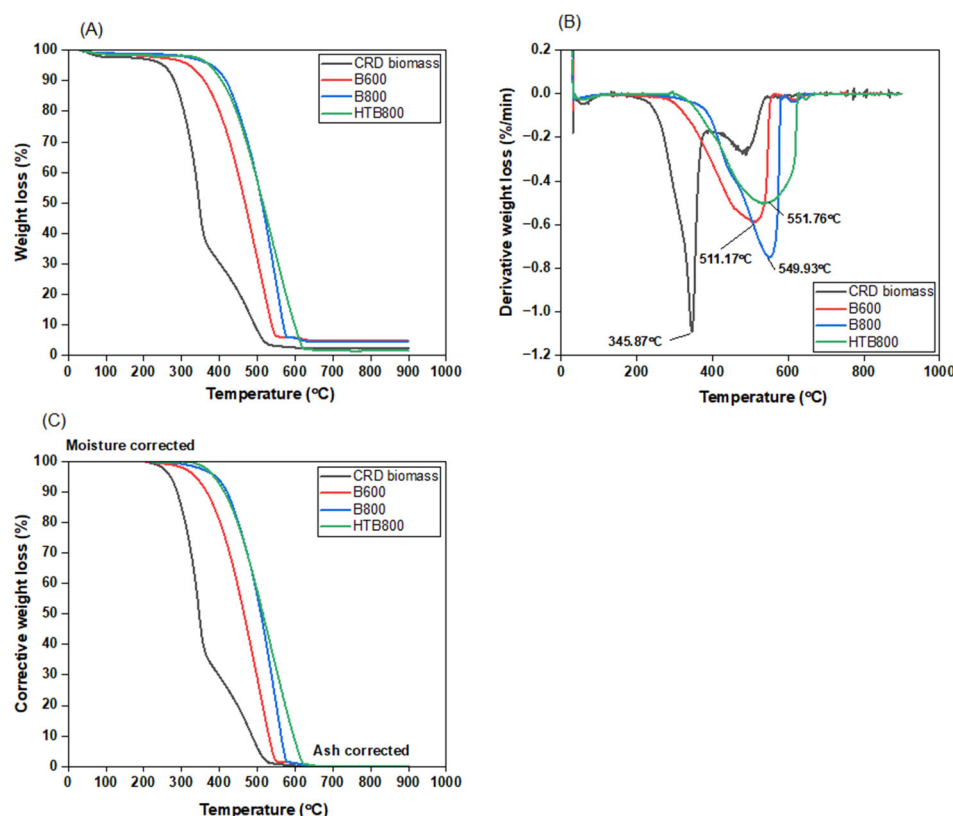


Figure 3. Thermal decomposition analysis of CRD wood biomass, B600, B800, and HTB800: (A): TGA curves; (B) DTG and associated melting temperatures; and (C) moisture and ash corrected TGA for calculating R50 index.

CRD wood biomass exhibits three distinct stages of decomposition during TGA as shown in Table 2. Below 150 °C, moisture and light extractive loss accounted for minimal weight reduction. Between 200 and 400 °C, major holocellulose breakdown dominated, yielding levoglucosan, CO, CO₂, and light gases [89]. All biochars showed reduced weight loss in these first two stages, reflecting advanced carbonisation and depleted VC relative to biomass. The marginally elevated second-stage loss in HTB800 is attributed to loosely attached residual volatiles from PHT remaining on pore surfaces rather than incomplete carbonisation. Peak degradation for all biochars occurred between 400 and 600 °C. DTG melting temperatures increased progressively with thermal treatment intensity, reaching 511 °C for B600, 550 °C for B800, and 552 °C for HTB800. This rightward shift reflects growing aromatic condensation and the higher bond dissociation energy required to cleave increasingly crystalline carbon structures [90]. Lignin depolymerisation, initiated in the 200–400 °C zone, reached completion within this phase [91]. HTB800 showed an 8.02% weight loss above 600 °C, attributed to decomposition of weakly aromatised carbon fractions and thermally labile ash constituents that survived PHT conditions.

Numerical deconvolution of the DTG curves into Gaussian or Fraser–Suzuki component peaks would improve the quantification of overlapping holocellulose and lignin contributions in the 200–600 °C zone. Given the heterogeneous, multi-component nature of the CRD feedstock, this refinement is recommended for future work.

From Figure 3C, R50 increased from 0.52 (B600) to 0.57 (B800) and 0.58 (HTB800), placing all biochars within Class B ($0.5 \leq R50 < 0.7$) according to the analysis procedure fully compliant with [63]. The thermograms were corrected for moisture and ash, and the graphite reference fixed at 886 °C. The marginal R50 increase, despite substantial improvement in H/C (from 1.83 in biomass to 0.21 in B800) and O/C (from 0.63 to 0.05),

reflects a known sensitivity limitation. The R50 is governed primarily by the degradation peak in the 400–600 °C zone, controlled by lignin-derived aromatic structures that shift relatively less between 600 °C and 800 °C pyrolysis. TSF, by contrast, showed a more resounding response, rising from 16.68% in biomass to 82.5% in HTB800. R50 and TSF correlated positively with FC and negatively with H/C, O/C, and VC, consistent with progressive deoxygenation and aromatization.

Table 2. TGA weight loss (%) per thermal stage for CRD wood biomass and biochars. Values are reported to two decimal places.

Sample Analyzed	Weight Loss in Each Phase of TGA (%)			
	First Phase (<150 °C)	Second Phase (200–400 °C)	Third Phase (400–600 °C)	600–900 °C
CRD wood biomass	2.38	66.95	27.80	0.09
B600	1.58	18.11	74.33	1.01
B800	1.07	5.83	87.40	1.09
HTB800	1.56	7.16	81.71	8.02

3.1.4. FTIR

FTIR spectral analysis of B600, B800, and HTB800 used band assignments from [92,93] to identify functional groups and their variations with increasing pyrolysis temperature and secondary treatment. The analysis is presented in Figure 4.

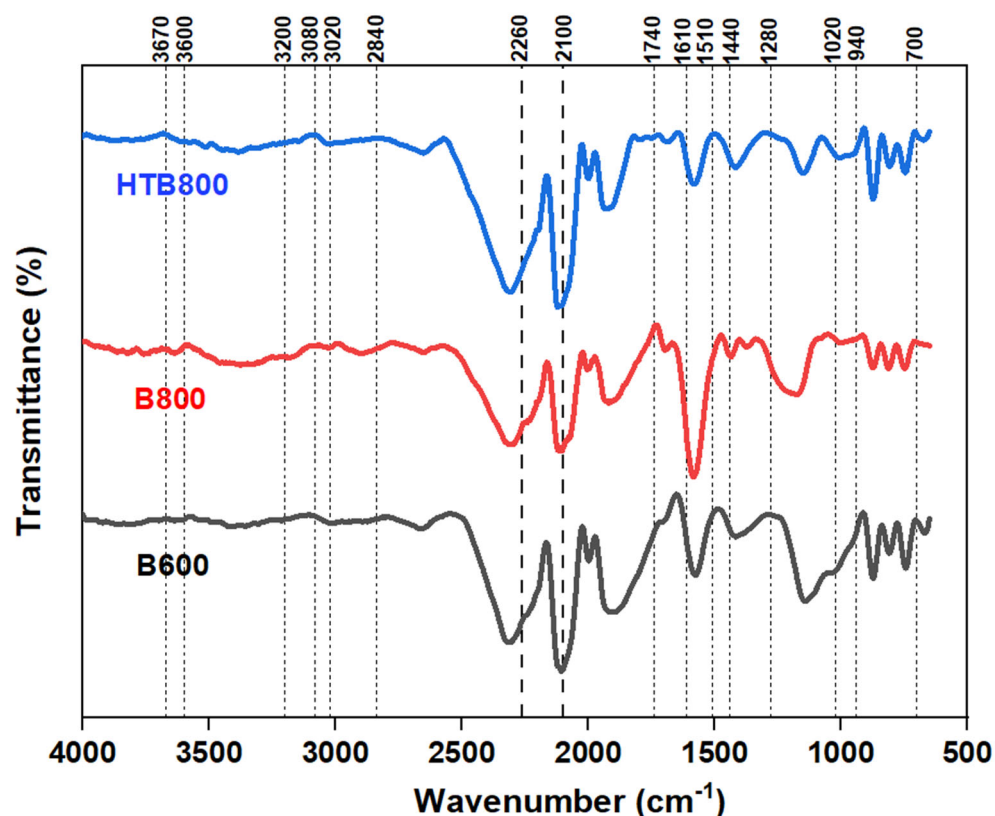


Figure 4. FTIR transmittance spectra of B600, B800, and HTB800, illustrating key functional group assignments.

FTIR spectra across all biochars reflect a progressive loss of oxygen-bearing functional groups and consolidation of aromatic structure with increasing pyrolysis temper-

ature and heat treatment. Aromatic C-H bending ($700\text{--}840\text{ cm}^{-1}$) and O-H vibrations in metal/mineral-O-H linkages ($800\text{--}940\text{ cm}^{-1}$) were present across all samples; the latter intensified in HTB800 as labile hydrocarbon decomposition concentrated inorganic constituents in the residual matrix. Diminishing peak intensity in the $1020\text{--}1280\text{ cm}^{-1}$ zone indicates progressive loss of polysaccharide-associated C-O and C-OH functionalities, with near-absent signals in B800 and HTB800 consistent with advanced decarboxylation, decarbonylation, and cracking reactions. B600, retaining more surface oxygenates due to milder conversion, may offer higher CEC potential, though this remains speculative without direct CEC measurements [50].

Aromatic backbone development is evidenced by O-H bending in phenols and C-H deformations below 1440 cm^{-1} , intensifying toward HTB800. Notably, B800 shows stronger C=C stretching ($1510\text{--}1610\text{ cm}^{-1}$) than HTB800, suggesting greater aromatic maturation and hydrophobicity [94]. The comparatively lower intensity in HTB800 here implies that post-heat treatment promotes conjugation rather than further aromatization. C=O vibrations ($1740\text{--}2100\text{ cm}^{-1}$) from lignin-derived aldehydes, ketones, and esters diminish in B800 and HTB800. C $\equiv$ C stretching ($2100\text{--}2260\text{ cm}^{-1}$) peaks in HTB800, confirming a positive relationship between heat treatment intensity and multi-aromatics development. Residual aliphatic C-H vibrations ($2840\text{--}3020\text{ cm}^{-1}$) signal incomplete polymer decomposition [95], while aromatic C-H stretching ($3020\text{--}3080\text{ cm}^{-1}$) confirms progressive carbonization from B600 to HTB800. The absence of distinct peaks beyond 3020 cm^{-1} indicates minimal hydrogen-bonded O-H groups and low residual moisture in high-temperature biochars [94,95].

3.1.5. SEM-EDX

To explain the positive impacts of PHT on slow pyrolysis biochar, SEM analyses of only B800 [Figure 5A–C] and HTB800 [Figure 5D–F] were considered, as they outlined some significant findings.

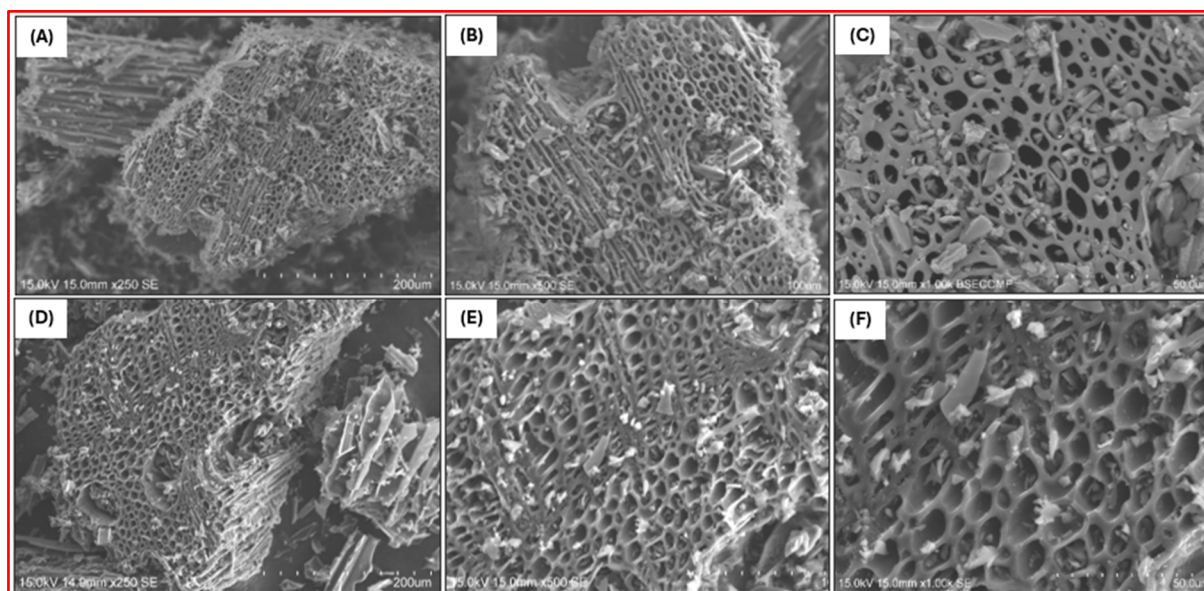


Figure 5. SEM micrographs of (A) 250X, (B) 500X, and (C) 1000X-B800, and (D) 250X, (E) 500X, and (F) 1000X-HTB800, illustrating the effect of PHT.

Micrographs revealed a rough, porous network at 250X and 500X magnifications for both biochars. Due to the long BRT and controlled heating rate, no sudden intra-particle explosions occurred, resulting in non-widened pore sizes. At 1000X magnification for B800 [Figure 5C], some hierarchical porosity was observed despite lower surface area, contrary to the findings in [96], where hierarchical porosity enhanced specific surface area. Some

pores appeared clogged with settled residual tar or ash constituents, given CRD wood's sizeable AAEM content. This is in line with [97] where it was noted that condensed volatiles can settle in pores and transform during secondary pyrolysis or carbonization cycles. In HTB800, PHT facilitated gas escape (e.g., CO_2 , CO , CH_4 , H_2O), volatilization of weak organics, and densification of microporosity, forming interconnected porous structures [Figure 5F] amid graphitized carbon, consistent with [98]. Glossy indentations across HTB800 may represent desorbed inorganic elements. These could have initially been intercalated within the matrix and later volatilized, leaving well-defined unclogged spaces following a pore reaming-like effect, while thermal activation also smoothened surface textures due to enhanced carbonization.

Unlike conventional metal salt impregnation approaches [99,100], AAEMs naturally present in CRD wood may have enabled mild in situ activation, improving surface area without introducing additional reactive surface groups. EDX confirmed a reduction in oxidative surface groups in HTB800 (Figure 6 (bottom)), supporting PHT's role in enhancing stability with minimal chemical intervention.

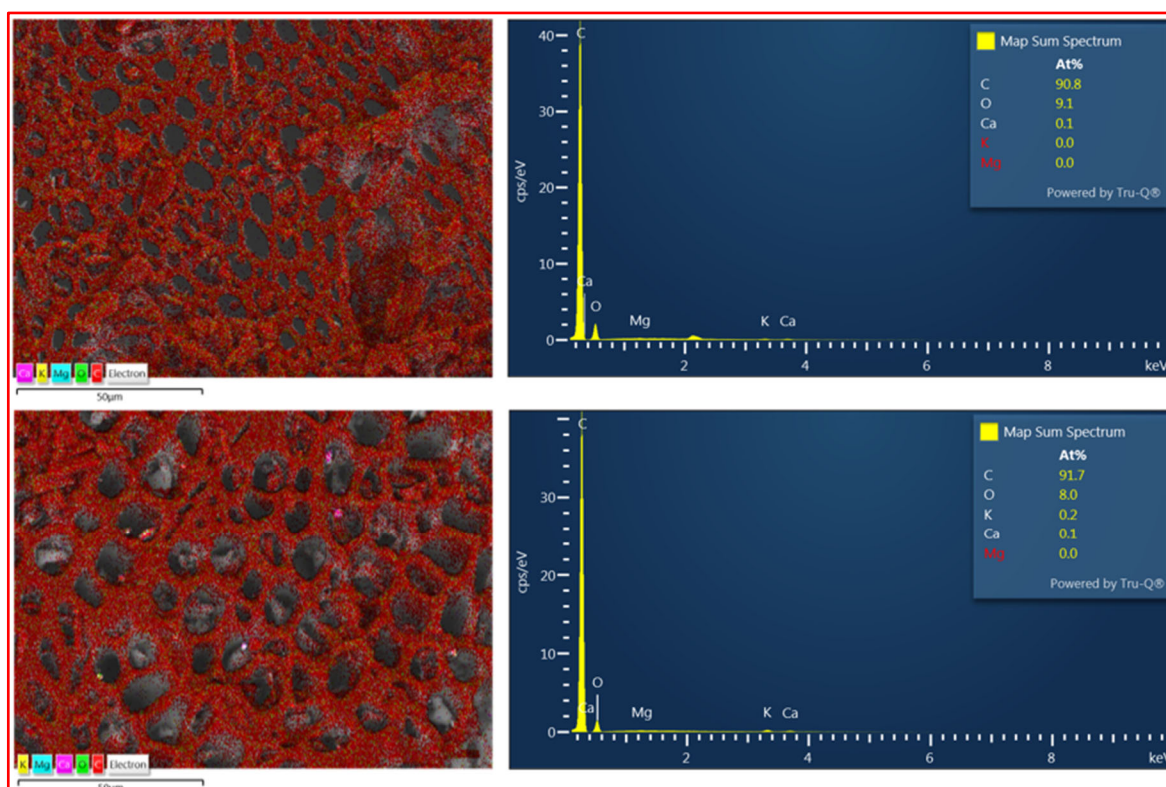


Figure 6. EDX spectra of B800 (top) and HTB800 (bottom).

EDX spectra confirmed progressive carbon enrichment from B800 (90.8%) to HTB800 (91.7%), consistent with volatile elimination and aromatic condensation during PHT. The higher EDX carbon values relative to bulk elemental analysis (85.11% and 87.00%, respectively) should not be interpreted as evidence of understatement by elemental analysis. EDX is a semi-quantitative, surface-sensitive technique whose shallow interaction space preferentially samples carbon-rich near-surface domains. In porous biochar, this potentially overestimates bulk carbon content relative to combustion-based elemental analysis, which remains the reference method for total carbon quantification. The discrepancy is, therefore, expected for surface versus bulk measurement rather than a reflection of the true degree of carbonization. The decreasing EDX oxygen trend from 9.1% (B800) to 8.0% (HTB800) is consistent with the elemental analysis trend (5.91% to 2.58%), with the offset, again,

attributable to EDX's surface sensitivity and preferential detection of oxidized near-surface functional groups. PHT-induced concentration of AAEM in the surface layer, as oxygen and VC were eliminated, contributed to localized compositional heterogeneity between surface and bulk phases.

3.2. Self-Heating Behavior

The self-heating behavior of B600, B800, and HTB800 is assessed here by systematically varying particle size, basket volume, and moisture content across triplicate basket heating tests. Tests were conducted under two protocol tiers: Tier 1 (140 °C oven, 5–12 h) applied to B600 and B800 for reactive screening assessment; Tier 2 (120 °C oven, ~24 h) applied to HTB800 to probe long-term oxidative stability under milder, prolonged thermal stress. The two tiers address different assessment objectives and direct cross-tier comparison of self-heating propensity is not made. B800 results at 140 °C can be compared to B600, while HTB800 results at 120 °C represent an independent, more stringent assessment of long-term safe storability.

3.2.1. B600

In the first batch of basket heating experiments, B600 was tested at an oven temperature of 140 °C with constant airflow for 5–7 h. As shown in Figure 7, when biochar lumps as is (<5% intrinsic moisture) occupied half the steel basket volume, the self-heating test showed an exponential trend and smoldering occurred, likely due to high surface oxygen, labile functionalities, and high VC, despite loose packing and sufficient air voids. When these lumps filled the entire basket, self-heating failure was more pronounced, as restricted inter-particle spacing led to faster heat transfer, poorer heat dissipation, and ignition in just over 3 h, indicating only a minor delay in heat conductivity but similar terminal outcomes. Adding 20–25% moisture to these biochar lumps did not prevent ignition but merely delayed heat absorption, with B600 still approaching the ignition threshold at around 4.5 h, confirming that moisture alone cannot mitigate self-heating risks. Once self-heating curves trend exponentially, plateauing behavior is unlikely. Since large lumps (with varying moisture content) failed the test, fines of B600 were not tested, as greater surface area would only accelerate air uptake and reactivity. The key takeaway is that biochar's self-heating tendencies could be primarily governed by its physicochemical properties, which are dictated by pyrolysis conditions.

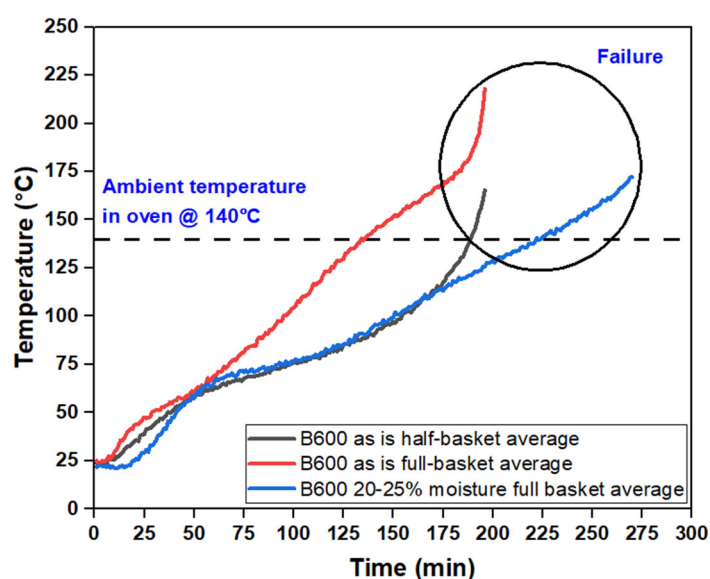


Figure 7. Self-heating curves for B600 with particle size as lumps (as is post-pyrolysis); occupying half and full volumes of the basket; with inherent moisture as is, and also with 20–25% moisture addition.

3.2.2. B800

From Figure 8, in Test 1, B800 lumps as-received (<5% moisture) passed at both half and full basket volumes after approximately 7 h at 140 °C. The full basket showed a brief temperature overshoot before stabilizing, reflecting packing-induced heat accumulation rather than exothermic onset, whereas the half-filled basket equilibrated more gradually through better heat dissipation. In Test 2, dried lumps (<1% moisture) reached oven temperature (~140 °C) within 2.5 h before stabilizing, with moisture-enhanced lumps (20–25%) showing delayed oxidation through oxygen diffusion blockage [101]. Excessive drying increased reactivity, consistent with [102], which noted that bituminous coal with 9.4–10.3% moisture maintains a stable combustion state as ambient oxygen equilibrates with oxygen in coal pores. Moisture beyond a critical threshold risks triggering wetting reactions via hydrophilic surface groups (–OH, –COOH, C=O, –SO₃H), generating localized exothermicity [103]. B800 passed under both moisture extremes, confirming that physicochemical properties govern self-heating behavior more decisively than moisture content alone. In Test 3, B800 fines at half and full basket volumes passed after 12 h, as low oxygen content, low VC, and elevated ash could have collectively suppressed reactive air adsorption despite increased surface area exposure. This is consistent with the known low reactivity of high-temperature biochars [77].

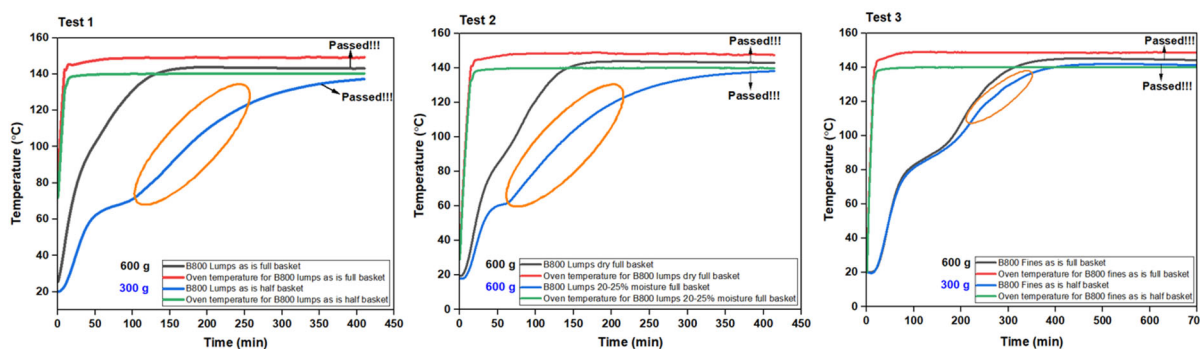


Figure 8. Three self-heating test batches (Tests 1–3) for B800 at 140°C. The orange oval highlights the region of notable temperature divergence between the two samples.

Another opening for deeper future investigations is biochar ash's role in reactivity and its influence on self-heating, i.e., whether or not they impart any specific inertness to the biochar based on their relative percentages.

3.2.3. HTB800

HTB800 self-heating behavior was evaluated through three targeted tests (Figure 9). All tests were conducted at 120 °C for ~24 h to monitor ignition trends. Test 1 assessed HTB800 fines as-received at half and full basket volumes. Test 2 compared wet fines (20–25% moisture) with as-received fines at full basket volume. Test 3 evaluated dry fines of B800 (as reference, despite being non-comparable) and HTB800 at full basket volume. Since HTB800 exhibits substantially reduced VC (16.19%) and high thermal maturity, reactive screening at 140 °C was less informative. Instead, the 120 °C, ~24 h protocol was selected to probe whether PHT-induced stabilization confers resistance to prolonged low-temperature oxidative stress, which is a more stringent and practically relevant indicator of long-term storage safety.

Across all three tests, HTB800 passed convincingly, including as-received dry fines at full basket volume which is the most conducive ignition scenario. This may indicate that PHT-induced stabilization collectively suppresses oxidative reactivity below the self-heating threshold regardless of particle geometry or packing.

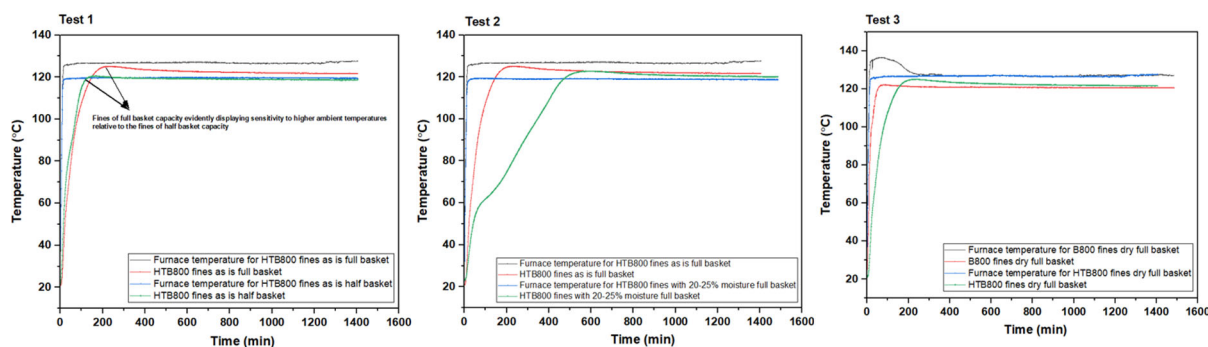


Figure 9. Three self-heating test batches (Tests 1–3) for HTB800 at 120°C.

In Test 1, the transient temperature overshoot slightly above 120 °C in the full basket reflected packing-induced heat accumulation rather than exothermic onset, with temperatures stabilizing without exponential progression. The low surface oxygen and reduced VC confirmed by elemental analysis are the underlying physicochemical drivers of this stability. In Test 2, moisture extended equilibration time from ~3 to ~3.5 h (as-received) to ~9 h (wet fines), confirming moisture's role as a thermal buffer that delays oxidative heat uptake. However, this may not totally prevent self-heating and remains a key distinction, which is critical for large-volume storage risk assessment. In Test 3, HTB800 dry fines at full basket volume approached oven temperature gradually over 3–3.5 h before plateauing. This is consistent with its reduced VC, elevated FC, TSF, and R50, and progressive deoxygenation and aromatization confirmed by FTIR signals between 1280 and 1610 cm^{-1} [104]. The elevated ash content of HTB800 (7.48%) likely contributed additionally, as inert mineral matter, metals, and inorganics could bind reactive organic carbon surface sites, collectively suppressing oxidative reactivity [15].

3.2.4. Comparison with Similar Biochar Self-Heating Tests

Self-heating propensity is governed by feedstock composition, pyrolysis conditions, moisture content, storage volume, and particle size (non-exhaustive). Heterogeneous CRD wood with high holocellulose and low lignin promotes tar and gas formation, reducing FC and chemical stability [105–107]. High pyrolysis temperatures and BRT reduce VC and reactivity [79,108,109]. PHT further passivates residual volatiles, as demonstrated by HTB800. Oxygen deprivation during pyrolysis can exacerbate reactive functional groups, while low-temperature biochars like B600 retain surface tars that initiate thermal runaway [39,110,111]. Smaller particles accelerate oxidation through higher surface area exposure [112,113]. However, B800 and HTB800 fines still passed due to their low VC.

Moisture buffers thermal stress by inhibiting oxygen diffusion, though excessive levels risk biological oxidation [104,108,114]. Packed volumes amplify heat build-up, yet this effect is secondary to biochar properties—B800 and HTB800 fines at full basket volume still passed [115,116]. Square basket geometry ensured uniform oxygen permeation per protocol [117]. The minimum testable particle size (~500 μm) precluded assessment of finer fractions (1–100 μm), which may behave differently and represent a future test case.

Lastly, biochar particles of finer size (e.g., 1 to 100 μm) may show large differences in self-heating results and could fail due to greater surface area exposure. The minimum particle size achievable with the current milling device in our laboratory was ~500 μm (as used in this study), preventing testing of such lower ranges—a potential future work package.

3.3. Characterization of B800 PHT at Longer Durations (30–90 min)

Two independent PHT runs were conducted on B800 (separately prepared 2 kg sub-batches processed sequentially) at an operating temperature of 600 °C across five residence

times (30, 45, 60, 75, and 90 min) to assess the proximate, stability, and surface area trends (shown in Table 3). The consistency of the trends across both runs demonstrates process replicability and reproducibility. Additional replicates were limited by mandatory equipment downtime for thermocouple repair. Advanced characterizations (TGA/DTG/R50, FTIR, SEM-EDX) are reported for the first PHT run only, as the trends were consistent across both runs.

Table 3. Proximate analysis, stability indices, surface area, and yield loss of B800 after PHT at 600 °C for 30–90 min (two independent runs). Metrics that show a declining trend with PHT duration are highlighted in red.

Metric	B800				
	30 min	45 min	60 min	75 min	90 min
First set of PHT runs					
VC (wt%DB)	16.17	15.81	15.64	14.92	14.43
Ash (wt%DB)	6.96	7.22	7.31	7.98	8.02
FC (wt%DB)	76.87	76.97	77.05	77.10	77.55
TSF (%)	82.62	82.96	83.13	83.79	84.31
BET surface area (m ² /g)	218.88	247.22	271.80	376.41	292.87
Micropore volume (cm ³ /g)	0.099793	0.111929	0.122945	0.158739	0.130419
Loss in yield (wt%)	15.21	16.95	17.65	18.70	20.80
Second set of PHT runs					
VC (wt%DB)	16.88	16.59	15.21	14.56	13.98
Ash (wt%DB)	7.08	7.21	7.23	7.61	8.13
FC (wt%DB)	76.04	76.20	77.56	77.83	77.89
TSF (%)	81.83	82.12	83.60	84.24	84.78
BET Surface area (m ² /g)	212.40	241.95	271.88	356.50	301.59
Micropore volume (cm ³ /g)	0.088228	0.115629	0.122093	0.149322	0.131855
Loss in yield (wt%)	14.05	15.95	16.65	17.9	20.15

3.3.1. Physicochemical Properties

In both rounds, similar trends were observed for VC, ash, and FC, with longer residence times promoting steady decomposition, carbon reinforcement, and microporosity development [93]. VC decreased by ~11% between 30 and 90 min in the first round and ~17% in the second, suggesting degradation of labile surface groups (e.g., –COOH, –C–OH) and formation of stable C–C and C=C bonds through dehydrogenation, deoxygenation, isomerization, and aromatization [118]. Pearson’s coefficient ($r = -0.98$) confirmed a strong negative correlation between VC and PHT duration. FC increased slightly with r values of 0.90 and 0.93 across both rounds, supporting gradual stacking of condensed aromatics, also explaining the rise in TSF from 81% to 85% with a highly positive correlation with PHT time ($r = 0.98$). As noted by [119], FC can also influence biochar yields. Ash increased steadily by a magnitude of 15.2% in the first round and 14.8% in the second, tracking inversely with VC decline. Biochar yield loss after PHT ranged from 14 to 21 wt%, peaking at 90 min, reflecting volatilization and thermal breakdown of carbon into gases, tars, and VOCs, and was strongly correlated with PHT time ($r = 0.98$).

PHT increased surface area microporosity between 30 and 75 min by 72% (218.88 to 376.41 m²/g) in the first run and 68% (212.4 to 356.5 m²/g) in the second, likely due to lignin degradation and aromatic condensation [73]. At 90 min, surface area declined to 292.87 and

301.59 m²/g in both rounds due to pore expansion and collapse, with moderate Pearson's *r* values (0.73 and 0.83) indicating a shift in correlation direction. SEM micrographs confirmed micropore loss and mesopore formation by etching. Surface areas were consistent with co-pyrolysis air activation results from [120] (110 to 330 m²/g), though no air was used in our study. Post-pyrolysis air activation at 400–600 °C can optimize surface area [45]. However, in this study, no external oxidant was intentionally introduced during PHT. This surface area increase could be attributed to three non-exclusive in situ mechanisms: (i) thermal decomposition of residual oxygen-containing volatile groups releasing CO and CO₂ through decarboxylation; (ii) AAEM-catalyzed carbon gasification by K and Na salts above 500 °C even under inert atmospheres; and (iii) potential trace oxygen ingress through imperfect pilot-scale retort sealing, which cannot be excluded. Off-gas oxygen monitoring during PHT was not performed and is recommended in future trials to distinguish these pathways and their relative influence.

The convergence of two independent indicators, i.e., surface area decline beyond 75 min, and yield loss exceeding 20% at 90 min, establishes 75 min as the empirical optimum for this system at 600 °C. The yield loss may also continue to rise, producing a net deterioration in product quantity. Formally optimizing these trade-offs requires a multi-variable approach. A response surface methodology (RSM) design across moderate PHT temperature (500–700 °C) and duration (15–90 min) is recommended as the logical next step, with surface area, yield retention, and stability parameters (like FC and R50) as simultaneous response variables. This would identify whether lower temperatures at longer durations, or higher temperatures at shorter durations, can achieve equivalent or superior activation outcomes with reduced yield penalty; a critical question for industrial process viability.

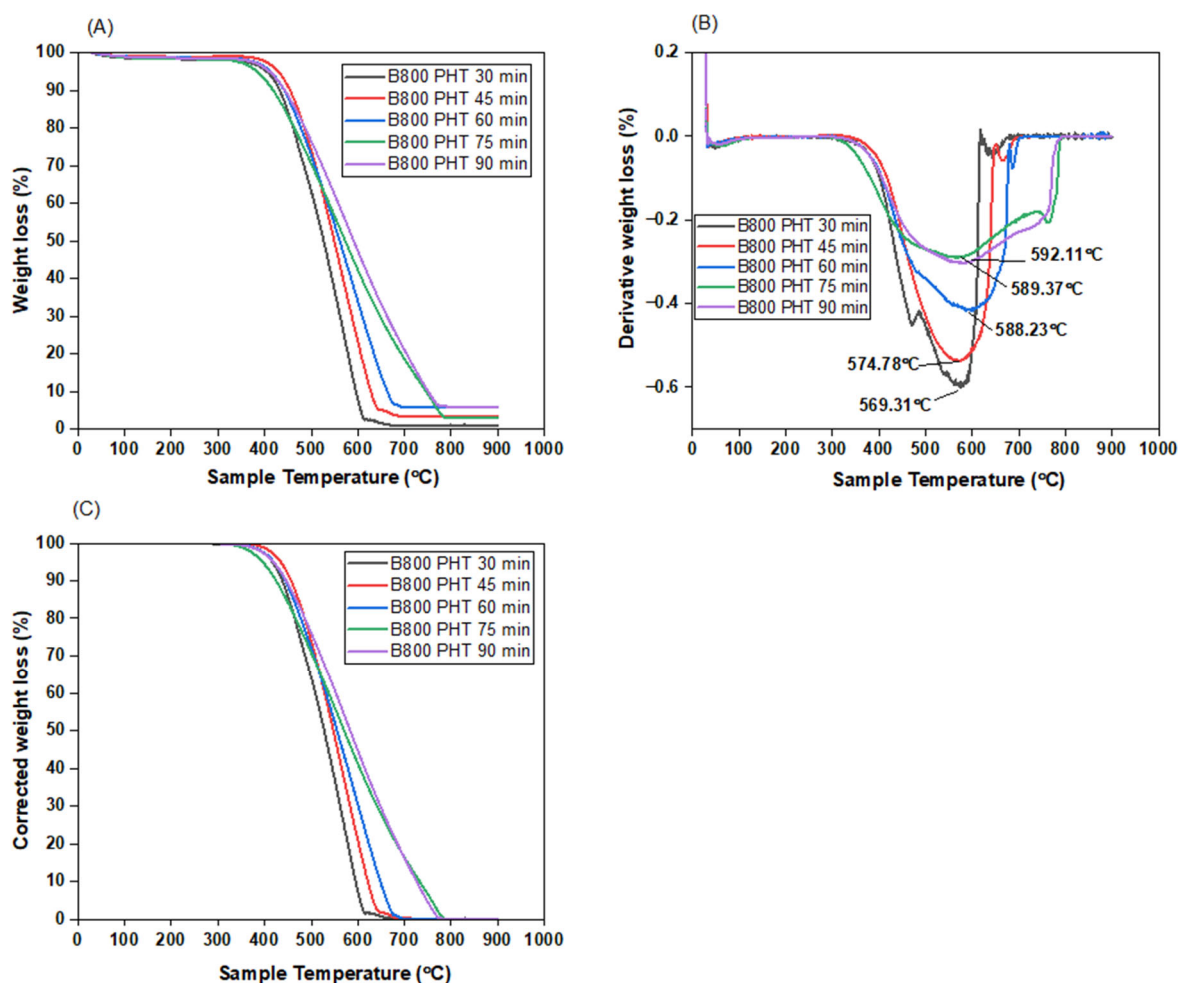
These experiments confirm that porosity, surface area, surface functional groups via VC, and charge via pH can be tuned depending on the target application. For metallurgical use, a moderately high surface area benefits oxidation–reduction reactions between biocoke, air, CO, slag, and metal ores (e.g., Fe₂O₃). Nevertheless, within foundry applications as a carbon-based reductant, excessive surface area may increase ignition risks during handling, and high porosity can also weaken structural integrity under heavy loads—affecting durability and compressive strength.

3.3.2. TGA/DTG/TGA R50

For B800, weight loss below 150 °C and between 200 and 400 °C remained low across all PHT durations (Table 4), reflecting reduced moisture and holocellulose residues. A dual-peak DTG pattern (471 °C and 569 °C), observed exclusively at 30 min PHT, collapsed to a single rightward-shifting peak at longer durations (575–592 °C), indicating progressive aromatic condensation and elimination of lower-stability carbon fractions (Figure 10B). Third-phase weight loss declined monotonically from 87.63% at 30 min to 48.71% at 90 min, confirming conversion of labile functional groups into stable aromatic rings. From [93], it was noted that full turbostratic carbonisation is rarely achieved; biochars retain a heterogeneous mix of amorphous and graphitic carbon. Above 600 °C, weight loss increased from 6.94% to 41.34% for 30–90 min of PHT. This could be attributed to oxidation of residual amorphous carbon and decomposition of heat-labile AAEM carbonates (e.g., CaCO₃ to CaO and CO₂ at >600 °C [121]), whose loss progressively exposed previously shielded biochar carbon to thermal degradation.

Table 4. TGA weight loss (%) per thermal stage for B800 at PHT durations of 30–90 min. Values reported to two decimal places.

Biochar Sample	Weight Loss in Each Phase of TGA (%)			
	First Phase (<150 °C)	Second Phase (200–400 °C)	Third Phase (400–600 °C)	600–900 °C
B800 PHT 30 min	1.60	2.79	87.63	6.94
B800 PHT 45 min	0.98	1.22	74.50	19.96
B800 PHT 60 min	1.18	2.39	62.28	28.21
B800 PHT 75 min	1.51	5.37	50.72	39.26
B800 PHT 90 min	1.24	2.64	48.71	41.34

**Figure 10.** Thermal decomposition analysis of B800 after PHT for 30–90 min. (A): TGA curves; (B) DTG and associated melting temperatures; and (C) moisture and ash corrected TGA for calculating R50 index.

R50 increased from 0.596 (30 min) to 0.659 (90 min), confirming that carbon maturity scales with PHT duration (Figure 10C). All values remain within Class B ($0.5 \leq R50 < 0.7$). Class A ($R50 \geq 0.70$) was not achieved within the tested range. Even if it were, the Class A boundary alone may not entirely constitute biochar's carbon stability.

3.3.3. FTIR

As in Figure 11, the FTIR analysis of B800 after PHT between 30 and 90 min showed consistent aromatic C-H bending ($700\text{--}840\text{ cm}^{-1}$) across all PHT durations, with progressively reduced C-O carbohydrate intensities ($1020\text{--}1280\text{ cm}^{-1}$) confirming steady holocellulose depletion with time. C=C stretching ($1510\text{--}1610\text{ cm}^{-1}$) showed no duration-dependent variation, confirming that aromatic condensation was largely complete beyond 30 min PHT. C $\equiv$ N vibrations ($\sim 2250\text{ cm}^{-1}$) strengthened at longer durations, indicating progressive denitrogenation, while the absence of O-H peaks beyond 3200 cm^{-1} across all durations confirmed sustained hydrophobicity.

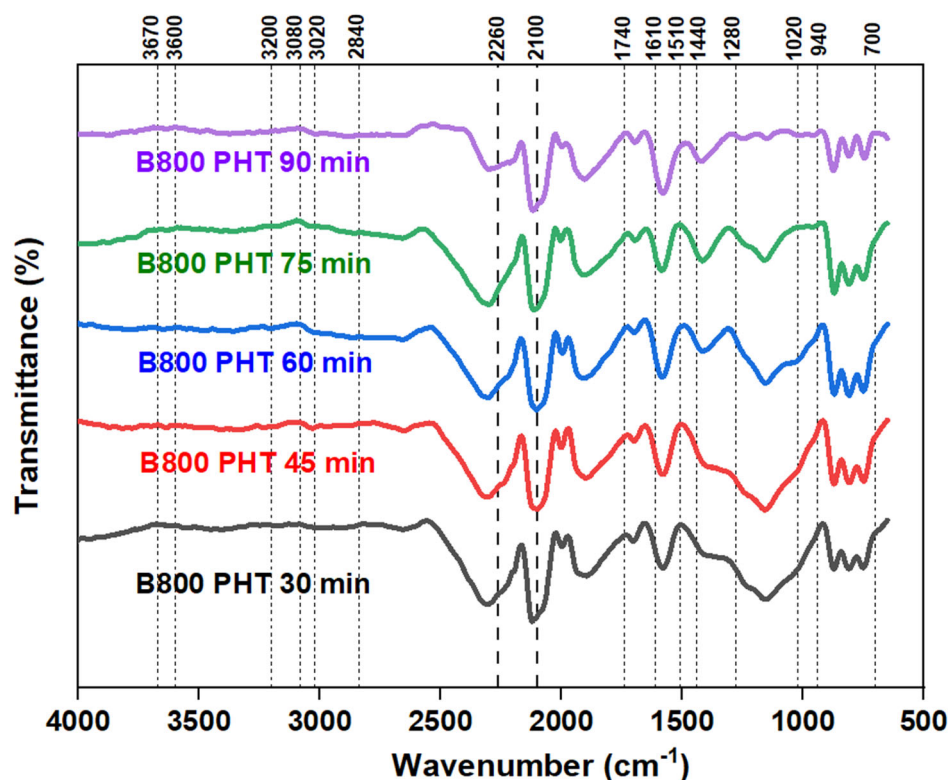


Figure 11. FTIR bands of B800 after PHT for 30–90 min.

3.3.4. SEM-EDX

The SEM micrographs at 250, 500, and 1000X magnifications for B800 at 60 and 90 min PHT (Figure 12) indicated that pore obstruction by volatiles and/or inorganics was greatly avoided. The porous structure at 60 min appears soft and ordered as heat treatment severity increases [122]. Pore sizes at 90 min showed higher heterogeneity as marked in Figure 12D,F. This was also corroborated via enlarged openings observed on biochar's surface as shown in Figure 13A–C. Such morphologies may indicate porosity generation from cracking of biochar carbon or tarry material, trapped gas evolution, removal of less stable inorganics, and/or bulk volatiles loss [123]. It may have also occurred through structural reorganization of unconverted biomass where thin fragile walls between adjacent micropores collapse under thermal stress causing pore coalescence from internal overpressure [124,125]. The resulting larger interconnected pores reduce surface area but enhance mass transport, supporting water/nutrient retention potential [126]. However, leaching studies circumventing heavy metal impacts need to be conducted. The key activation trade-off is preserving stable FC while eliminating volatiles as treatment beyond 75 min reduces surface area and incurs yield losses exceeding 20%, without proportional gains in carbon maturity.

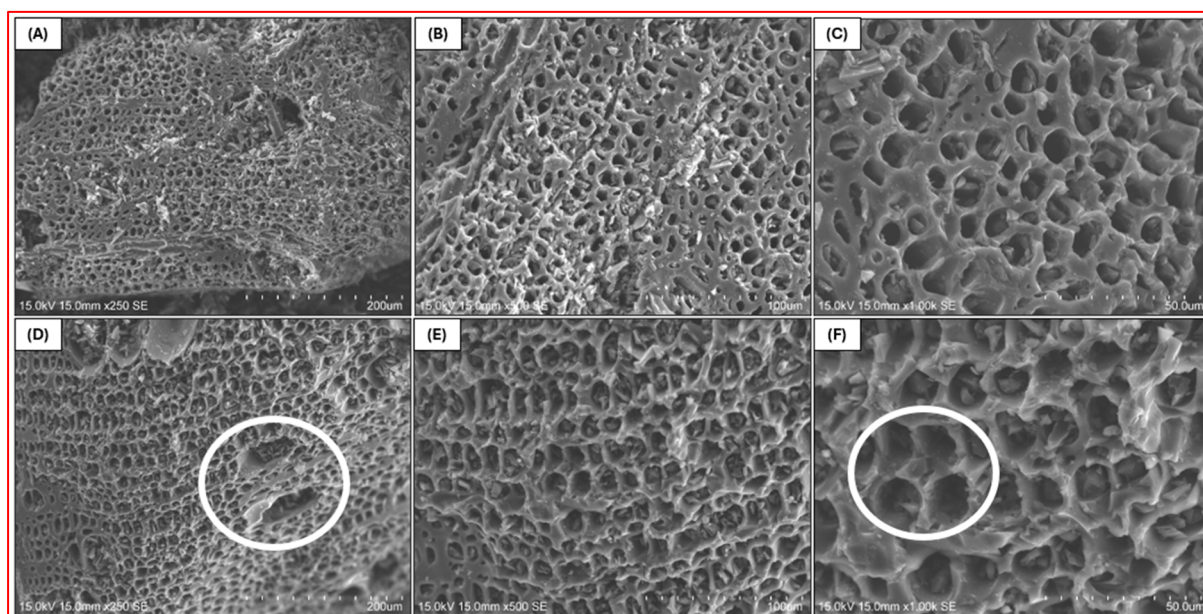


Figure 12. SEM micrographs of: (A) 250X, (B) 500X, (C) 1000X-B800 PHT at 60 min; and (D) 250X, (E) 500X, (F) 1000X-B800 PHT at 90 min, to illustrate the effect of duration.

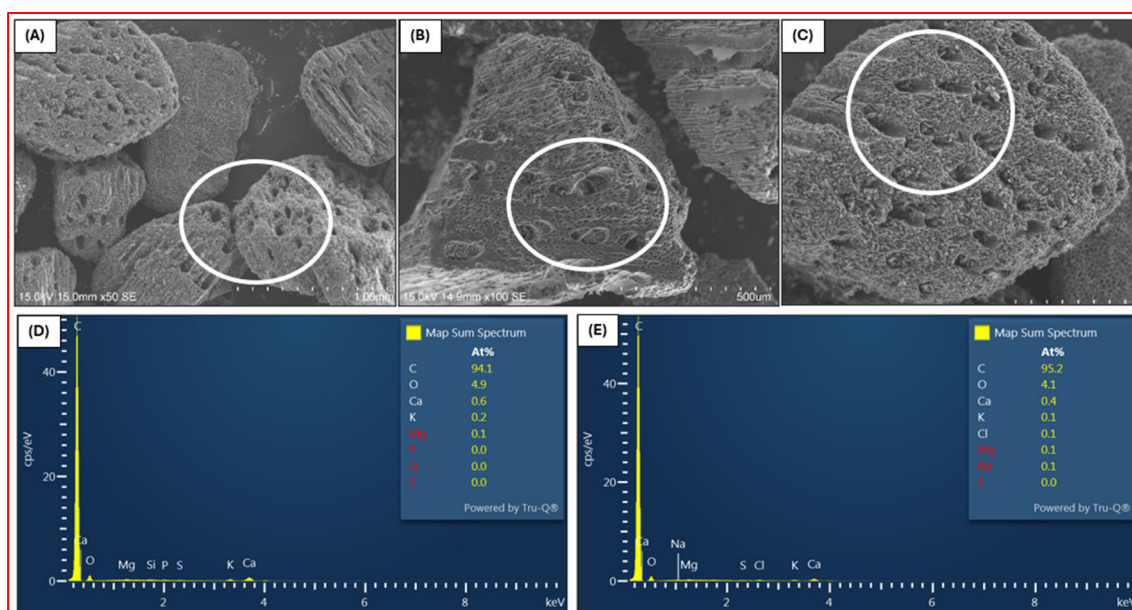


Figure 13. SEM micrographs of: (A) 50X, (B) 100X, and (C) 100X-B800 PHT at 90 min (to depict pore rupture and widening); (D) EDX spectra of B800 PHT at 60 min; and (E) PHT at 90 min.

EDX analysis in Figure 13D,E confirmed that PHT of B800 at 60 and 90 min increased carbon content in the biochar matrix to 94.1% and 95.2%, respectively. This validated that prolonged heat treatment critically improved carbon conversion. Surface oxygen was limited to 4.9% at 60 min PHT with an even lower concentration of 4.1% at 90 min, confirming the positive role of secondary thermal activation in tailoring chemical composition. A longer heat treatment time also reduced AAEM in ash, with Ca decreasing from 0.6% to 0.4% and K from 0.2% to 0.1% at 90 min. The presence of Cl at 90 min PHT suggests AAEM existed in chloride salt forms, likely trapped within the biochar carbon structure before volatilizing as chlorinated hydrocarbons or organo-chloride compounds at high temperatures and residence times.

4. Conclusions

CRD wood waste, which is compositionally heterogeneous and largely non-recyclable, represents an underutilized feedstock whose landfill trajectory generates avoidable GHG emissions, groundwater contamination, and soil degradation. Pilot-scale slow pyrolysis of CRD wood demonstrated that these risks can be addressed through thermal valorisation with pyrolysis temperature, BRT, and feedstock variability as the primary determinants of biochar quality. These factors govern carbon maturity, thermal stability, and oxidative resistance more decisively. Recycled pyrolysis gas directed to the combustion chamber to partially offset natural gas input, constitutes the bioenergy co-product of this process. The persistent thermocouple displacement in sealed retorts remains a fundamental instrumentation limitation requiring resolution before pilot-scale data can be benchmarked against laboratory studies. Multiple replicates of production trials are also recommended to compare biochar properties across different runs.

Thermal-only PHT requiring no reagents, reactive gases, or water proved a credible and resource-lean activation pathway. An empirical optimum at 75 min balanced surface area, FC, and product yield retention. Beyond this, pore coalescence and yield losses exceeding 20% defined the practical activation boundary. Formally resolving this trade-off requires a RSM design across PHT temperature (500–700 °C) and duration (15–90 min) along with self-heating tests correlating activation conditions directly with combustion vulnerability and biochar properties. Self-heating behavior confirmed pyrolysis severity as the overriding determinant of ignition propensity. Low-temperature biochar failed unconditionally while high-temperature and PHT-treated biochars passed under all conditions tested. Moisture content, particle size, and volume/capacity of biochar are other dependent factors for self-heating. Elevated Cr and Cu concentrations in CRD wood biochar necessitate careful application selection. Metallurgical reductant use and energy co-firing with mandatory emission controls represent the most immediately viable pathways, while soil amendment cannot be recommended at this stage without dedicated leaching and risk assessment studies to confirm regulatory compliance. Carbon sequestration application remains conditional on incubation validation.

Furnace natural gas demand decreased during peak pyrolysis gas evolution for both B600 and B800, confirming that recycled pyrolysis gas offset external fuel demand under both pyrolysis conditions. The magnitude of this offset was temperature dependent. For B800, natural gas demand decreased by approximately 50%, from approximately 400 to 200 standard cubic feet on the flow indicator. B600 showed a similar trend but at a much smaller magnitude. This pattern is consistent with greater devolatilization at higher pyrolysis temperature, producing a larger volume of pyrolysis gas available for recycling through the suction and recycling system. The continuous extraction of pyrolysis gas under negative pressure, therefore, may serve a dual role. It could support biochar quality by limiting tar redeposition and PAH formation, and it may also reduce external fuel demand during active devolatilization. A complete equipment level energy balance is identified as a priority for future work, incorporating calibrated flow metering and gas calorimetry on the recycled pyrolysis gas stream to quantify its calorific contribution against natural gas demand at each set point temperature. Feedstock supply variability and energy return on energy invested also remain critical uncertainties for scale up, where supportive policy frameworks will be essential for industrial adoption.

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Data Availability Statement: Only the data presented in this study are available on request from the corresponding author due to ongoing validation, as subsequent rigorous testing with different materials is being conducted for the standardisation of the experimental protocols described in this study.

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