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RESEARCH ARTICLE

REVISED Thermal carbonization of woody biomass under inert atmosphere with temperature-dependent variation in the effects of Cu and Ti additives

[version 2; peer review: 2 approved with reservations]

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Abstract

Background

Carbonization of woody biomass under inert atmospheres is a practical route to producing functional carbon materials. However, carbon yield and microstructural development are strongly influenced by temperature and by the presence of metal additives. The temperature-dependent differences in the effects of such additives on carbonization behavior remain insufficiently understood.

Methods

The effects of copper and titanium additives were systematically examined during heat-induced carbonization of Todo fir (*Abies sachalinensis*) wood flour at 500 °C and 800 °C under nitrogen using controlled heating rates. Carbonization behavior was analyzed by thermogravimetric–differential thermal analysis. The resulting char was characterized by elemental analysis, scanning electron microscopy, and transmission electron microscopy.

Results

At 500 °C, copper addition was associated with the formation of partially layered turbostratic carbon structures with expanded interlayer spacing, suggesting possible stabilization of carbon frameworks with reduced bond cleavage. In contrast, titanium addition was associated with increased devolatilization and

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fragmentation, leading to lower carbon retention and more heterogeneous microstructures. At 800 °C, thermally stable, carbon-rich residues were obtained largely independent of heating rate, indicating that the final hold temperature was the primary factor influencing bulk carbon ordering. Under these conditions, copper was associated with higher char retention, whereas titanium was associated with enhanced interfacial reactions and decomposition-related behavior at carbon interfaces. Transmission electron microscopy showed that overall structural ordering was primarily determined by the final temperature rather than by the additive. These findings indicate temperature-dependent variation in additive effects, with copper favoring solid carbon retention at moderate temperatures and titanium showing stronger decomposition-related effects at elevated temperatures.

Conclusions

The results suggest distinct temperature-dependent differences in the effects of copper and titanium during biomass carbonization and provide a basis for considering additive selection and thermal design in controlling carbon yield and microstructure.

Keywords
carbonization; thermal treatment under inert atmosphere; transition metal additive; copper catalyst; titanium catalyst; turbostratic carbon; temperature-dependent catalytic role switching

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REVISED **Amendments from Version 1**

This version has been revised in response to peer review comments. The title, abstract, and discussion have been updated to emphasize temperature-dependent variation in the effects of Cu and Ti additives rather than catalytic role switching. The terminology has been revised throughout the manuscript for consistency. Experimental details have been clarified, including the numbers of TG–DTA, elemental analysis, SEM, and TEM measurements. Figure 5 has been revised to present a conceptual summary consistent with the revised interpretation. Limitations of the study have also been clarified, particularly regarding the lack of direct identification of Cu and Ti phases after carbonization. These revisions improve the clarity and interpretation of the results without changing the underlying experimental data or the main conclusions.

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1. Introduction

The depletion of fossil resources and the increasing severity of environmental degradation have accelerated global efforts to develop sustainable technologies for the production of energy, chemicals and functional materials from renewable resources. Among the various alternatives, woody biomass has attracted significant attention due to its abundance, renewability and carbon-neutral nature. However, the efficient utilization of this resource will require the development of conversion technologies capable of producing value-added products while minimizing waste generation.

The thermochemical conversion of biomass under oxygen-limited conditions enables the formation of liquid products, solid carbonaceous residues (char) and gaseous species.[1] One of the key advantages of such thermal processes is the potential to simultaneously form liquid chemicals and solid functional materials. The liquid products can be utilized as renewable fuels or chemical feedstocks, while biomass-derived char has applications in environmental remediation, carbon sequestration, energy storage and catalysis.[2] Despite these advantages, controlling the yield and quality of thermochemical conversion products remains a challenge. Product distribution depends on a range of operational parameters, including heating rate, residence time, final temperature, and the presence of catalysts or additives. Among these factors, temperature plays a decisive role in governing the balance between primary volatilization reactions and secondary processes, including condensation, further devolatilization and carbonization. Thermal treatment of biomass at temperatures in the vicinity of 500 °C typically generates liquids as the major products together with char having relatively disordered carbon structures. In contrast, higher temperatures, generally above 700–800 °C, are associated with enhanced devolatilization, secondary cracking reactions, and structural changes in carbon frameworks.[3,4]

Carbonization of biomass in the presence of metal additives under an inert atmosphere has emerged as an effective strategy for tailoring product distributions and improving the properties of the resulting materials.[5] Transition metals such as copper (Cu) and titanium (Ti) are of particular interest because of the unique chemical reactivities and interactions with carbonaceous intermediates of these elements. Cu has been reported to be associated with structural evolution toward more ordered carbon arrangements and stabilization of carbon structures, whereas Ti has been associated with bond cleavage and gasification-related reactions.[5,6] However, the majority of studies to date have focused on single temperature regimes and have not sufficiently addressed the manner in which the effects of these additives vary with increasing temperature.

Previous work by the authors suggested that, at 800 °C, Cu addition was associated with increased char yield, whereas Ti addition was associated with greater mass loss and increased formation of gas and liquid phase products.[7] Observations using electron microscopy have also revealed distinct features between the metal additive and the carbonized matrix under high-temperature conditions. Building on these findings, the goal of the present study was to integrate both moderate- and high-temperature processing (500 and 800 °C) into a unified framework to elucidate the temperature-dependent differences in the effects of Cu and Ti additives during the thermal treatment of woody biomass.

2. Materials and methods

2.1 Raw materials and additive preparation

Wood flour was prepared from Todo fir (*Abies sachalinensis*) wood specimens harvested in Hokkaido, Japan. The wood was mechanically ground by ball milling and sieved to obtain a particle size fraction of less than 500 μm, following the procedure reported previously.[8] The wood material was supplied by the Forest Products Research Institute, Hokkaido Research Organization (HRO), Japan. The species identification was confirmed based on supplier documentation and macroscopic anatomical characteristics according to standard wood identification references used in Japanese wood science research. Therefore, no voucher specimen was deposited in a public herbarium. Species identification was confirmed by the supplier (HRO) and verified by the authors based on macroscopic anatomical characteristics. The wood was mechanically ground and then sieved to obtain a uniform particle size fraction. Copper powder (99.9%, average particle size 75 μm) and titanium powder (99.9%, average particle size 45 μm) were used as additives. The wood flour was

mixed with either Cu or Ti powder at a mass ratio of 7:3 using an agate mortar to ensure that homogeneous dispersions were obtained. A portion of additive-free wood flour was used as a control sample.

2.2 Carbonization under an inert atmosphere

Carbonization experiments were conducted using a thermogravimetry-differential thermal analysis (TG–DTA) apparatus (TG8120, Rigaku Corporation, Japan). In each trial, a sample mass of approximately 10 mg was placed in an alumina crucible and heated under nitrogen at a flow rate of 200 mL min^{-1}. Heating rates of 10, 20 or 40 °C min^{-1} were applied and the material was heated to a final temperature of either 500 °C to generate primarily liquid products or 800 °C to produce primarily char. After reaching the target temperature, each specimen was held at that temperature for 3 min and then allowed to cool naturally while maintaining the flow of nitrogen. For each experimental condition, TG–DTA measurements were conducted three times. Representative thermogravimetric profiles are presented in this study.

2.3 Elemental analysis

Elemental compositions (that is, the C, H and N proportions) of char residues were determined using a CHN analyzer (MT-5, Yanako Co., Ltd.). Oxygen contents were calculated by difference following these analyses. Elemental compositions were determined from duplicate measurements, and the reported values represent the average of the two measurements.

2.4 Electron microscopy

The morphology of the carbonized samples and the interactions between the metal additives and the carbonized matrix were observed using scanning electron microscopy (SEM; JEM-5310, JEOL, Japan) operated at an accelerating voltage of 15 kV. Carbonized specimens were sufficiently conductive and therefore examined without additional coating.

Transmission electron microscopy (TEM; JEM-2100F, JEOL, Japan) was employed to investigate the carbon microstructure and to evaluate the interlayer spacing of turbostratic carbon domains. TEM observations were performed at an accelerating voltage of 200 kV to minimize beam-induced structural damage. SEM and TEM observations were conducted at multiple locations within each sample. Representative images showing the characteristic microstructural features are presented in the manuscript.

Two-dimensional fast Fourier transform (FFT) analysis was applied to high-resolution TEM images, and the resulting power spectra were rotationally integrated to obtain interlayer spacing distributions. The peak maxima in the rotationally integrated FFT profiles were used as apparent structural spacing parameters reflecting disordered fringe spacing and nanoscale periodicity in the carbon structure. These values do not represent ideal graphite interlayer spacing.[9]

3. Results

3.1 Thermogravimetric behavior at 500 °C and 800 °C

Supplementary Figures 1 and 2 present the thermogravimetric (TG–DTA) behavior of char residues obtained at 500 °C and 800 °C, respectively, highlighting the influence of Cu and Ti additives under an inert atmosphere. At 500 °C (Supplementary Figure 1), clear differences in thermal decomposition behavior were observed depending on the catalytic metal added.

The TG curves indicate that the incorporation of Cu reduced the overall mass loss and resulted in higher char yields compared with the untreated samples. In contrast, the addition of Ti led to increased mass loss, suggesting enhanced devolatilization during carbonization. These trends were consistently observed across different heating rates (r10, r20, and r40), indicating that the observed differences among additive treatments were consistently observed across different heating rate under the present conditions.

A quantitative comparison of the mass loss data further supports these observations: Cu-containing specimens exhibited systematically lower mass losses, whereas Ti-containing specimens showed higher mass losses relative to the non-catalyzed samples. This behavior is consistent with greater carbon retention in Cu-containing specimens, and greater mass loss in Ti-containing specimens at intermediate temperatures. Overall, these results indicate that different additive treatments were associated with distinct char yields and mass-loss behaviors at 500 °C.

Supplementary Figure 2 shows the TG–DTA profiles of char residues obtained at 800 °C under an inert atmosphere. The TG curves indicate enhanced mass loss at this higher temperature, reflecting more extensive thermal decomposition compared with the behavior observed at 500 °C (Supplementary Figure 1).

The elemental compositions of char residues at 500 and 800 °C results are summarized in Tables 3 and 4, respectively. The char residues produced at 800 °C exhibited substantially higher carbon contents than those obtained at 500 °C, reflecting the greater degree of carbonization achieved at the higher temperature. Notably, even at 800 °C, the Cu-containing specimens retained higher carbon contents than both the Ti-containing and untreated samples. This trend is consistent with the TG–DTA results and provides quantitative support for the role of Cu in stabilizing the solid carbon phase at elevated temperatures. In contrast, Ti addition promoted further decomposition, leading to reduced carbon retention.

3.2 Elemental composition of char residues at 500 and 800 °C

Table 3 summarizes the elemental compositions of the char residues obtained at 500 °C under different heating rates (r10, r20, and r40), together with those of untreated Fir. After carbonization at 500 °C, the char residues exhibited markedly higher carbon contents (approximately 79–81 wt%) than the untreated material (50.1 wt%), accompanied by substantial reductions in hydrogen and oxygen contents. These results indicate effective carbon enrichment during carbonization at this temperature.

The carbon content of the char residues at 500 °C showed only minor variations with heating rate, whereas the oxygen (+ ash) content ranged from 16.0 to 18.1 wt%. Hydrogen contents decreased to approximately 3 wt%, and nitrogen contents remained low (<0.5 wt%) in all cases. These trends suggest that the influence of heating rate on elemental composition was relatively limited at 500 °C under the present experimental conditions.

Table 4 presents the elemental compositions of the char residues obtained at 800 °C. In contrast to the samples carbonized at 500 °C, the char residues produced at 800 °C exhibited substantially higher carbon contents, reaching approximately 93 wt% irrespective of heating rate. Correspondingly, hydrogen contents were reduced to approximately 1.3–1.4 wt%, while the combined oxygen and ash contents decreased to around 5 wt%. Nitrogen contents remained consistently low (<0.3 wt%).

At 800 °C, variations in elemental composition with heating rate were negligible, indicating that differences associated with heating rate became less pronounced under the present experimental conditions. The consistently high carbon content and low heteroatom concentrations are consistent with extensive devolatilization and deoxygenation occurred at this temperature, resulting in the formation of a highly carbonized solid residue. Overall, the elemental analysis results indicate that increasing the carbonization temperature from 500 to 800 °C was associated with higher carbon content and reduced variation in elemental composition, while the influence of heating rate became less pronounced at the higher temperature.

3.3. Microstructural features of char at 500 °C

Figure 1 presents a representative SEM cross-sectional image of a Cu-containing char residue prepared at 500 °C. The image illustrates the typical microstructural features observed after Cu-assisted carbonization, including the direct contact between Cu particles and the carbonized matrix derived from *Abies sachalinensis.* The region indicated as the reaction area highlights localized morphological modifications associated with the presence of Cu.

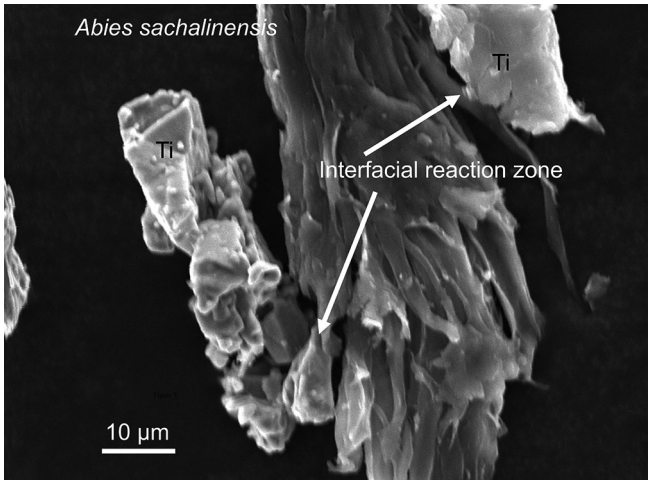

Figure 1. Scanning electron microscopy image of char derived from *Abies sachalinensis* wood flour carbonized at 500 °C under a nitrogen atmosphere with Cu addition. The arrow indicates the interaction region between the Cu particles and the carbonized wood structure. Scale bar: 10 µm.

In the additive-free samples (Figures 2 (1)–(3)), the carbon structure is highly disordered, and the interlayer spacing increases systematically with heating rate, ranging from approximately 0.84 to 1.12 nm. The observed increase in interlayer spacing suggests a change in carbon microstructure with heating rate and is consistent with general interpretations of disordered and turbostratic carbon structures based on interlayer spacing analyses.[10]

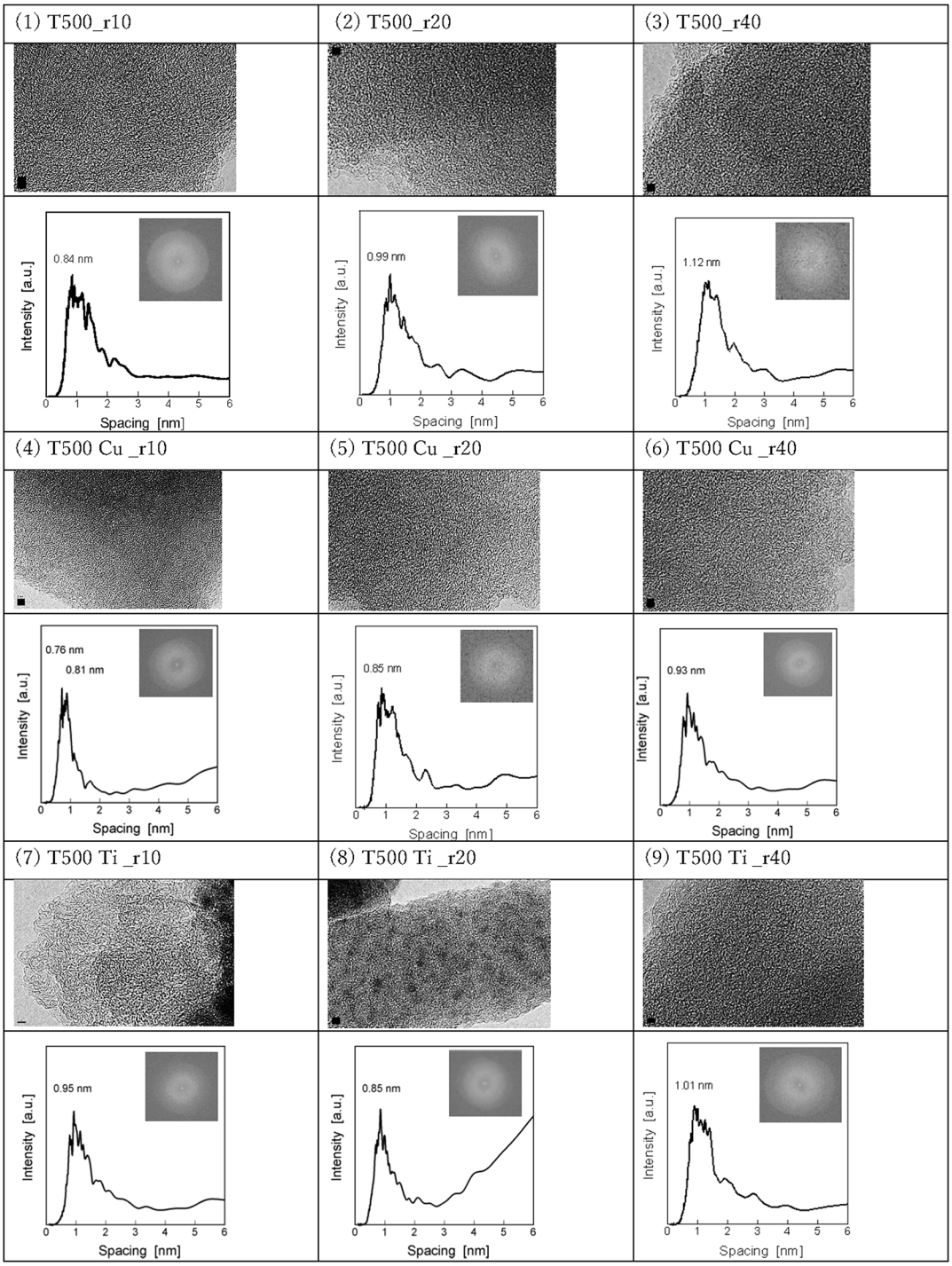

Figure 2. Transmission electron microscopy images of char derived from *Abies sachalinensis* wood flour carbonized at 500 °C under a nitrogen atmosphere with different heating rates and additive treatments. Panels (1–3) show samples without additives (T500_r10, T500_r20, and T500_r40), panels (4–6) show Cu-added samples (T500_Cu_r10, T500_Cu_r20, and T500_Cu_r40), and panels (7–9) show Ti-added samples (T500_Ti_r10, T500_Ti_r20, and T500_Ti_r40). The corresponding FFT analysis and rotationally integrated radial intensity profiles are presented below each image. The peak positions in the rotationally integrated radial intensity profiles were used to estimate apparent interlayer spacing associated with disordered turbostratic carbon domains. Scale bar: 2 nm.

In contrast, Cu-assisted samples (Figures 2 (4)–(6)) exhibit partially developed layered carbon domains at all heating rates. The corresponding radial intensity profiles show relatively constrained interlayer spacings of approximately 0.76–0.93 nm. Notably, increasing the heating rate does not lead to a pronounced expansion of the interlayer spacing, suggesting that Cu was associated with less pronounced interlayer expansion during carbonization at 500 °C.

Ti-assisted samples (Figures 2 (7)–(9)) show heterogeneous carbon structures with no systematic dependence of interlayer spacing on heating rate. The interlayer spacings vary irregularly, suggesting greater structural heterogeneity in the Ti -containing samples under the present experimental conditions.

A direct comparison across Figure 2 indicates that partially layered carbon structures were observed more frequently in the Cu-containing samples at 500 °C, whereas additive-free samples and Ti-containing samples exhibited different structural features. These observations suggest that Cu-containing samples tended to retain partially layered carbon structures and relatively smaller changes in interlayer spacing under the conditions examined.

3.4 Microstructural features of char at 800 °C

Figure 3 shows a cross-sectional SEM image of a typical specimen exhibiting the effects of interactions between the Ti and the carbon matrix after the high-temperature treatment. Distinct reaction zones are observed at the Ti–carbon interface, accompanied by pronounced fragmentation of the carbon framework. This SEM image is intended to provide a qualitative illustration of the characteristic morphology induced by Ti at elevated temperatures and does not imply uniform behavior across all samples.

Figure 4 shows TEM images and corresponding interlayer spacing distributions of carbon residues formed at 800 °C under different heating rates, without additives and with Cu or Ti addition.

In the additive-free samples (Figures 4 (1)–(3)), relatively compact carbon structures are observed, with apparent interlayer spacings centered at approximately 0.44–0.50 nm. No clear systematic dependence on heating rate is evident, suggesting that the carbon microstructure becomes less sensitive to heating-rate variations at 800 °C under the present experimental conditions.

In Cu-assisted samples (Figures 4 (4)–(6)), partially disrupted carbon structures are observed, accompanied by a moderate increase in apparent interlayer spacing to approximately 0.63–0.74 nm. Although some variation with heating rate is present, the overall interlayer spacing remains constrained compared with lower-temperature carbonization. According to established interpretations of disordered turbostratic carbon structures based on TEM analyses, such constrained interlayer spacing is consistent with modification of nanoscale carbon organization.[11] In the present study, these features indicate that Cu modifies the nanoscale carbon structure even at elevated temperatures.

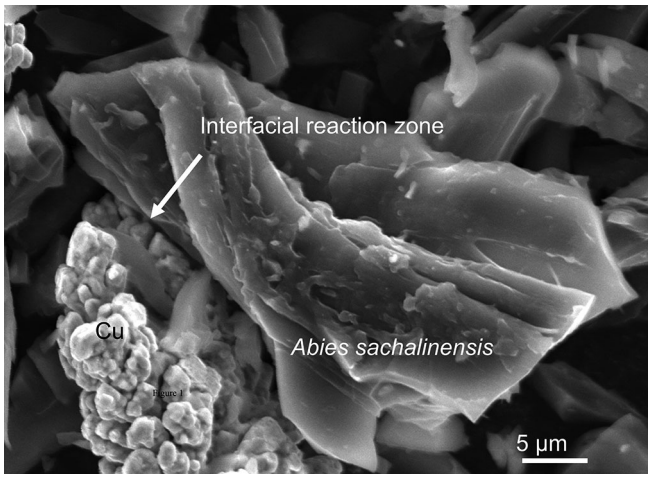

Figure 3. Scanning electron microscopy image showing the morphology of char derived from *Abies sachalinensis* wood flour carbonized under a nitrogen atmosphere with Ti addition. The catalyst–char interaction and associated surface structural modification are visible. The arrow indicates a reaction zone on the cell wall surface. Scale bar: 10 μm.

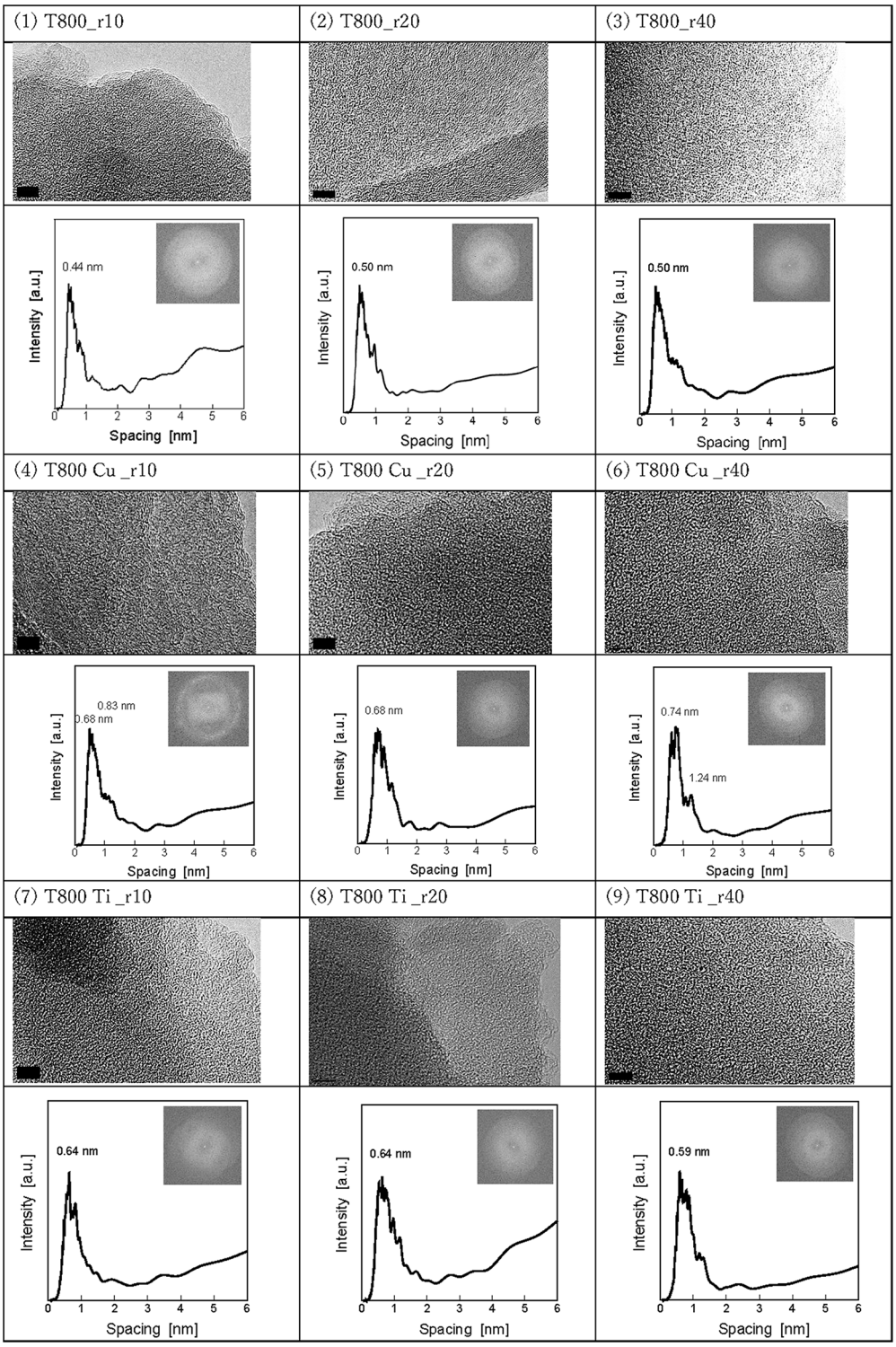

Figure 4. Transmission electron microscopy images of char derived from *Abies sachalinensis* wood flour carbonized at 800 °C under a nitrogen atmosphere with different heating rates and additive treatments. Panels (1–3) show samples without additives (T800_r10, T800_r20, and T800_r40), panels (4–6) show Cu-added samples (T800_Cu_r10, T800_Cu_r20, and T800_Cu_r40), and panels (7–9) show Ti-added samples (T800_Ti_r10, T800_Ti_r20, and T800_Ti_r40). The corresponding FFT analysis and rotationally integrated radial intensity profiles are shown below each image. The peak positions in the radial intensity profiles were used to estimate apparent interlayer spacing associated with disordered turbostratic carbon domains. Heating rates r10, r20, and r40 denote 10, 20, and 40 °C min^{-1}, respectively. Scale bar: 2 nm.

Ti-assisted samples (Figures 4 (7)–(9)) exhibit heterogeneous carbon structures with irregular interlayer spacing distributions. The interlayer spacings range from approximately 0.63 to 0.82 nm and show no systematic dependence on heating rate, suggesting that Ti induces localized structural perturbations rather than uniform microstructural reorganization at 800 °C.

Overall, the TEM observations at 800 °C indicate differences in carbon microstructure among the samples. Cu-containing samples exhibited more consistent interlayer spacing characteristics than Ti-containing samples. The observed differences suggest that the effects of Cu and Ti on carbon microstructure The observed differences suggest that the effects under high-temperature The observed differences suggest that the effects conditions.

4. Discussion

4.1 Temperature-dependent variation in the effects of Cu and Ti additives

Based on the experimental results summarized in Figures 1–4 and Tables 1–4, a conceptual model describing temperature-dependent differences in the effects of Cu and Ti additives is proposed, as schematically illustrated in Figure 5. Rather than interpreting the effects of Cu and Ti as definitive catalytic functions, the present results suggest temperature-dependent differences in their influence on carbonization behavior under nitrogen atmospheres. These observations can be interpreted within a temperature-oriented framework, in which thermal decomposition behavior, elemental composition, and microstructural evolution are considered together to understand the observed trends.

Table 1. Weight loss ratios of carbonized fir samples under different catalyst conditions and heating rates at 500 °C.

Sample ID	Heating rate (°C min^{-1})	Catalyst	Weight loss ratio (%)[†]	Weight loss ratio (%)[‡]
r10	10	None	78.2	78.2
r20	20	None	79.7	79.7
r40	40	None	79.9	79.9
Cu r10	10	Cu	52.0	74.3
Cu r20	20	Cu	51.0	72.8
Cu r40	40	Cu	58.0	82.9
Ti r10	10	Ti	65.2	93.1
Ti r20	20	Ti	63.1	90.1
Ti r40	40	Ti	66.7	95.3

[†]Cu- or Ti-treated samples.
[‡]Metal-free fir samples.

Table 2. Weight loss ratios of carbonized fir samples under different catalyst conditions and heating rates at 800 °C.

Sample ID	Heating rate (°C min^{-1})	Catalyst	Weight loss ratio (%)[†]	Weight loss ratio (%)[‡]
1 (r10)	10	None	82.1	82.1
2 (r20)	20	None	82.3	82.3
3 (r40)	40	None	81.7	81.7
4 (Cu r10)	10	Cu	61	89.3
5 (Cu r20)	20	Cu	55.9	81.9
6 (Cu r40)	40	Cu	57.2	83.9
7 (Ti r10)	10	Ti	59.3	86.8
8 (Ti r20)	20	Ti	57.7	84.6
9 (Ti r40)	40	Ti	58.4	85.6

[†]Cu- or Ti-treated samples.
[‡]Metal-free fir samples.

Table 3. Elemental composition of char residues at 500 °C.

Element (wt%)	r10	r20	r40	Fir (untreated)
Hydrogen (H)	3.4	2.9	3.1	6.1
Carbon (C)	78.7	78.8	80.5	50.1
Nitrogen (N)	0.3	0.2	0.4	0
Oxygen (+ ash)*	17.5	18.1	16	43.7

Elemental compositions are given on a weight percentage basis.
*Oxygen content was calculated by difference and includes ash.

Table 4. Elemental composition of char residues at 800 °C.

Element (wt%)	r10	r20	r40
Hydrogen (H)	1.4	1.3	1.3
Carbon (C)	93.4	93.5	93.2
Nitrogen (N)	0.2	0.3	0.2
Oxygen (+ ash)*	5.0	4.9	5.3

Elemental compositions are given on a weight percentage basis.
*Oxygen content was calculated by difference and includes ash.

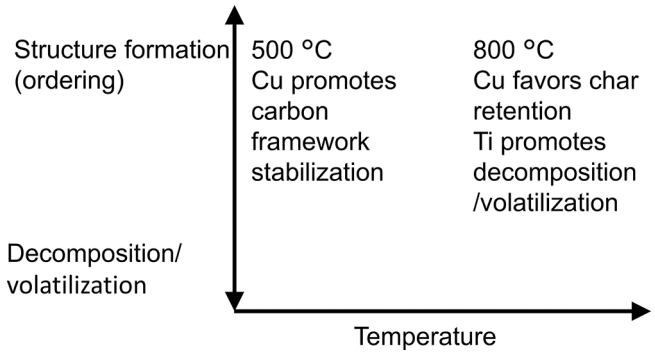

Figure 5. Schematic illustration of temperature-dependent variation in the effects of Cu and Ti additives during carbonization of woody biomass. The diagram summarizes the observed differences in carbon retention and carbonization behavior among Cu- containing and Ti-containing, and additive-free samples at 500 °C and 800 °C.

The TG–DTA, elemental analysis, and SEM/TEM results consistently show that the apparent additive-associated effects of Cu and Ti during woody biomass carbonization under nitrogen are strongly influenced by temperature. Temperature-dependent differences in the effects of Cu and Ti were observed between 500 and 800 °C. Rather than showing a monotonic enhancement or decrease in decomposition-related behavior, both metals exhibited temperature-dependent behavior, suggesting that their influence on carbonization behavior may vary according to the thermal conditions.

Cu-containing samples at 500 °C were associated with reduced mass loss and higher carbon retention. SEM and TEM observations suggest partial preservation of the carbon framework and the presence of partially layered turbostratic carbon structures in Cu-containing samples. These observations are consistent with possible moderation of bond cleavage and partial stabilization of carbonaceous intermediates during intermediate-temperature carbonization under an inert atmosphere.

In contrast, Ti-containing samples treated at 500 °C exhibited increased mass loss, lower carbon retention, and more heterogeneous microstructures. These observations suggest enhanced devolatilization and fragmentation behavior during carbonization under the present conditions. The absence of well-developed layered carbon domains suggests that Ti-containing samples were associated with less preservation of the carbon framework at this temperature.

At 800 °C, carbonization proceeds under conditions where differences associated with heating rate become less pronounced.[4] Elemental analyses show that the char residues reach carbon contents of approximately 93 wt%, with only minor variations associated with heating rate. Under these conditions, Cu-containing samples still exhibited slightly higher carbon contents than Ti-containing or additive-free samples, suggesting that Cu-containing samples continued to show relatively high carbon retention at 800 °C, although its structural influence appeared less pronounced than at 500 °C.

Ti-assisted samples at 800 °C exhibited extensive fragmentation of the carbon framework and distinct reaction zones at the Ti–carbon interface in SEM and TEM observations. Together with the increased mass loss observed in TG–DTA measurements, these findings suggest decomposition-related interfacial behavior at elevated temperatures, possibly associated with reactions at the metal–carbon interface.

Taken together, these results are consistent with temperature-dependent differences in additive-associated behavior, in which Cu-containing samples were generally associated with greater solid carbon retention at intermediate temperatures, whereas Ti-containing samples exhibited greater decomposition-related behavior, with these tendencies becoming more apparent at elevated temperatures. These findings suggest the importance of temperature-specific additive selection when controlling char yield, composition, and microstructure during woody biomass carbonization under inert atmospheres.

4.2 Implications for functional carbon materials

The temperature-dependent variation in the additive effects of Cu and Ti has important implications for the rational design of functional carbon materials derived from woody biomass. In particular, carbonization at 500 °C in the presence of Cu tended to produce partially layered, turbostratic carbon structures with relatively preserved frameworks and expanded interlayer spacing. Such structural characteristics are commonly associated with enhanced accessibility and reactivity in disordered biomass-derived carbons.[12] These microstructural features may be advantageous for applications requiring accessible active sites, such as gas adsorption, energy storage electrodes, and catalyst supports.[2,13,14]

The disordered stacking and enlarged interlayer gaps observed in Cu-containing chars at intermediate temperatures are consistent with structures that may be favorable for ion and gas transport in carbon materials reported in previous studies. In contrast, Ti-containing samples exhibited greater mass loss and lower carbon retention, particularly at elevated temperatures, leading to extensive fragmentation and reduced solid carbon retention. While this behavior is unfavorable for maximizing char yield, it may be associated with enhanced devolatilization or gas-phase product formation during carbonization.

At 800 °C, differences in carbon structure among samples with different heating rates became less evident. The observed results suggest that temperature had a greater influence on carbonization behavior under these conditions, while differences associated with additive type were less pronounced. Nevertheless, Cu-containing samples still exhibited relatively high carbon retention compared with the other samples.

Overall, these findings suggest that the properties of biomass-derived carbon materials may be influenced by appropriate combinations of additive selection and carbonization temperature. Cu-assisted carbonization at intermediate temperatures may be suitable for producing turbostratic carbon structures with potential functional utility, whereas Ti incorporation may be more appropriate for applications emphasizing devolatilization and volatile formation. This temperature-specific additive selection concept provides a practical framework for controlling both the yield and functionality of biomass-derived carbon materials.

Because the oxidation states and phases of Cu and Ti after carbonization were not directly determined in this study, the proposed interpretations should be regarded as possible explanations rather than definitive mechanistic conclusions.

The present study was designed as an exploratory investigation focusing on comparative trends in carbonization behavior under different additive and temperature conditions. TG–DTA measurements were repeated three times for each condition, while elemental analyses were performed in duplicate. SEM and TEM observations were conducted at representative locations within each sample. The results are therefore intended to provide qualitative and comparative insights into temperature-dependent changes in carbonization behavior. Future studies incorporating larger datasets and more extensive statistical analyses will be valuable for further quantitative validation of the observed trends.

5. Conclusions

This study suggests that the effects of Cu and Ti additives during the thermal treatment of woody biomass are temperature dependent. Cu addition was associated with the formation of partially layered carbon structures and relatively higher char

retention under the present conditions, whereas Ti addition was associated with increased devolatilization and carbon consumption, particularly under high-temperature conditions.

These findings may provide a practical framework for designing biomass carbonization processes under inert atmospheres aimed at controlling carbon yield and microstructural characteristics through additive selection and thermal conditions. Cu containing samples were associated with partially layered carbon structures and relatively high solid carbon retention at moderate temperatures, whereas Ti-containing samples exhibited greater decomposition-related behavior, particularly under high-temperature conditions.

Overall, the present results suggest that temperature-dependent additive selection may influence carbonization behavior and product distributions under the conditions examined in this study. Because the oxidation states and phases of Cu and Ti after carbonization were not directly determined in this study, the proposed interpretations should be regarded as possible explanations rather than definitive mechanistic conclusions.

Additional information

FFT analysis was performed using a custom script provided by Prof. Kyoichi Oshida. While the script is not publicly available, the radial profile data derived from the FFT analysis are included in the dataset, allowing reproduction of the figures presented in the manuscript.

Supplementary Figure S1. TG–DTA curves of woody biomass during carbonization at 500 °C under a nitrogen atmosphere with heating rates of 10, 20, and 40 °C min^{-1} (r10, r20, and r40). Panels (1–3) show untreated wood samples (T500), panels (4–6) show Cu-added samples (T500Cu), and panels (7–9) show Ti-added samples (T500Ti). Green, blue, and red lines represent TG, DTA, and temperature profiles, respectively.

Supplementary Figure S2. TG–DTA curves of woody biomass during carbonization at 800 °C under a nitrogen atmosphere with heating rates of 10, 20, and 40 °C min^{-1} (r10, r20, and r40). Panels (1–3) show untreated wood samples (T800), panels (4–6) show Cu-added samples (T800Cu), and panels (7–9) show Ti-added samples (T800Ti). Green, blue, and red lines represent TG, DTA, and temperature profiles, respectively.

Data availability

Underlying data

Zenodo: Dataset supporting the article: Thermal carbonization of woody biomass under inert atmosphere with temperature-dependent switching of catalytic effects of Cu and Ti. https://doi.org/10.5281/zenodo.18912773[15]

The dataset includes:

- Tables 1–4: Weight loss and elemental composition data of fir-derived carbonized samples at 500 °C and 800 °C (XLSX and UTF-8 CSV formats).
- TEM line-profile data corresponding to Fig. 2 ((2) T500_r20, (5) T500_Cu_r20, (8) T500_Ti_r20) and Fig. 4 ((2) T800_r20, (5) T800_Cu_r20, (8) T800_Ti_r20), including interlayer spacing (nm) and grayscale intensity (a.u.).

Extended data

Zenodo: same repository as above

- Processed TG–DTA curves corresponding to Supplementary Figures 1 and 2.

Data not included.

The raw numerical TG–DTA data are currently not available in digital format.

Acknowledgements

The authors sincerely thank Dr. Aya Yanagawa, the late Prof. Takeshi Yoshimura, and the late Mr. Joko Sulistyo for their valuable guidance during this work. The authors also thank Prof. Kyoichi Oshida for providing the custom FFT analysis script used in this study. This research was conducted within the framework of the Research Unit for Realization of Sustainable Society (RURSS), Kyoto University.

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Publisher Full Text

Open Peer Review

Current Peer Review Status: ? ?

Version 2

Reviewer Report 22 July 2026

https://doi.org/10.5256/f1000research.204911.r498445

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Diakaridia Sangaré
CIRAD, French Agricultural Research Centre for International Development, Montpellier, France

I thank the authors for the revisions. Most of my previous comments have been satisfactorily addressed. However, the following points still require correction:

1. Section 3.1 states that the Cu-containing samples had higher carbon contents than the Ti-containing and untreated samples. However, Tables 3 and 4 do not distinguish between Cu, Ti, and untreated treatments. Therefore, this comparison cannot be verified from the presented elemental data. The authors should provide the corresponding data or revise this statement.
2. The selected biomass-to-metal ratio of 7:3 is reported, but its justification is still absent from Section 2.1. Considering the high metal loading, the authors should briefly explain why this ratio was selected and acknowledge that physical effects, including biomass–metal contact and heat-transfer changes, may also influence the observed carbonization behavior.
3. The final paragraph of Section 3.4 contains an incomplete and repeated sentence concerning the effects of Cu and Ti on carbon microstructure. This sentence should be corrected.

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Thermochemical biomass conversion, bioenergy, high-value products, product characterization (solid, liquid, gas), kinetic modeling, and numerical simulations of biomass processes

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.

Version 1

Reviewer Report 11 May 2026

https://doi.org/10.5256/f1000research.195280.r477227

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Diakaridia Sangaré
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The manuscript investigates the carbonization of *Abies sachalinensis* wood flour under nitrogen at 500 °C and 800 °C with Cu and Ti additives. The topic is relevant, but several internal inconsistencies and missing methodological clarifications should be addressed before indexing. My comments are as follows:

1. There is an inconsistency in the interpretation of elemental composition. In Section 3.1, p. 4, the authors state that the char residues produced at 500 °C contained higher carbon contents, whereas those obtained at 800 °C exhibited lower carbon contents. However, Tables 3 and 4 show the opposite trend: approximately 78–80 wt% C at 500 °C and approximately 93 wt% C at 800 °C. This contradiction should be corrected because it directly affects the interpretation of carbon enrichment during carbonization.
2. The order and presentation of the tables are confusing. Table 2, corresponding to the 800 °C experiments, appears before Table 1, which corresponds to the 500 °C experiments. This disrupts the logical flow of the results, especially because the discussion first describes 500 °C and then 800 °C. The authors should reorder the tables or revise the text to ensure that the numbering follows the sequence of presentation.
3. The FTIR method is described in Section 2.4, p. 4, but no FTIR spectra or FTIR-based discussion are presented in the results. If FTIR was performed, the spectra should be included and interpreted, particularly because the manuscript discusses functional groups, carbon stabilization and structural evolution. If FTIR data are not used, this section should be removed from the methodology.
4. The particle size of the wood flour is not sufficiently specified. In Section 2.1, p. 3, the authors indicate that the wood was ground and sieved, and they report the particle sizes of Cu and Ti powders, but not that of the wood flour. This information is important because the relative particle size of biomass and metal additives may affect biomass–metal contact and, consequently, the apparent catalytic effect. The authors should provide the wood flour particle size range.
5. The use of the term “catalyst” should be reconsidered. In Section 2.1, p. 3, the authors report a biomass-to-metal mass ratio of 7:3, corresponding to about 30 wt% Cu or Ti. At this relatively high loading, the metals may act not only as catalysts but also as metal additives that modify physical contact, heat transfer, and mass-loss behavior. The authors should justify the selected loading and use the term “catalyst” more cautiously, or alternatively describe Cu and Ti as metal additives throughout the manuscript.
6. The interpretation of the TEM-derived interlayer spacings requires more clarification. Figures 2 and 4 report relatively large spacing values, especially at 500 °C, ranging from approximately 0.76 to 1.12 nm. The authors should clarify whether these values represent

true carbon layer spacing, apparent fringe spacing, pore-related periodicity or image-processing-derived structural distances. Without this clarification, the link between FFT-derived spacing and turbostratic carbon ordering remains ambiguous.

7. Some statements about applications are broader than the results support. In Section 4.2, p. 11, the authors suggest potential utility for gas adsorption, energy storage electrodes and catalyst supports. However, no surface area, porosity, adsorption capacity, electrical conductivity or electrochemical performance is reported. These application claims should be moderated or clearly presented as possible future directions rather than conclusions supported by the present data.
8. The distinction between the Results and Discussion sections is not sufficiently clear. In Section 3.1 and Sections 3.3–3.4, the authors already include interpretative statements on carbon stabilization, decomposition, and structural organization, which belong more appropriately in the Discussion. Conversely, Section 4.1 largely repeats the results instead of providing a deeper mechanistic interpretation or a stronger comparison with previous literature. The authors should reorganize these sections by keeping the Results more descriptive and using the Discussion to critically interpret the findings, address limitations, and relate them to existing studies.

Is the work clearly and accurately presented and does it cite the current literature?
Partly

Is the study design appropriate and is the work technically sound?
Partly

Are sufficient details of methods and analysis provided to allow replication by others?
Partly

If applicable, is the statistical analysis and its interpretation appropriate?
Not applicable

Are all the source data underlying the results available to ensure full reproducibility?
Partly

Are the conclusions drawn adequately supported by the results?
Partly

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Thermochemical biomass conversion, bioenergy, high-value products, product characterization (solid, liquid, gas), kinetic modeling, and numerical simulations of biomass processes

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.

Author Response 15 Jul 2026

俊充 畑

We sincerely thank Reviewer 2 for the careful evaluation of our manuscript and for the constructive comments. We apologize for the delay in posting this response due to a technical issue with the editorial system. We have revised the manuscript accordingly. Detailed responses to each comment are provided below.

Response to Reviewer 2

Comment 1:
The terminology “catalyst”, “catalytic effects”, and “catalytic role switching” is too strong because catalytic mechanisms were not directly demonstrated.

Response:
We appreciate this important comment. We agree that the terminology may imply mechanistic conclusions that are not directly supported by the present experimental evidence. Therefore, expressions such as “catalyst,” “catalytic effects,” and “catalytic role switching” were revised to more neutral terminology including “additive,” “additive-assisted behavior,” and “temperature-dependent variation in additive effects.” The manuscript now focuses on observed carbonization behavior rather than mechanistic interpretation.

Revision:
Terminology was revised throughout the manuscript, including the Title, Abstract, Results, Discussion, Conclusions, and Keywords.

Comment 2:
The carbon-content interpretation in Section 3.1 was inconsistent with the values shown in Tables 3 and 4.

Response:
We thank the reviewer for identifying this inconsistency. The relevant description was corrected to match the numerical values reported in Tables 3 and 4. The revised text now correctly indicates that carbonization at 800 °C produced higher carbon contents than carbonization at 500 °C.

Revision:
Section 3.1 was revised accordingly.

Comment 3:
FTIR was not used in this study, although FTIR-related descriptions were included in the methodology.

Response:
We appreciate the reviewer’s careful reading. Because FTIR measurements were not performed in the present study and no FTIR data were discussed, the FTIR-related

description was removed from the Methods section to improve consistency between methodology and reported results.

Revision:
FTIR-related text was removed from Section 2.4.

Comment 4:
The relationship between particle size and additive effects was not sufficiently described.

Response:
We thank the reviewer for this suggestion. To improve reproducibility and clarify the experimental conditions, the particle-size range of the wood flour used in this study has been added to the Materials and Methods section.

Revision:
Particle-size information was added to Section 2.1.

Comment 5:
The apparent structural spacing obtained from FFT profiles should not be interpreted as ideal graphite interlayer spacing.

Response: We appreciate this important comment. Additional clarification has been added to the Methods and Results sections. The manuscript now explicitly states that the reported spacing values were derived from rotationally integrated FFT profiles and represent apparent structural spacing associated with disordered carbon structures and nanoscale periodicity. These values should not be interpreted as ideal graphite interlayer spacing.

Revision:
Clarifying statements were added to the Methods and Results sections.

Comment 6:
Several statements concerning future applications were overly speculative.

Response:
We agree with the reviewer that the discussion should remain consistent with the experimental evidence. Therefore, statements concerning potential applications were revised to describe future possibilities rather than conclusions directly supported by the present study.

Revision:
Relevant statements in the Discussion and Conclusions sections were revised.

Comment 7:

Interpretations should be separated from observations, and speculative discussion should be moved to the Discussion section.

Response:
We appreciate this constructive comment. To improve clarity, descriptive observations were retained primarily within the Results section, whereas interpretation, comparison with previous studies, limitations, and future perspectives were reorganized into the Discussion section.

Revision:
The Results and Discussion sections were revised and reorganized accordingly.

Comment 8:
The manuscript should acknowledge that the study is preliminary and that limitations regarding replication and statistical evaluation remain.

Response:
We thank the reviewer for this valuable comment. The revised manuscript now explicitly states that this work was conducted as a preliminary exploratory investigation focusing on comparative trends in carbonization behavior. Additional methodological information regarding TG–DTA triplicate measurements, duplicate elemental analyses, and SEM/TEM observations at multiple locations has been added. The limitations associated with replication and statistical evaluation have also been acknowledged in the Discussion section.

Revision:
Additional statements were added to the Materials and Methods and Discussion sections.

Competing Interests: No competing interests were disclosed.

Reviewer Report 22 April 2026

https://doi.org/10.5256/f1000research.195280.r477228

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Sathish Raam Ravichandran
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[2] Kongu Engineering College, Erode, Tamil Nadu, India

General Comments about the article:

- This manuscript investigates the effects of Cu and Ti additives on the carbonization of Todo

fir wood flour under nitrogen at 500 °C and 800 °C, using TG-DTA, elemental analysis, SEM, and TEM.
- The authors conclude that Cu promotes char retention, while Ti promotes devolatilization, and propose a temperature-dependent catalytic role-switching mechanism.
- However, the central mechanistic claims are stronger than the data support, and several methodological issues limit the scientific soundness of the conclusions.
- Major revision is required before the work can be considered scientifically sound.

Specific comments for the authors:
- Though the article is well written and structured, the main claim of "temperature-dependent switching of catalytic effects" is not accurately supported by the results.
- At 500 °C, Cu increases char retention and Ti increases mass loss and at 800 °C, Cu still increases char retention and Ti still increases mass loss. This indicates persistent catalytic behavior, not "switching."
- The literature review relies heavily on older references.
- The biomass:catalyst ratio used is 7:3 (30 wt%), which is unusually high. At this loading, the additive significantly alters the physical behavior of the biomass, rather than acting as a conventional catalyst. No justification is provided for choosing this catalyst loading.
- The manuscript claims Cu stabilizes carbon frameworks, Ti promotes interfacial catalytic decomposition, Cu promotes aromatization. but these claims are not directly measured. It also misses gas product analysis, bio-oil analysis, aromaticity analysis and catalyst phase analysis.
- The oxidation state and phase of Cu and Ti after carbonization are unknown.
- Number of replicates not reported, No standard deviation values that lacks for reproducibility.
- Processed tables and selected TEM profile data are available.
- The data support that cu gives higher char retention and Ti gives greater mass loss but the data do not fully support "catalytic role switching", "Cu promotes aromatization" and "Ti promotes interfacial catalytic decomposition" as highlighted in the abstract and conclusion.

Is the work clearly and accurately presented and does it cite the current literature?
Partly

Is the study design appropriate and is the work technically sound?
Partly

Are sufficient details of methods and analysis provided to allow replication by others?
Partly

If applicable, is the statistical analysis and its interpretation appropriate?
No

Are all the source data underlying the results available to ensure full reproducibility?
Partly

Are the conclusions drawn adequately supported by the results?
Partly

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: My research area is Chemical Engineering, with specialization in biomass thermochemical conversion, catalytic pyrolysis/carbonization, biofuel production, membrane technology, and biomass-derived functional carbon materials

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.

Author Response 15 Jul 2026

俊充 畑

We sincerely thank Reviewer 1 for the careful evaluation of our manuscript and for the constructive comments. We apologize for the delay in posting this response due to a technical issue with the editorial system. We have revised the manuscript accordingly. Detailed responses to each comment are provided below.

Response to Reviewer 1
Comment 1:
The main claim of “temperature-dependent switching of catalytic effects” is not accurately supported by the results. The observed behavior indicates persistent effects rather than true switching.

Response:
We thank the reviewer for this important comment. We agree that the term “switching” may imply a mechanistic transition that is not directly demonstrated by the present experimental results. To avoid overinterpretation, we have replaced the expression “temperature-dependent switching of catalytic effects” throughout the manuscript with “temperature-dependent variation in the effects of Cu and Ti additives.” We also revised related statements in the Abstract, Introduction, Discussion, Conclusions, Keywords, and Dataset title to emphasize observed trends rather than mechanistic switching.

Revision:
The Title, Abstract, Introduction, Discussion, Conclusions, Keywords, Figure 5 caption, and Zenodo dataset title were revised accordingly.

Comment 2:
The literature review relies heavily on older references.

Response:
We appreciate this suggestion. To improve the relevance and timeliness of the literature review, recent review articles on biomass-derived carbon materials and energy-storage applications have been added and discussed where appropriate.

Revision:
Additional references, including Li et al. (2020) and Biswal and Balasubramanian (2026), were incorporated into the Discussion section.

Comment 3:
The biomass:catalyst ratio used is 7:3 (30 wt%), which is unusually high. No justification is provided.

Response:
We thank the reviewer for this observation. The additive loading was intentionally selected to maximize observable additive-related effects on carbonization behavior and to maintain consistency with our previous studies employing similar experimental conditions. The purpose of this study was to comparatively evaluate the effects of Cu and Ti rather than to optimize the additive loading.

Revision:
An explanation of the rationale for the selected additive loading has been added to the Materials and Methods section.

Comment 4:
At this loading, the metals may act as additives rather than conventional catalysts.

Response:
We agree with the reviewer that the term “catalyst” may imply a mechanistic role that cannot be conclusively demonstrated under the present conditions. Therefore, the terminology has been revised throughout the manuscript, and Cu and Ti are now primarily described as “additives,” except when referring to previous literature.

Revision:
The terms “catalyst” and “catalytic” were revised where appropriate throughout the manuscript.

Comment 5:
The claims that Cu stabilizes carbon frameworks, promotes aromatization, and that Ti promotes interfacial catalytic decomposition are not directly measured.

Response:
We agree that these interpretations should be presented more cautiously. The manuscript has been revised to distinguish direct observations from possible interpretations. Statements implying definitive mechanisms were modified to emphasize associations suggested by the experimental results.

Revision:
Expressions such as “promoted,” “stabilized,” and “demonstrated” were replaced, where

appropriate, with more cautious wording such as “was associated with,” “suggested,” “indicated,” or “may contribute to.”

Comment 6:
The oxidation state and phase of Cu and Ti after carbonization are unknown.

Response:
We appreciate this comment. Determination of the oxidation states and crystalline phases of Cu and Ti would provide valuable mechanistic information. However, such analyses were beyond the scope of the present exploratory study, which focused on comparative carbonization behavior and microstructural development. We have acknowledged this limitation and identified it as an important topic for future investigation.

Revision:
A statement describing this limitation has been added to the Discussion section.

Comment 7:
Number of replicates not reported. No standard deviation values that lacks for reproducibility.

Response:
We thank the reviewer for highlighting the importance of reproducibility. TG–DTA measurements were conducted three times under representative conditions, and elemental analyses were performed in duplicate. SEM and TEM observations were conducted at multiple locations within each specimen, and representative images together with averaged elemental compositions were reported. Because the present work was designed as an exploratory investigation focusing on comparative trends, standard deviation values were not included. This limitation has now been acknowledged in the revised manuscript.

Revision:
Additional methodological details regarding replicate measurements, averaging procedures, and study limitations have been added to the Materials and Methods and Discussion sections.

Competing Interests: No competing interests were disclosed.

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