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Mechanisms of Biochar Structural Evolution and Carbon Stability During Biomass Pyrolysis

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Abstract. Biomass pyrolysis has great application potential in the high-value utilization of renewable carbon resources. The microstructure of biochar formed during pyrolysis is jointly affected by the composition of raw materials and pyrolysis conditions, and is further related to the formation of carbon stability. This paper focuses on the main line of "raw material composition - pyrolysis process - structural evolution - carbon stability", summarizes the pyrolysis differences and interactions of the three major components of hemicellulose, cellulose and lignin, and also analyzes the regulatory effects of pyrolysis temperature, heating rate, residence time and raw material composition on the structural evolution of biochar. On this basis, the variation characteristics of the carbon skeleton, pore structure and surface functional groups, as well as the chemical connotation and evaluation methods of carbon stability, were summarized. Overall, the growth of aromatic structure, the reduction of oxygen-containing functional groups and the high condensation of carbon skeleton will have a more direct impact on the formation of stable carbon, while the pyrolysis of lignin and the high-temperature aromatization process are usually more closely related to the formation of highly stable biochar. In the future, further research on the quantitative correlation between structural parameters and long-term stability is still needed.

Keywords: Biomass pyrolysis, Biochar, Structural evolution, Carbon stability, Aromatization

1. Introduction

Biomass is a widely available, renewable and carbon-rich natural organic resource. Its efficient conversion and utilization are of great significance for energy substitution, carbon reduction and resource recycling. Pyrolysis is an important way of biomass resource utilization, which can convert biomass into gas, liquid, and solid products under anaerobic or anaerobic conditions. Among them, biochar has received widespread attention due to its high carbon content, rich pore structure, and certain carbon fixation potential [1-3]. At present, biochar has been applied in fields such as soil improvement, pollutant adsorption, and carbon sequestration [1,3].

The properties of biochar are influenced by both the composition of raw materials and pyrolysis conditions. Biochar prepared from different raw materials and under different pyrolysis conditions often exhibit differences in microstructure and carbon stability. The structures and pyrolysis characteristics of cellulose, hemicellulose, and lignin, the three main components in biomass, are not the same. Factors such as pyrolysis temperature, heating rate, and residence time further affect the carbon structure transformation process, thereby changing the pore structure, surface functional groups, and aromatization degree of biochar [1-4].

At present, relevant research mainly focuses on changes in pyrolysis yield, elemental composition, and surface properties, but the systematic sorting of the logical chain of "raw material composition-pyrolysis process-structural evolution-carbon stability" is still relatively insufficient. This article focuses on the structural evolution and carbon stability of biochar during the biomass pyrolysis process. Analyze the thermal decomposition characteristics of the main components of biomass and the regulatory role of thermal decomposition conditions. Also, the intrinsic relationship between the microstructure and the stability of carbon is explored. This provides a reference for the targeted preparation and stability control of biochar.

2. The pyrolysis reaction mechanism of the main components of biomass

The reaction behavior and carbonization contribution of the three major components of biomass during pyrolysis are different. The early release of volatile matter and initial pore formation are mainly influenced by hemicellulose, which mainly provides the main carbon skeleton precursor. Lignin is conducive to the formation of stable carbon structures with high aromaticity and high shrinkage [5-10]. The three components are not independent of each other, but are coupled with each other during the pyrolysis process, together shaping the subsequent structural evolution path of biochar [5,6,11]. Therefore, to analyze how biochar forms a specific structure, how its stability evolves, the prerequisite is to grasp the differences in pyrolysis of the three major components and their mutual influence.

2.1. Collaborative pyrolysis behavior of biomass components

The volatile components, intermediates, and free radicals generated by the pyrolysis of different components will continue to undergo re cracking, condensation, and cross-linking reactions, thereby jointly affecting the behavior of volatile analysis, tar generation, and solid-phase residual carbon structure [5,6]. Therefore, biochar is not a simple superposition of the thermal behavior of each component, but the result of the continuous interaction between each component. Bielecki and Zubkova pointed out that the pyrolysis of lignocellulose is essentially a process of multi-component cross reactions working together [5]; Giudicianni et al.'s research also suggests that the interactions between components can affect the characteristics of solid and gas products [6]. Therefore, a deep understanding of collaborative pyrolysis behavior is an important prerequisite for clarifying the actual biomass carbonization pathway [11].

2.2. Thermal decomposition differences and functional division of the three major components

Hemicellulose is an amorphous, branched heteropolysaccharide with the lowest thermal stability and usually decomposes first [6,7]. Its pyrolysis mainly releases volatile products such as CO_2, CO, and organic acids. Although it has a weak direct contribution to the high condensed carbon skeleton, it is beneficial for the early formation of pores during pyrolysis. Cellulose is a linear polysaccharide formed by the connection of β -1,4-glycosidic bonds. During the pyrolysis process, it first breaks the chain and depolymerizes to produce intermediates such as L-glucan, and then undergoes dehydration and rearrangement [7,8]. Compared with hemicellulose, cellulose pyrolysis is more concentrated, producing more volatile products and providing key skeleton precursors for char formation. Lignin is a complex aromatic polymer characterized by a wide decomposition temperature range and a strong tendency to char [9,10]. During the initial stage of pyrolysis, ether bonds are broken to generate phenols and free radicals. Subsequently, through cross-linking condensation and aromatic ring rearrangement, a highly condensed and aromatic stable carbon structure is formed, which is the core contributor to the stable carbon skeleton [9,10]. Overall, the pyrolysis differences of the three major components can be summarized as hemicellulose dominating early devolatilization and pore initiation, cellulose dominating the formation of carbon skeleton precursors, and lignin dominating the aromatization and stabilization of carbon structures [5-10].

3. The regulatory effect of pyrolysis conditions on structural evolution

The influence of pyrolysis conditions on the structural evolution of biochar is distinct, with temperature being the core dominant factor, directly determining the depth of carbon skeleton rearrangement; The heating rate mainly affects the speed of volatile matter release and the opportunity for secondary reactions; The residence time mainly affects whether the later condensation and aromatization are sufficient; The composition of raw materials is the reaction basis that determines whether these process parameters are effective [1,2,12]. Therefore, the formation of the structure of biochar is essentially a comprehensive evolutionary outcome resulting from the joint regulation of the raw material properties and the pyrolysis conditions. The differentiated effects produced under different conditions further determine the subsequent characteristics of the microstructure. It also determines the formation path of carbon stability.

3.1. The dominant role of pyrolysis temperature

Among various process parameters, pyrolysis temperature is the most critical factor affecting the structural evolution of biochar [13,14]. The reason is that temperature directly determines the order of chemical bond breaking, the degree of volatile release, the removal of oxygen-containing functional groups, and the strength of aromatic structure condensation. The low-temperature stage system mainly undergoes dehydration, decarboxylation, and primary carbonization reactions, and the resulting biochar still retains many oxygen-containing functional groups and amorphous structures;After entering the medium temperature stage, structural rearrangement gradually increases, aromatic clusters begin to form, and the carbon skeleton transitions from a relatively disordered state to a higher degree of aromatization [1,14]; During the high temperature stage, the continuous removal of oxygen-containing functional groups and condensation reactions are significantly enhanced, resulting in an increase in the size of aromatic structures and a higher degree of orderliness of carbon skeletons [1,13,14]. Therefore, the temperature critical factor essentially determines the depth of carbon skeleton rearrangement and the degree to which the carbon structure transitions from a low condensation and high reactivity state to a high aromaticity and strong chemical inertness state.

Although high temperature is beneficial for aromatization and enhanced carbon stability, it may also cause some pore structures to shrink or even collapse, reducing surface oxygen-containing functional groups and weakening certain surface reactivity [1,12,13]. This means that the essence of temperature regulation is not simply to increase the pyrolysis intensity, but to find a balance between stable carbon formation and surface structural functionality

3.2. The synergistic effect of heating rate, residence time, and raw material composition

Unlike the temperature dominated carbon skeleton rearrangement depth, the heating rate and residence time are more reflected in regulating the rhythm of the pyrolysis process and the adequacy of the later reactions [1,2,12]. The heating rate mainly affects the release rate of volatile matter and its opportunity to participate in secondary reactions. Rapid heating causes volatile matter to quickly escape, reducing the possibility of its residence and recondensation on the solid phase surface; Slow heating is more conducive to the intermediate staying in local areas and participating in secondary reactions, thereby promoting local structural reorganization [2]. In contrast, the residence time mainly affects whether the condensation and aromatization in the later stage of pyrolysis can be fully completed. Extending the residence time appropriately is usually beneficial for further removal of oxygen-containing groups and growth of aromatic structures, but this effect is usually established on the basis that the temperature has reached sufficient reaction strength [12].

The effect of process parameters cannot be separated from the constraints of raw material composition. Different biomass species have differences in cellulose, hemicellulose, lignin, and ash content, so even under the same pyrolysis conditions, their structural evolution paths may be different [1,12,13]. For example, high lignin raw materials are more likely to form high aromatic carbon at higher temperatures; High hemicellulose raw materials tend to release volatile compounds in the early stages of pyrolysis, which has a more significant impact on the formation of pore structures; Minerals in high ash raw materials may also catalyze devolatilization and char formation reactions, further altering local structural rearrangement pathways [1,12]. Therefore, pyrolysis conditions are not independent variables that exist separately from the raw materials, but rather regulatory factors that play a role based on the properties of the raw materials.

4. Formation and evolution of microstructure of biochar

4.1. Evolution of carbon skeleton and pore surface structure

The degree of pyrolysis deepens, and the internal carbon skeleton of biochar continues to undergo rearrangement. The carbon samples obtained during the low-temperature stage still retain a significant amount of oxygen-containing structures and amorphous features, resulting in a lower overall degree of condensation; After entering the medium high temperature stage, deoxygenation and condensation reactions are enhanced, the size of aromatic clusters gradually increases, and the carbon skeleton gradually transitions from a low condensation state to a high condensation aromatic network [10,14]. Compared with low-temperature carbon, high-temperature carbon usually exhibits a higher degree of aromatization and stronger chemical inertness, which is also an important structural basis for its higher stability.

Accompanying the evolution of the carbon skeleton is the synchronous change of pore structure and surface structure. The pore structure of biochar is mainly derived from the combined effects of volatile matter release, skeleton contraction, and local structural rearrangement [1,12]. In the early stage of pyrolysis, the release of a large amount of volatile compounds is beneficial for the formation of initial pore channels. As the temperature increases, the pore structure can further develop. However, when the degree of pyrolysis is too high, local pore walls may also collapse due to shrinkage [12]. At the same time, the oxygen-containing functional groups on the surface will continue to decrease, leading to a decrease in surface polarity. It is worth noting that although the development of pore structure is beneficial for improving specific surface area and adsorption performance, it does not necessarily equate to the enhancement of long-term carbon stability.

Compared to others, the high condensation of carbon skeleton is the more critical foundation for stable carbon formation.

4.2. Structural characterization and its chemical significance

The evolution of biochar structure requires the joint analysis of multiple characterization methods, among which Raman and XRD are mainly used to determine the aromatization and ordering trends of carbon skeleton [14]. FTIR can track the changes in surface oxygen-containing functional groups, while BET is used to characterize pore structure and specific surface area characteristics [1,3]. The significance of these methods lies not in describing a single indicator separately, but in jointly supporting the judgment of structural evolution and its stability effects from different scales.

5. The chemical essence and evaluation methods of carbon stability

5.1. The chemical connotation of carbon stability

From a chemical perspective, the key to the stability of biochar lies in whether its internal carbon structure is sufficiently inert [3,4]. Generally speaking, carbon structures with higher aromatic condensation degree, fewer edge active sites, and lower surface polarity are less likely to undergo oxidation or be utilized by microorganisms under long-term environmental conditions, and therefore are more likely to exhibit higher stability [3].On the contrary, if there are still many oxygen-containing functional groups retained in the carbon structure, or if the edge active sites are relatively abundant, the possibility of its subsequent participation in chemical reactions and environmental transformation is usually higher [4].

In other words, the core of carbon stability does not lie in whether a carbon sample looks complex or not, but in whether its carbon skeleton has transformed from a highly reactive primary carbonization structure to a higher aromaticity, higher condensation degree, and lower reactivity structural state. Therefore, when discussing the long-term stability of biochar, what is truly worth paying attention to is the degree of structural maturity reflected behind these indicators

5.2. Common evaluation methods and their limitations

The commonly used methods for evaluating the stability of biochar currently include elemental ratio method, chemical oxidation method, thermal analysis method, long-term mineralization experiment, and newer methods such as reflectivity [3,4,15]. Among them, the H/C and O/C element ratio methods are simple and convenient to operate, and are also suitable for quickly comparing the potential stability differences between different carbon samples. However, they are essentially indirect judgments; The chemical oxidation method can quickly evaluate the ability of carbon samples to resist chemical transformation, but there may still be differences between the experimental system and the real natural environment; Thermal analysis can reflect the trend of thermal stability, but thermal stability itself cannot be completely equated with persistence in long-term environments; The long-term mineralization experiment is more closely related to real environmental behavior, but the experimental period is long and time-consuming; Reflectance and other methods provide new judgment ideas from the perspectives of structural maturity and persistence [15].

From a comparative perspective, these methods are not entirely suitable for answering the same questions. The element ratio method is more suitable for preliminary screening, long-term mineralization experiments are closer to real long-term behavior, while thermal analysis and chemical oxidation methods are more suitable for relative stability comparison [3,4]. However, a single method often fails to fully reflect the true long-term stability of biochar. For example, some carbon samples may exhibit relatively stable behavior in thermal analysis, but their actual behavior in complex environments is still influenced by various factors such as pore structure, surface chemistry, and external conditions [3,4]. So, instead of searching for a "unique and best" indicator, a more reasonable approach is to combine different methods and improve the accuracy of long-term stability assessment of biochar through joint evaluation of multiple indicators.

6. Formation mechanism and prospects of microstructure carbon stability relationship

6.1. The decisive role of microstructure in carbon stability

From a structural comparison perspective, the aromatization and high condensation of carbon skeletons are directly related to long-term stability. The changes in pore structure and surface functional groups are reflected in the regulation of interfacial reactivity and environmental behavior [10,14,15]. As the degree of pyrolysis deepens, the size of aromatic clusters in biochar increases, the number of edge active sites decreases, oxygen-containing functional groups continue to be removed, and the carbon structure changes from primary carbonization products to highly condensed aromatic networks [10,14]. This change indicates a decrease in units in the structure that are easily oxidized or utilized by microorganisms, thus enhancing their antioxidant and anti degradation capabilities [15]. In contrast, although the development of pore structure is beneficial for improving specific surface area and interfacial reactivity, it does not necessarily equate to the synchronous enhancement of long-term carbon stability. Therefore, it is generally believed that carbon skeleton aromatization is the more fundamental basis for stability improvement.

6.2. Current research deficiencies and future prospects

The synergistic mechanism between raw material composition and pyrolysis conditions determines stable carbon formation, rather than the result of a single factor [1,2,10,12,13]. Raw materials with high lignin content are usually more conducive to the formation of highly aromatic structures, and temperature determines whether this potential can be achieved through sufficient deoxidation and condensation. The heating rate and residence time will further affect the opportunity for secondary reactions and the degree of aromatization completion [1,2,12]. At present, the quantitative relationship between aromatization degree, pore structure parameters, and long-term stability is still unclear, and there is a lack of a unified explanatory framework between different characterization results. In the future, multi-scale characterization, in-situ monitoring, and model coupling research should be strengthened to establish a more reliable structure stability prediction system.

7. Conclusion

This article summarizes the evolution of biochar structure and the formation process of carbon stability in biomass pyrolysis. The roles of hemicellulose, cellulose, and lignin in pyrolysis are not the same, but they jointly affect the formation of biochar structure during pyrolysis. Among them, hemicellulose has a greater impact on early volatilization analysis and initial pore formation, while cellulose mainly provides the main carbon skeleton precursor, and lignin is more conducive to high condensation aromatic structure and stable carbon formation.

In pyrolysis conditions, the most direct influence on the rearrangement and aromatization degree of the carbon skeleton is temperature. The heating rate and residence time mainly affect the reaction rhythm and the degree of later condensation. The composition of raw materials further determines the response basis of different process conditions. As the degree of pyrolysis deepens, biochar will gradually transform from primary carbon with low condensation and high oxygen content to carbon samples with higher aromaticity and a more stable structure.

Overall, the growth of aromatic structures, reduction of oxygen-containing functional groups, and high condensation of carbon skeletons are important chemical foundations for enhancing the stability of biochar. In the future, it is still necessary to strengthen the quantitative correlation research between structural parameters and long-term stability.

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