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Biochar Production, and Use: A Detailed Review of the Art

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Biochar Production, and Use: A Detailed Review of the Art

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Abstract: This study presents a detailed description of the technologies and processes for obtaining biochar and its formation from the fundamental structures of aromatic groups. These aromatic groups come from biomass pyrolysis; therefore, this document explores the complex relationship between biochar structural characteristics and the reactions involved in its formation during the pyrolysis process, specifically: analysis of the generation of a cross-linked network, structural features, and the impact of free radicals on biochar formation. This study will culminate with an analysis of microwave absorption and heat transfer dynamics among microwave absorbing materials and biomass or plastic particles. This examination aims to understand the temperature profiles in various heating modes, providing insights into their impacts on the overall performance of microwave-assisted reactors dedicated to these processes. Through this narrative, this study intends to provide an understanding of the multifaceted world of biochar and its diverse applications, drawing meaningful connections between its formation, structural attributes, and practical implementations.

Keywords: Biochar Production, Biochar Characterization, Biochar Application

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Introduction

Biochar has many applications, including carbon storage and sequestration, soil enhancement, and pollution remediation [1]. Knowledge of its molecular structure and functionality is needed to engineer biochar for specific applications [2].

Biomass can be municipal, animal, forest, agroindustry, pulp and paper, industrial biowaste, and thermochemically or biologically treated food waste. Thermochemical processes (pyrolysis, gasification, combustion, hydrothermal carbonization) are suitable for dried waste; on the other hand, wet wastes are recommended for use in the biological processes route (extraction processing, anaerobic digestion, fermentation, microbial fuel cell, transesterification).

Biochar Production

Various thermochemical techniques convert waste polymer and lignocellulosic biomass into valuable products: syngas, hot gas, biochar, and bio-oil (pyrolysis oil). These products could become new, such as heat, power, fine chemicals, etc. The plastic waste can be mixed with biomass to increase the synergy between both to achieve products like biochar for multiple applications.

The type of thermochemical process depends on the operation conditions (see Figure 1). Torrefaction is a heating process at the lowest temperature (290°C) that is carried out at a slow heat rate (0.01-0.05°C/s) and long residence time (10-60 min) to obtain mostly solid products [5-7].

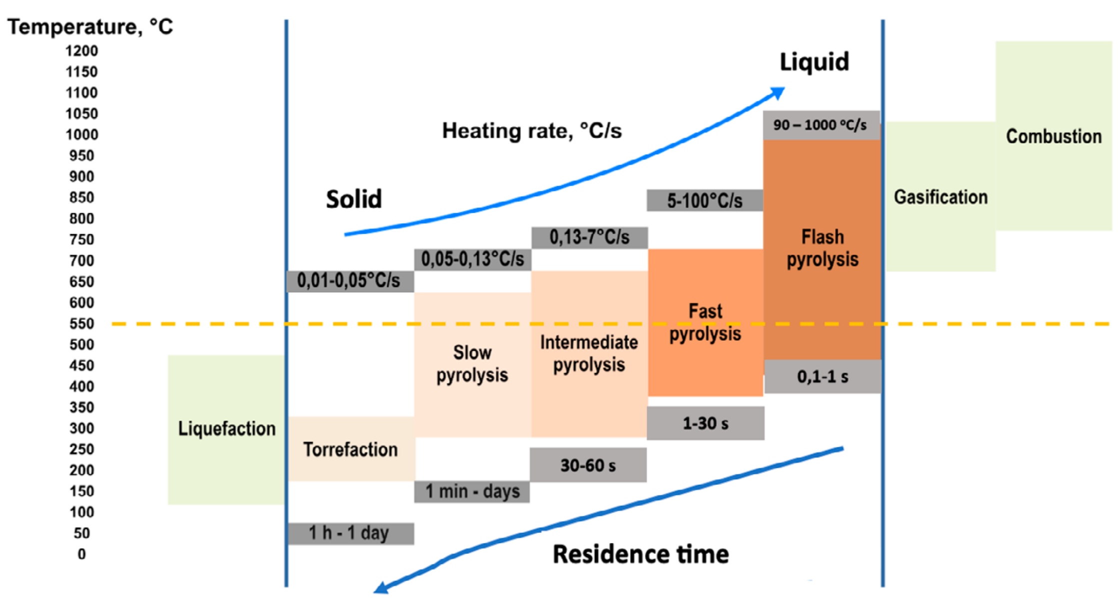

Figure 1. Description of figure above (prepared by authors and modified from [5]).

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The products formed during the pyrolysis of biomass and commercial plastics depend on pyrolysis severity. Primary processes are carried out at the lowest heating rate and temperature. Still, when the severity is increased (e.g., increasing the heating rate and the temperature), secondary char, condensed oil (phenolics, aromatic), and low molecular weight products are formed.

Biomass is transformed during the heating process, e.g., condensation of aliphatic chains for ring formation from cellulose and hemicellulose become a solid part and all the benzene rings from lignin remain at low temperature (200-400°C). Condensation of branched structure for ring enlargement and polymerization of benzene rings by removing ether bonds occur as temperature increases up to 500°C. The organization process, removal of the ether bond of the interlayer sheet, condensation, and enlargement of fused rings occur at temperatures above 700°C.

The route to produce biochar from lignocellulosic biomass initializes with dehydration and cracking of functional groups from cellulose and hemicellulose will occur to permit the aromatization process and then the biochar formation [8-11]. Regarding lignin, its functional groups undergo cracking and heteroatoms are removed, resulting in the formation of biochar.

Concerning the pyrolysis of plastic material, it can be said that it is a depolymerization process in the formation of smaller polymers according to elementary reactions, such as those involved in the pyrolysis of Polystyrene (PS) [12]:

$$\begin{array}{ll}
\textbf{end initiation:} & P_n \rightarrow R_{n-1} + R_1 \\
\textbf{random initiation:} & P_n \rightarrow R_{n-i} + R_i \\
\textbf{hydrogen abstraction:} & R_i + P_n \rightarrow P_i + R_n \\
\boldsymbol{\beta}\textbf{-scission:} & R_n \rightarrow P_{n-j} + R_j \\
\textbf{depropagation:} & R_n \rightarrow R_{n-1} + P_1 \\
\textbf{termination by disproportionation:} & R_i + R_j \rightarrow P_i + P_j \\
\textbf{termination by recombination:} & R_i + R_j \rightarrow P_{i+j}
\end{array}$$

Polystyrene (PS) pyrolysis is considered to proceed via type-free radical reactions that include β-scission, hydrogen abstraction, hydrogen transfer, radical recombination, and disproportionation with the aromatic monomer, dimer, and trimer as the main products. Aromatic monomers are mainly produced via an unzipping reaction, where the terminal aromatic ring falls off due to the fracture of the C–C linkage between two aromatic rings.

Previously, the torrefaction process affected the biochar formation. This prior process increases biochar formation due to the last formation of crosslinking, depolymerization, and charring processes. In general terms, the pyrolysis of biomass is a process in which the oxygen and hydrogen are removed to obtain a product that seems like coal, kerogens, etc.

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LDPE-biomass mixtures generated more char products than MBr-Np and MBr-Np-LDPE. In contrast, literature reports that co-pyrolysis of poly-olefinic plastics (such as LDPE) with biomass promotes bio-oil production. Some volatiles from biomass degradation were trapped within the residual solid, where they further reacted with the residual char and other volatiles to recombine. Such reactions led to the formation of secondary char, which is consistent with increased char yield at the expense of bio-oil production.

There are batch and continue reactors, such as screw kiln reactors, fluidized bed reactors, etc. The heating process can be external electric power by electrical resistance, hot gas from an external combustion process or a carrier that was hot outside a screw kiln, or by using microwaves, etc.

Screw kiln reactors can be used for slow pyrolysis to produce biochar if the raw material remains inside the kiln for an extended period (more than 20 minutes). However, they can also be used for fast pyrolysis to produce bio-oil, provided a short residence time for the gases inside the reactor (less than 1 second) is ensured. In the case of fluidized bed reactors, the residence times of solids and vapors are nearly identical and very brief (less than 1 second), making them well-suited for bio-oil production. Biochar can also be obtained through the gasification process, with a significant BET surface area that depends on the type of biomass used. This approach is essential for thermochemical processes aimed at simultaneously producing energy, liquid fuels, and biochar.

Biochar Characterization

It is essential to know what kind of biochar we are generating; it is therefore, necessary to characterize it in order to decide on a suitable application (see Figure 2). The physicochemical, surface, and structural/molecular characteristics make it possible to know the composition, pH, electrical conductivity, physical properties, internal structure and morphology, decomposition temperature, functional groups, aromaticity, etc. [9].

The biomass transforms the heating process, e.g., in biochar, the carbon increases, oxygen and hydrogen decrease, and several functional groups disappear, like the C=O group. Other data related to DTG analysis are necessary to determine the degradation temperature. Several plastic materials degrade at a single temperature and at temperatures higher than those of lignocellulosic biomass.

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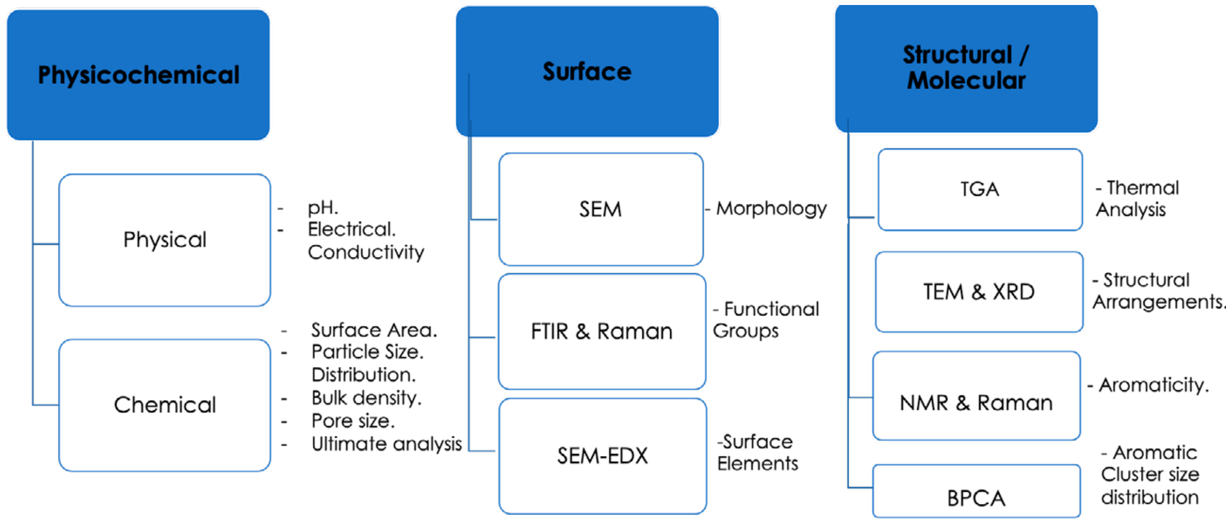

Figure 2. Analytical technique for characterization the biochar (prepared by authors).

The aromatic molecular structures within biochar can be defined by their aromaticity indices (the proportion of aromatic carbons) and their aromatic domain sizes (the number of conjugated aromatic rings within polyaromatic domains). ^{13}C Solid-State Nuclear Magnetic Resonance (ssNMR) can detect the different chemical environments within a biochar sample. The other most straightforward measure of aromaticity is to know the H/C ratio, which is related to aromatic domain size (n) by using the equation:

$$\frac{H}{C} = \frac{2\sqrt{n}+1}{2\sqrt{n}+n}$$

SEM analysis allows us to observe the structural change and transformation of the internal morphology of the biomass until it becomes biochar. On the other hand, theoretical analysis can determine how pyrolysis conditions influence the biochar structure. Simulation of the transformation of the biochar structure at different temperatures can be observed in Figure 3.

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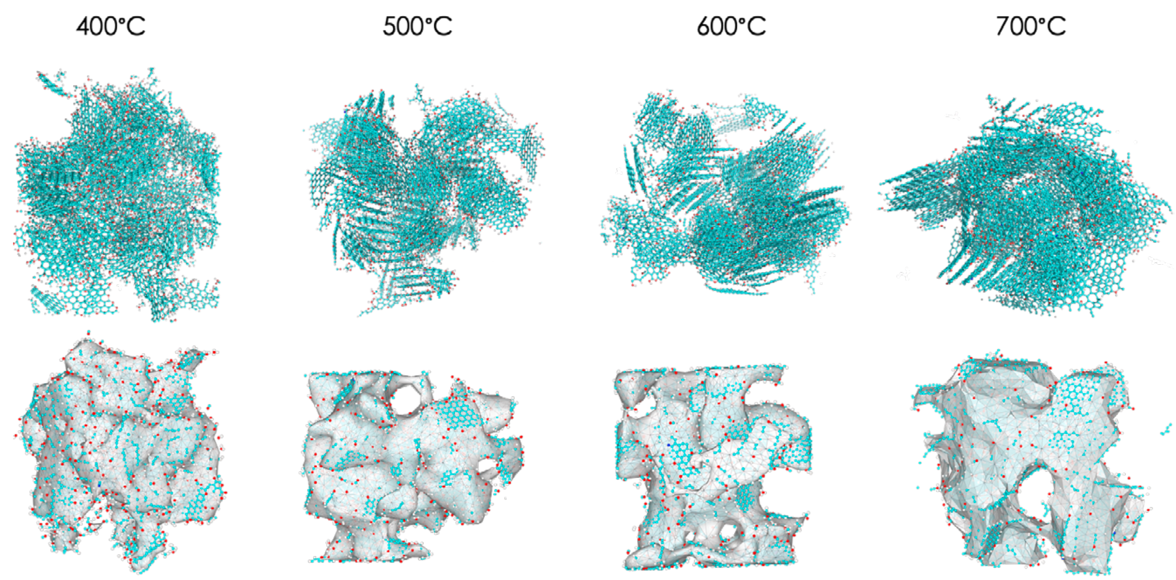

Figure 3. Simulation of biochar structure at different temperature (taken from [9]).

The internal surface of biochar depends on the thermochemical process [13,14]. It can increase from the slowest area of torrefied material to about 50 m2/g more than 2000 m2/g for activated biochar [14]. The internal surface of the biochar plays a crucial role in anaerobic digestion processes. The microporous can trap the smallest particles, the mesoporous can absorb medium sized particles, and the microporous provide a space for bacterial colonies to form. This high degree of selectivity significantly enhances methane production yields.

Biochar Application

Biochar has several applications. It can be used as an adsorbent, fuel, catalyst, catalyst support, soil amendment and additives. Modern application includes:

1. Using biochar derived from biomass waste as a catalyst provides the opportunity to develop a sustainable and efficient process to add value to plastic waste.

2. CO2 capture.

3. Biochar is a low-cost absorbent material.

4. Biochar contains significantly fewer functional groups than its biomass precursors. Depending on the nutrient composition of the initial biomass, a variety of nitrogen-, phosphorous- and sulfur-based functionalities may also appear. Nevertheless, those are found in significantly lower quantities than in oxygen-based groups.

5. Biochar as the conductive medium. The adsorption mechanism on the biochar surface is at two temperature ranges. The higher the pyrolytic temperature, > 450°C, the more suitable the biochar is for the adsorption of organic contaminants because of the improved surface area, the increased distribution of micropores, and the higher level of hydrophobicity. Biochar produced at lower temperatures, < 450°C, is suitable for the adsorption of inorganic and polar organic contaminants. The absorption rate that biochar creates over low temperatures is facilitated by electrostatic attraction, precipitation, and O- O-containing functional groups.

   The conductive properties of biochar could play an essential role in soil biogeochemistry and the microbial community, for instance, by promoting direct interspecies electron transfer (DIET), a mechanism for electron exchange between different species of microorganisms. After accepting electrons from an electron-donating microorganism, the conductive graphite-like sheet structures allow electrons to migrate to electron-accepting microorganisms, linking both metabolisms.

6. Role of biochar in anaerobic digestion processes [15]:

   - Improved digestion performance: accumulation of volatile fatty acids.
   - Improvement of the anaerobic environment: inhibitor adsorption, load shock resistance.
   - Promotion of substance exchange: increases the speed of transport of substances and direct interspecific electron transfer.
   - Biochar is very useful for integrating different technologies (see Figure 4).
   - Use of biochar for potable water production.
   - Use of biochar in the cement industry.
   - Production of nanostructures from tar using biochar.

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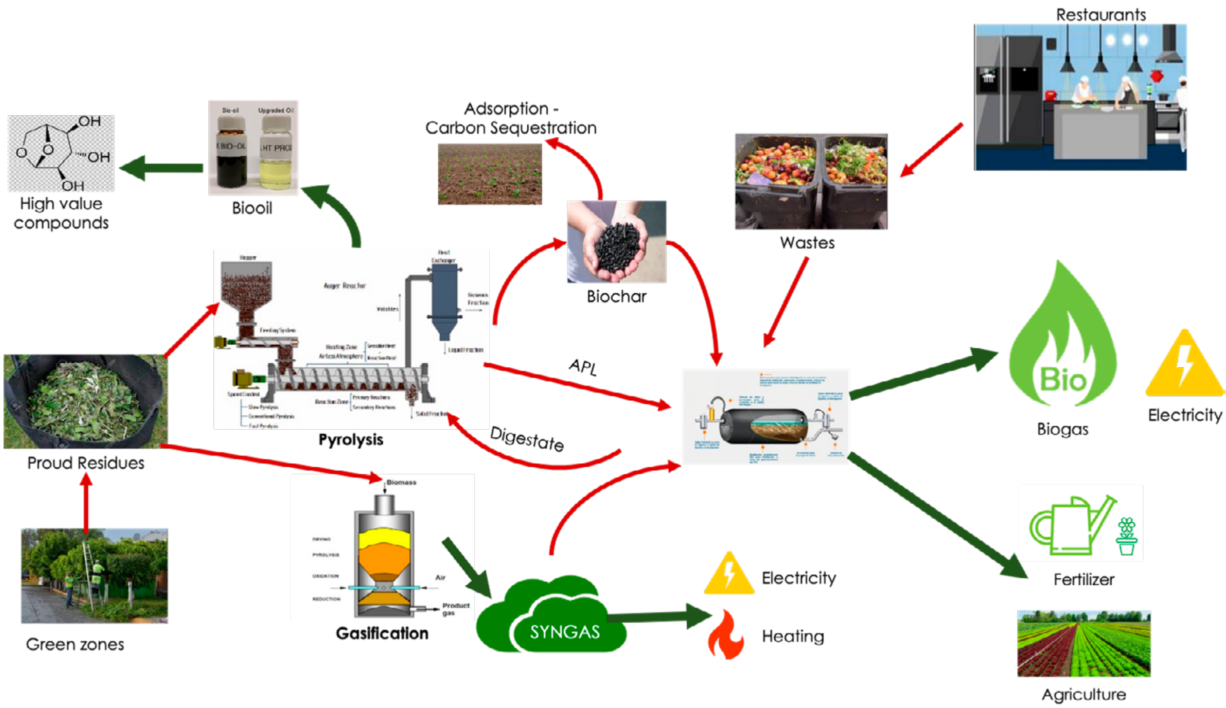

Figure 4. Outline of potential integrations between anaerobic digestion and pyrolysis (prepared by authors).

Conclusion

The second law of thermodynamics limits exploitation of agriculture and heat waste. Carrying out any process is linked to entropy generation due to irreversibility; therefore, this entropy creation means resources are lost, including materials, minerals, metals, and energy. It is vital to focus on developing complex engineering and high-level technology; working on soft engineering, specifically in advanced mathematical modeling; and developing the basic science for generating new efficient processes. These aspects are necessary to take advantage of biomass to implement a circular economy and reduce harmful environmental impacts.

Acknowledgments

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References

1. A. Jain, S. Sarsaiya, M. K. Awasthi, R. Singh, R. Rajput, U. C. Mishra, J. Chen, and J. Shi, "Bioenergy and bio-products from bio-waste and its associated modern circular economy: Current research trends, challenges, and future outlooks," *Fuel*, vol. 307, p. 121859, 2022.
2. O. Dogu, M. Pelucchi, R. Van de Vijver et al., "Progress in Energy and Combustion Science," *Progress in Energy and Combustion Science*, vol. 84, p. 100901, 2021.
3. X. Zhou, L. J. Broadbelt, R. Vinu, and K. M. Van Geem, "Mechanistic understanding of thermochemical conversion of polymers and lignocellulosic biomass," in *Advances in Chemical Engineering*, vol. 49, Academic Press, 2016, pp. 95–198.
4. A. G. Adeniyi et al., "Green Chemical Engineering," *Green Chemical Engineering*, vol. 5, pp. 31–49, 2024.
5. F. Chejne J., M. García Pérez, and M. del P. Noriega E., *Applications of Biomass Derived Materials for Bioproducts and Bioenergy*, Hanser, Munich, Germany, 2024.
6. A. V. Bridgwater, "Review of fast pyrolysis of biomass and product upgrading," *Biomass and Bioenergy*, vol. 38, pp. 68–94, 2012, https://doi.org/10.1016/j.biombioe.2011.01.048
7. M. Sharifzadeh, M. Sadeqzadeh, and M. Guo et al., "Progress in Energy and Combustion Science," *Progress in Energy and Combustion Science*, vol. 71, pp. 1–80, 2019.
8. Y. Li, B. Xing, Y. Ding, X. Han, and S. Wang, "A critical review of the production and advanced utilization of biochar via selective pyrolysis of lignocellulosic biomass," *Bioresource Technology*, p. 123614, 2020, https://doi.org/10.1016/j.biortech.2020.123614
9. V. Sierra-Jimenez, J. P. Mathews, F. Chejne, A. Dufour, and M. Garcia-Perez, "Atomistic modeling of lignocellulosic and carbonaceous fuels and their pyrolysis reactions: A review," *Energy and Fuels*, 2024, https://doi.org/10.1021/acs.energyfuels.3c02901
10. A. Ngambia, O. Mašek, and V. Erastova, "Development of biochar molecular models with controlled porosity," *Biomass and Bioenergy*, vol. 184, p. 107199, 2024.
11. R. Wood, O. Mašek, and V. Erastova, "Biochars at the molecular level. Part 1 – Insights into the molecular structures within biochars," *ArXiv preprint arXiv:2303.09661*, 2023, https://doi.org/10.48550/arXiv.2303.09661
12. G. Martínez-Narroa, P. Prasertcharoensuk, L. S. Diaz-Silvarrey, L. Dixon, and A. N. Phan, "Chemical recycling of mixed plastic waste via catalytic pyrolysis," *Journal of Environmental Chemical Engineering*, vol. 10, p. 108494, 2022, https://doi.org/10.1016/j.jece.2022.108494
13. Y. P. Rago, F.-X. Collard, J. F. Görgens, D. Surroop, and R. Mohee, "Torrefaction of biomass and plastic from municipal solid waste streams and their blends: Evaluation of interactive effects," *Fuel*, vol. 277, p. 118089, 2020, https://doi.org/10.1016/j.fuel.2020.118089
14. M. Córdoba-Ramirez, F. Chejne, J. Alean, C. A. Gómez, Á. Navarro-Gil, J. Abrego, and G. Gea, "Experimental strategy for the preparation of adsorbent materials from torrefied palm kernel shell oriented to CO2 capture," *Environmental Science and Pollution Research*, 2024, https://doi.org/10.1007/s11356-024-32028-3
15. Z.-W. He et al., "Biochar regulates anaerobic digestion: Insights into the roles of pore size," *Chemical Engineering Journal*, vol. 480, p. 148219, 2024.