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Biochar

REVIEW **Open Access**

Preparation of bio-carbon by polymerization of bio-tar: a critical review on mechanisms, processes, and applications

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Abstract

Biomass pyrolysis serves as a pivotal technology in renewable energy development, yet persistent bio-tar formation remains a critical challenge in pyrolysis processes. The innovative strategy of converting bio-tar into bio-carbon presents a promising pathway for technological advancement. To assess the efficacy and value of this approach, a comprehensive analysis of existing research advancements is warranted. This review systematically elucidates the polymerization mechanisms, polymerization process regulation, and application potential of derived bio-carbon. Notably, oxygenated compounds containing carbonyl groups and furan rings serve as critical precursors in bio-tar polymerization, where their unsaturated oxygen-containing functional groups facilitate bond cleavage and recombination. The main methods for regulating polymerization were analyzed by considering interactions between multiple influencing factors during polymerization. Reaction parameters significantly modulate bio-carbon yield by altering bio-tar component states and polymerization reaction, while additive incorporation enhances the physicochemical characteristics of bio-carbon. Crucially, bio-carbon produced through secondary biomass thermoconversion emerges as a novel carbon material, with its primary applications focusing on high-performance carbon material synthesis via value-added utilization pathways. This work establishes a theoretical framework for both bio-tar treatment and advanced carbon material development, offering systematic insights into polymerization mechanisms and application prospects.

Highlights

- The reaction mechanism, pathways and product applications on bio-tar polymerization have been summarized.
- Active oxygenated functional groups such as carbonyl and furan rings play a crucial role in bio-tar polymerization.
- High-value utilization pathways to produce high-performance carbon materials are the main applications of bio-carbon.

Keywords Bio-tar, Bio-carbon, Polymerization mechanism, Key components, Polymerization process, Potential applications

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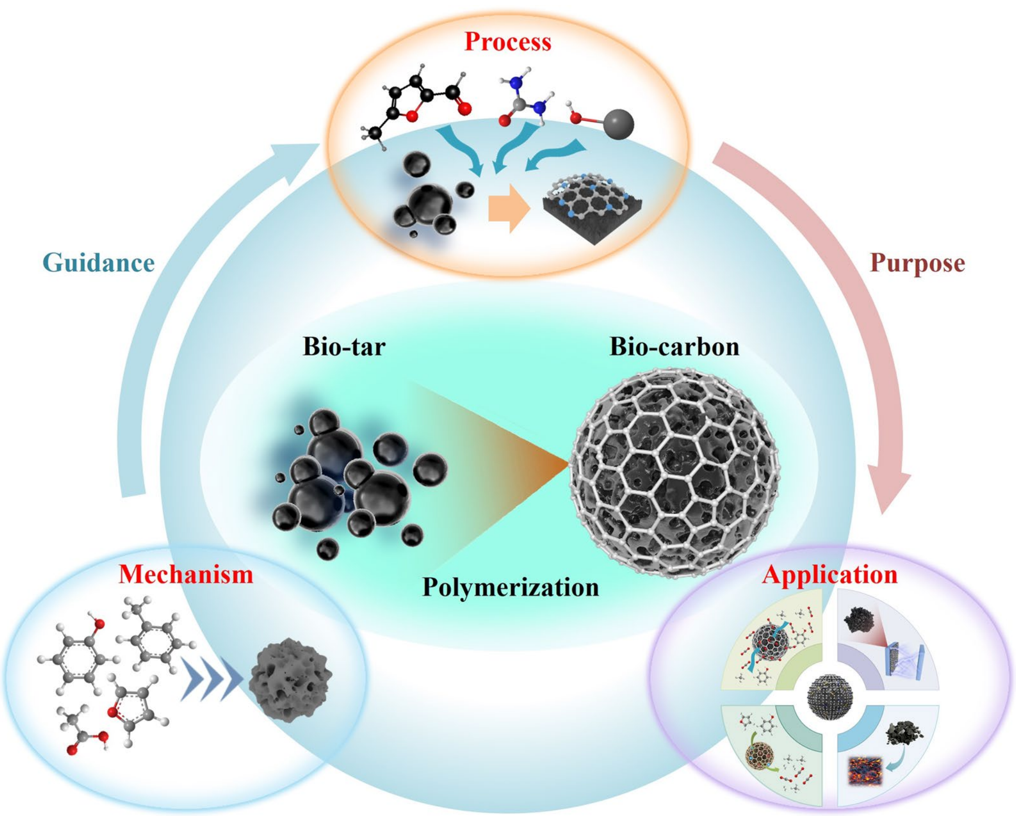
Graphical Abstract



1 Introduction

Biomass pyrolysis serves as a pivotal technology in renewable energy development, which can process different types of biomass and convert them into high-quality biochar and pyrolysis gas, but this also produces bio-tar as a by-product (Guan et al. 2016). The treatment of bio-tar has greatly limited the further development of pyrolysis technologies (Li and Suzuki 2009). During biomass pyrolysis, the bio-tar yield typically ranges from 10% to 20%. Although most bio-tar components (excluding a small fraction of heavy polycyclic aromatic hydrocarbons (HPAHs) with 4–7 rings) exhibit dew point temperatures below 100 °C, the pipeline temperature is often maintained below this critical threshold during gaseous bio-tar transport (Shen et al. 2014a, b). This operational condition leads to undesirable tar condensation in downstream equipment, resulting in persistent pipeline clogging issues. Furthermore, the condensed bio-tar predominantly consists of aromatic compounds, whose direct emission poses significant environmental risks due to their persistent and ecotoxic characteristics (Palma 2013). Therefore, researchers have explored efficient bio-tar treatment technologies to ensure clean and stable operation during pyrolysis.

Bio-tar, an inevitable liquid by-product generated during high-temperature pyrolysis of biomass, is characterized by complex composition, high viscosity, and volatility (Brzozowska et al. 1998; Delgado et al. 1997; DiBlasi 1996). Its component distribution is influenced by pyrolysis conditions, primarily consisting of aromatic compounds with minor aliphatic constituents (Huang et al. 2021; Jia et al. 2016; Jin et al. 2019; Krerkkaiwan et al. 2013). The inherent complexity of bio-tar composition poses significant challenges for direct treatment through simple material separation (Jia et al. 2022; Yao et al. 2021). Current treatment strategies encompass physical methods, non-catalytic thermal cracking, and catalytic reforming (Guan et al. 2016; Guo et al. 2020). While filters and scrubbers represent the most prevalent physical removal technologies that recover bio-tar through cooling of high-temperature gas–liquid mixtures, these approaches substantially increase overall system energy consumption (Han and Kim 2008). Non-catalytic thermal cracking requires extreme temperatures (> 1000 °C) for complete bio-tar decomposition, resulting in similarly high energy demands (Palma 2013). Catalytic reforming emerges as a more efficient strategy through temperature reduction enabled by catalyst introduction, though catalyst deactivation remains a critical technological bottleneck (Guo et al. 2014; Heidenreich and Foscolo 2015; Hosseini and Wahid 2016). Zhang et al. (2021) demonstrated 91.75% catalytic reforming efficiency using activated biochar catalysts derived from KOH/phosphoric acid-treated rice husk feedstock. Shen et al. (2016) systematically reviewed advancements in bio-tar catalytic reforming technology, highlighting that both carbon-based and metallic catalysts experience deactivation during prolonged operation. The high carbon content and polymerization propensity of bio-tar make coking through polymerization a primary factor compromising treatment efficacy (El-Rub et al. 2008). Given the physicochemical similarities between polymerized coking products and biochar, researchers have explored a novel approach integrating high-temperature polymerization treatment of bio-tar with bio-carbon production (Lv et al. 2010; Ni et al. 2006). As illustrated in Fig. 1, this technology utilizes condensed and accumulated bio-tar as feedstock for direct thermal polymerization into bio-carbon. The resulting products exhibit superior application potential compared to conventional biochar, attributable to their higher carbon content and reduced ash characteristics. This innovative methodology holds significant importance for developing novel carbon materials while addressing bio-tar treatment challenges.

The oxygenated organic compounds in bio-tar, including furans, acids, ketones, and aldehydes, can promote hydrocarbon polymerization at elevated temperatures to form bio-carbon with graphitic structure enrichment. Shukla and Koshi (2011) investigated the decomposition and secondary polymerization processes of biomass pyrolysis/gasification-derived bio-tar, revealing that aliphatic hydrocarbons and low-ring compounds (e.g., benzene, phenol, toluene, biphenyl, anthracene) undergo secondary polymerization reactions such as addition and condensation upon heating. These reactions generate polycyclic aromatic hydrocarbons (PAHs), which further polymerize into bio-carbon as reactions progress. Cheng et al. (2020) achieved rapid polymerization of bio-tar to produce bio-carbon with stabilized structural and chemical properties, employing life cycle assessment (LCA) to verify net-positive energy, economic, and environmental benefits in this process. Notably, Hu et al. (2019) achieved cross-linked polymerization between bio-tar and biochar through the addition of oxygenated organic compounds as polymerization agents. Their findings confirm the feasibility of bio-tar polymerization for bio-carbon preparation, while emphasizing the critical role of bio-tar component distribution patterns and polymerization pathways in developing novel bio-based carbon materials. Current research on this technology primarily focuses on experimental studies, including preliminary investigations into bio-tar component distribution mechanisms, polymerization characteristics, and application-oriented evaluations based on bio-carbon properties. However, systematic summarization remains lacking to consolidate fundamental understandings of bio-tar polymerization. Addressing these knowledge gaps could significantly advance the rational design of bio-tar treatment strategies and high-value bio-carbon synthesis.

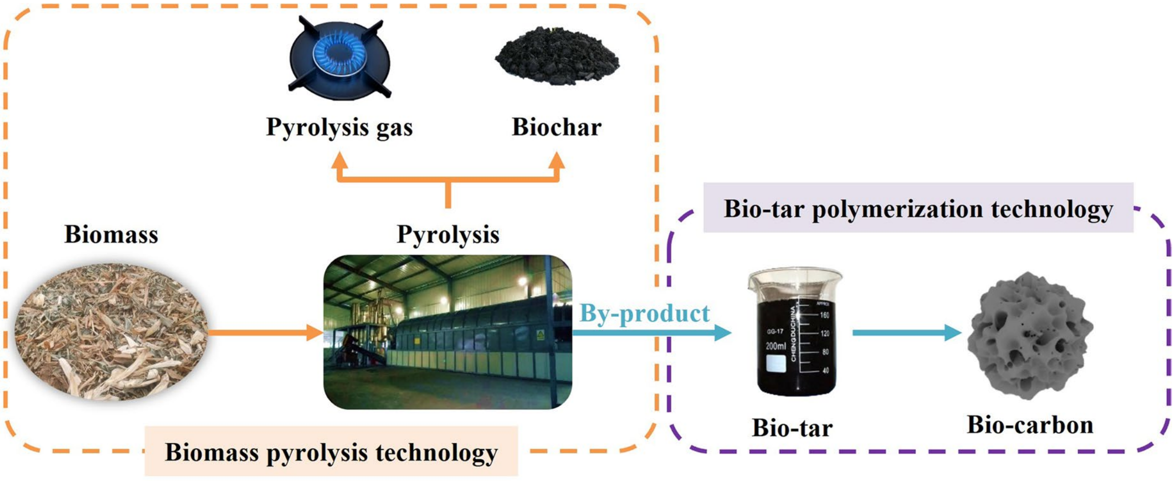


Fig. 1 Overview of bio-tar polymerization technology

This article systematically analyzes and summarizes the technological framework for bio-carbon production via bio-tar polymerization based on current research advances. It elucidates the component distribution mechanisms of bio-tar and the polymerization pathways of critical constituents, while investigating the influence of key factors (e.g., reaction conditions and additives) on polymerization efficiency and the physicochemical properties of bio-carbon. Furthermore, the potential applications of bio-carbon and future research directions for this technology are thoroughly discussed. These findings provide theoretical and technical foundations for the sustainable treatment of bio-tar and the development of novel bio-based carbon materials, highlighting their critical significance in advancing biomass energy utilization.

2 Research design

This research provides a systematic and critical review of bio-carbon production technology through bio-tar polymerization, with a focus on biomass pyrolysis tar generation processes, compositional characteristics, and polymerization mechanisms. The literature search in this study was conducted using the Web of Science database, with the keywords "tar", "polymerization", and "biomass" employed to systematically retrieve relevant scientific publications. The literature survey prioritized English-language publications, potentially omitting contributions from non-English sources. Our search strategy specifically targeted biomass pyrolysis tar (i.e., bio-tar), restricting topics to polymerization or thermochemical conversion. To comprehensively summarize physicochemical properties, compositional patterns, and polymerization behaviors of bio-tars, we selectively incorporated indexed studies examining alternative tar categories and treatment technologies. The search encompassed publications through December 2024, resulting in 210 relevant papers after rigorous screening and consolidation (Fig. 2). Although not all retrieved studies are explicitly cited, this corpus collectively establishes the evidence base for our systematic evaluation of technological progress in this field.

3 Polymerization mechanism of bio-tar

Due to the high complexity of bio-tar components, clarifying the distribution pattern of bio-tar components and the polymerization reactions is key to analyzing the bio-tar polymerization mechanism. Many studies have analyzed the bio-tar components generated during different pyrolysis reactions, and the results have shown that the reaction conditions during pyrolysis are the main factor affecting the distribution of bio-tar components. The polymerization of key components is still in the exploratory stage, and due to the complexity of the reaction process, the crosslinking mechanism of specific components is still under research.

3.1 Characteristics of bio-tar components

Bio-tar is a complex organic mixture mainly composed of aromatic compounds and a small amount of aliphatic compounds (Fagbemi et al. 2001), including insoluble substances such as esters, furan, phenol, toluene, naphthalene, long-chain fatty hydrocarbons, and other aromatic compounds. Soluble substances include aldehydes, ethers, alcohols, acids, and ketones (Patwardhan et al. 2009; Worasuwannarak et al. 2007). The component distribution of different bio-tars is shown in Table 1 (Saires

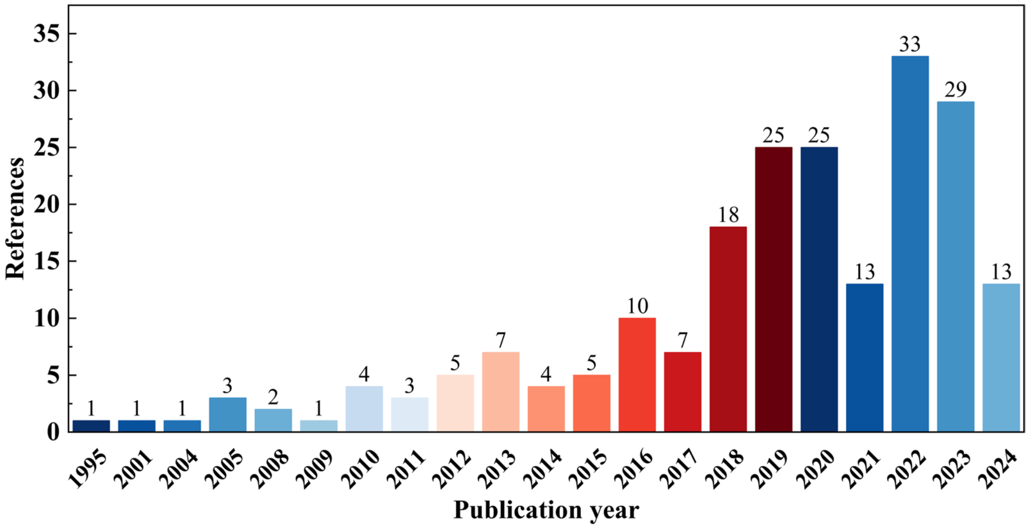


Fig. 2 References from different publication years

Table 1 Component distribution of different bio-tars

Chemical composition (%)	Biomass^a		
	Rice husk	Zoita wood sawdust	Pine wood sawdust
Acids	4.2	2.3	2.4
Aldehydes	0.4	0	0
Ketones	10.3	6.7	5.9
Esters	1.3	0.5	0.6
Ethers	1.2	5.8	5.3
Furans	11.4	2.9	3.4
Pyrans	0.8	0.5	0.3
Alcohols and sugars	5.0	2.6	4.7
Phenols	52.6	60.7	60.7
Hydrocarbons	0.1	8.3	8.8
Others	1.9	0	0.8
Unknown	10.8	9.7	7.3

[a] The temperature for biomass pyrolysis reaction is 500 °C and the residence time is 5 h

et al. 2024). The total carbon content is about 60–70%, the ash content is less than 1%, and aromatic compounds account for about 60–70% (Saires et al. 2024). It is a carbon-rich, low-ash material that readily polymerizes (Li et al. 2024a, b). Because biomass is mainly composed of cellulose, hemicellulose, and lignin, analyzing the conversion pathways of its monomers or conversion intermediates can provide deeper insights into the generation of biomass bio-tar (Rubin 2008). The pyrolysis of cellulose generates levoglucose through glycosidic bond cleavage and converts it into alcohols and furfural, and it also generates aldehydes and ketones through ring-opening and reforming (Zhou et al. 2014). Pyrolysis of hemicellulose is the main pathway for generating organic acids, of which acetic acid has the highest proportion in bio-tar (Lopez et al. 2018; Sansaniwal et al. 2017; Shen and Yoshikawa 2013). Acetyl groups connecting xylose in hemicellulose are cleaved to produce acetic acid, which is accompanied by the production of small molecules such as methanol and furfural. Lignin is the most difficult component to pyrolyze among the three biomass components, and it consists of three monomers: guaiacyl propane, syringal propane, and *p*-hydroxyphenylpropane. The main pyrolysis products in bio-tar are aromatic compounds such as phenols and other aromatics (Lu et al. 2010; Morf et al. 2002; Vitolo et al. 2001).

The pyrolysis reaction temperature affects the distribution of bio-tar components. The intensity of the pyrolysis reaction increases with the temperature, and the bio-tar components gradually transform from unstable small-molecule compounds to stable long-chain hydrocarbons and polycyclic aromatic hydrocarbons. The generation path of bio-tar is shown in Fig. 3. When the pyrolysis temperature is in the range of 200–500 °C, cellulose, hemicellulose, and lignin in biomass are first converted into intermediates such as xylan and levoglucan. Then, pyrolysis generates bio-tar components whose composition mainly includes aromatic hydrocarbon derivatives with oxygen-containing branched substituents, including aldehydes, phenols, furans, alcohols, and acid organic compounds. As the temperature rises to 500–700 °C, oxygen-containing functional groups undergo decarboxylation, and primary bio-tar is converted into secondary bio-tar components with lower oxygen content, higher molecular weight, and improved thermal stability, accompanied by the production of small-molecule gases. When the temperature exceeds 700 °C, secondary bio-tar undergoes further chemical bond breaking

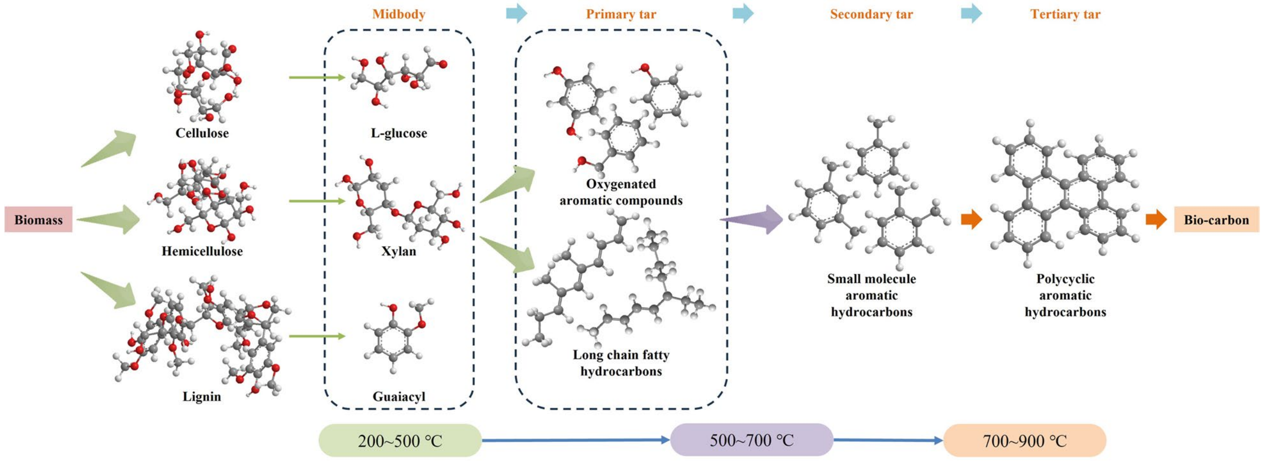


Fig. 3 Bio-tar generation process

and recombination to generate higher-molecular-weight tertiary tar that has a more stable molecular structure. During the conversion of bio-tar, each component undergoes simultaneous cracking and polymerization. Cracking mainly involves the gradual decomposition of heterocyclic compounds into aromatic rings and numerous branched-chain groups, including demethylation, hydroxyl dehydration, deethylation, and decarboxylation. Polymerization mainly occurs through reactions such as aromatic hydrocarbon addition, dehydrogenation cyclization, and dehydrogenation addition of acetylene. As the temperature further increases, the bio-tar components polymerize into bio-carbon with a more stable structure (Xiong et al. 2018a, b).

3.2 Polymerization reactions of key components

The pyrolysis polymerization reaction path of the key components of bio-tar is shown in Fig. 4, which involves complex chemical reactions such as the cyclization of linear hydrocarbons, the conversion of single rings to multi-ring aromatic hydrocarbons, and the conversion of phenol (Shen et al. 2014a, b; Wang et al. 2011). Cross-linking also occurs during each reaction. Palma (2013) summarized the formation and further polymerization mechanisms of bio-tar, and the results showed that the conversion mechanism of phenol to polycyclic aromatic hydrocarbons in bio-tar is that the CO and H atoms are first removed to form cyclopentadiene radicals that collide to form naphthalene via single-ring to multi-ring conversion. Short-chain aliphatic hydrocarbons decompose into small unsaturated hydrocarbons upon heating and then undergo dehydrogenation and acetylation to form a benzene ring (Dilks et al. 2016). Further dehydrogenation cyclization generates polycyclic aromatic hydrocarbons with a higher polymerization degree. Different oxygen-containing organic compounds play different functions during polymerization (Hu et al. 2013), while glucose plays a crucial role in the formation of polymers by forming active compounds with multiple hydroxyl groups, carbonyl groups, or conjugated π bonds during decomposition. Among them, hydroxyaldehydes and hydroxyacetone both contain a hydroxyl group, a carbonyl group, and an active α-H, which promote electrophilic substitution and aldol condensation reactions (Xu et al. 2017). In contrast, cyclopentanone contains a single carbonyl group, but its complex unsaturated bonds tend to undergo breakage and recombination during reactions to form long-chain or multi-ring structures (Vitolo et al. 1999; Yu et al. 2017). Formic acid and acetic acid, as representative organic acids in bio-tar, do not directly participate in polymerization reactions, but instead act as catalysts (Shi et al. 2016; Sun et al. 2021a, b). Therefore, oxygen-containing compounds such as aldehydes, ketones, furans, monosaccharides, oligosaccharides, and phenols in bio-tar are the main substances that promote bio-tar polymerization (Tang et al. 2024). These compounds are particularly prone to polymerization reactions under acidic conditions. Therefore, small-molecule compounds featuring unsaturated oxygen-containing functional groups (particularly furan rings and carbonyl moieties) significantly facilitate bio-tar polymerization through radical initiation and electron-deficient site

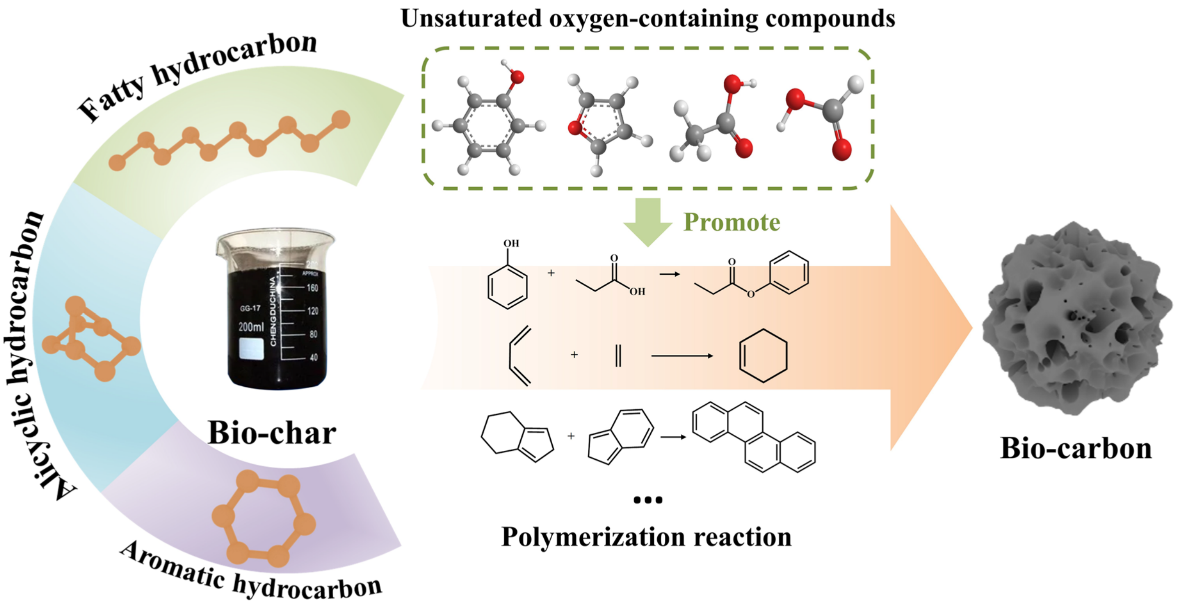


Fig. 4 Pyrolysis polymerization reaction pathway of key components in bio-tar

interactions, while macromolecular hydrocarbons primarily contribute to the carbon skeleton framework formation via Diels–Alder-type condensation and aromatic stacking mechanisms during bio-tar aggregation.

To verify the role of oxygen-containing compounds in bio-tar polymerization, Hu et al. (2019) selected xylose, methanol, hydroxyacetone, vanillin, *o*-methoxyphenol, and furfural as model compounds to investigate the mechanism of different polymerization agents during bio-tar polymerization. The results showed that furfural exhibited better polymerization effect by promoting the cross-polymerization of bio-tar and biochar, which combined bio-tar and biochar to form a cross-linked structure. Xiong et al. confirmed these results (Xiong et al. 2020). Among these highly-active light components in bio-tar, furan is an effective polymerization agent during bio-tar pyrolysis, of which furfural is the most common furan. Its active carbonyl group and electron-rich furan ring activate the polymerization of bio-tar. Although existing research has revealed the polymerization reaction pathways of the main components of bio-tar and verified the polymerization effects of furan-like components such as furfural, the components of bio-tar are complex. Most light components are prone to volatile overflow during polymerization (Sun et al. 2021a, b; Wu et al. 2017). Therefore, the interaction mechanism of the condensation chemical reaction of the key components of bio-tar to synthesize carbon skeletons is still unclear. The polymerization reaction mechanism and methods to regulate the mechanism of carbon skeleton growth and evolution require further exploration.

4 Polymerization process regulation of bio-tar

Because various components have different effects during bio-tar polymerization, the different component distribution is the main factor affecting the polymerization and quality of bio-carbon. In addition to the application of exogenous additives, bio-tar pretreatment technology can also be used to regulate the distribution of bio-tar components. Therefore, pre-treating bio-tar, changing the polymerization conditions, and using polymerization additives can be used to alter the bio-tar polymerization process. It is important to explore the effects of these different factors on the polymerization of bio-tar and the quality of bio-carbon. The latest developments of polymerization process regulation of bio-tar are shown in Table 2.

4.1 Polymerization reaction conditions

The polymerization reaction temperature, residence time, and heating rate affect the polymerization effect of bio-tar and the quality of the resulting bio-carbon (Shen et al. 2010). The influence mechanism of polymerization reaction conditions is shown in Fig. 5. Although bio-tar polymerizes to form stable bio-carbon at higher reaction temperatures, the components of bio-tar are highly volatile and are not retained at such high reaction temperatures. Thus, the yield of bio-carbon after polymerization is reduced (Miller and Bellan 1997; Park et al. 2010). Mochizuki et al. (Mochizuki and Tsubouchi 2019) investigated the influence of bio-tar polymerization temperature (200–500 °C) on polymerization efficiency during bio-carbon preparation. The results indicated that low temperatures (< 300 °C) were unfavorable for carbonization reactions, yielding bio-carbon with higher viscosity and non-graphitic structures. Furthermore, as the reaction temperature increased from 200 to 500 °C, the bio-carbon yield decreased by over 49%. As the reaction temperature increased, although the carbon content and graphitization degree of bio-carbon significantly increased, the yield decreased due to the escape of some components of bio-tar (Prauchner et al. 2001; Yang et al. 2020). Wu et al. (2020) obtained similar results, in which significant bio-tar polymerization occurred above 420 °C. A longer reaction time promoted the polymerization of bio-tar components, thereby improving the bio-carbon yield. Wang et al. (2013) investigated the pyrolysis polymerization of different fractions of tar and showed that synergistic effects between key components of bio-tar under low temperatures played a major role in the polymerization process, which improved the bio-carbon yield. In addition, the heating rate mainly influenced the decomposition and polymerization reactions. Xiong et al. (2018a, b) used a fixed-bed reactor to explore how the heating rate affected bio-tar polymerization. The results indicated that a lower heating rate promoted polymerization, which was more pronounced at lower temperatures (< 500 °C). In addition, a higher heating rate directly led to the decomposition and escape of bio-tar components and coking in pipelines, which greatly reduced the yield of bio-carbon. With the increase of heating rate, the yield of bio-carbon decreased by more than 30%. Therefore, without additives, maintaining a lower reaction temperature and heating rate and using a higher reaction time can improve the bio-carbon yield. In addition, the bio-carbon produced through direct polymerization of bio-tar exhibits limited surface functional groups and low specific surface area, with temperature variations during polymerization resulting in negligible improvements to these properties. Therefore, reducing temperatures to enhance bio-carbon yield offers minimal cost-benefit advantages. To meet application requirements, introducing additives is necessary to improve the physicochemical characteristics of bio-carbon, thus increasing its functional value.

Table 2 Polymerization process regulation of bio-tar

Raw material	Polymerization conditions	Additive	Regulation methods	Effect	References
Pine tree sawdust bio-tar	Polymerization at 200–500 °C	–	• Regulating reaction temperature	• Temperature is positively correlated with the effect of polymerization reaction • Temperature is negatively correlated with bio-carbon yield	(Mochizuki and Tsubouchi 2019)
Woody bio-tar	Polymerization at 500 °C	Crab shell	• Regulating residence time	• Residence time is positively correlated with the effect of polymerization reaction and bio-carbon yield • Crab shell is beneficial for polymerization reactions and improves the pore structure of bio-carbon	(Wu et al. 2020)
Rice husk bio-tar	Polymerization at 300–800 °C	–	• Regulating heating rate	• Heating rate is negatively correlated with the effect of polymerization reaction • Heating rate is positively correlated with bio-carbon yield	(Xiong et al. 2018a, b)
Bio-tar	Polymerization at 750 °C	–	• Air pre-oxidation	• Pre-oxidation is beneficial for improving the yield of bio-carbon	(Yang et al. 2022a, b)
Bio-tar	Polymerization at 800 °C	–	• Pretreating by hydrogen peroxide and nitric acid	• Pretreating is beneficial for improving the yield and porosity of bio-carbon	(Yang et al. 2022a, b)
Rice husk bio-tar	Polymerization at 500 °C	Furfural	-	• Furfural is beneficial for improving the yield of bio-carbon	(Xiong et al. 2020)
Pine tree sawdust bio-tar	Polymerization at 550 °C	Lignocellulosic biomass	-	• Lignocellulosic biomass promoted the formation of polymeric bio-carbon	(Mochizuki and Tsubouchi 2022)
Bio-tar	Polymerization at 550 °C	Crayfish shell and NaOH	• Chemical activation	• Crayfish shells and NaOH is beneficial for improving the porosity of bio-carbon	(Luo et al. 2021)
Corn straw bio-tar	Polymerization at 800 °C	Urea and KOH	• Nitrogen doping and chemical activation	• Urea improves the functional group properties of bio-carbon • KOH is beneficial for improving the porosity of bio-carbon	(Jia et al. 2023)

4.2 Component distribution regulation

Because it is difficult to directionally adjust bio-tar components by changing the pyrolysis conditions, bio-tar pretreatment has received widespread attention. The component distribution regulation path is shown in Fig. 6. Due to the crucial role of oxygen-containing compounds in bio-tar polymerization, the main goal of pretreatment is to improve the composition and distribution

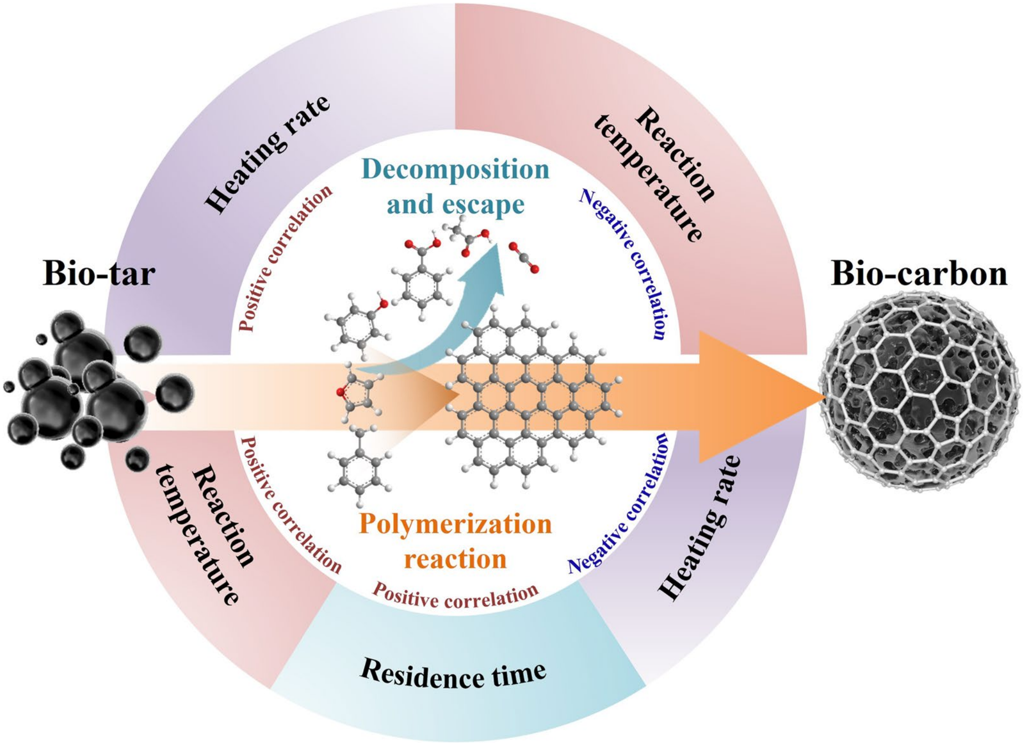


Fig. 5 Influence mechanism of polymerization reaction conditions

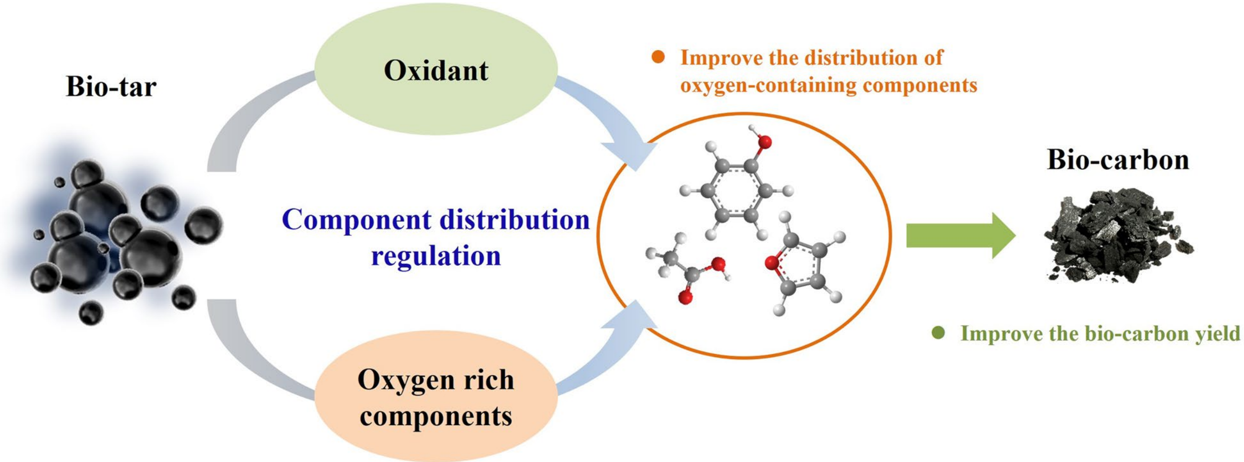


Fig. 6 Component distribution regulation path

of oxygen-containing compounds in tar. This can help enhance the polymerization effect of bio-tar and improve the yield and physicochemical properties of bio-carbon. Yang et al. (2022a, b) used air pre-oxidation to treat bio-tar, which promoted the polymerization reaction of bio-tar and increased the content of oxygen-containing functional groups in the polymerization products. The introduced oxygen-containing functional groups mainly existed as hydroxyl, carbonyl, carboxyl, and methoxy groups, and the morphology of the functional groups was greatly affected by the air pre-oxidation temperature. As the air pre-oxidation temperature increased, bio-tar underwent both deoxygenation and oxidation reactions. More stable oxygen-containing functional groups are enriched, and unstable oxygen-containing functional groups produce oxygen, which forms porous polymerization products. In addition, a higher pre-oxidation temperature (350 °C) will cause the oxygen-containing functional groups to undergo polymerization to form a cross-linked network. This is conducive to the directional construction of pores during subsequent carbonization, similar to the polymerization of bio-tar at this temperature. Air pre-oxidation further enhances the polymerization effect of bio-tar and enriches the content of oxygen-containing functional groups such as carbonyls, which show a high polymerization activity.

In addition, Yang et al. (2022a, b) pretreated bio-tar with strongly-oxidizing hydrogen peroxide and nitric acid. Hydrogen peroxide treatment increased the introduction of oxygen-containing functional groups such as carbonyl and hydroxyl groups, which improved the polymerization effect of bio-tar. Nitric acid treatment increased the number of oxygen-containing functional groups and introduced nitrogen-containing functional groups such as pyridine, pyrrole, and nitroso. This promoted polymerization reactions while incorporating heteroatoms, further improving the polymerization effect and functional group characteristics of the polymerization products. Similar to air pre-oxidation treatment, the introduced oxygen-containing and nitrogen-containing structures were prone to gas overflow during subsequent carbonization, which increased the porosity of the bio-carbon product. Therefore, while introducing oxygen-containing functional groups to promote bio-tar polymerization, pretreatment also improved the pores and functional groups of the polymerization products.

Chemical additives rich with oxygen-containing functional groups can promote polymerization (Zheng et al. 2017), of which furfural is a widely used additive. Xiong et al. (2020) conducted polymerization experiments using bio-tar as the raw material and pure furfural as an additive. Although the reaction temperature is higher than the boiling point of furfural, interactions between furfural and bio-tar promoted the smooth polymerization reaction. This inhibited the evaporation of furfural and bio-tar components, which increased the bio-carbon yield. The addition of furfural also delayed the carbonization temperature, which ensured that the aromatic hydrocarbon polymerization reactions occurred at higher temperatures. This is the main reason for the increased bio-carbon yield.

4.3 Modification regulation strategy

Although the introduction of chemical additives can directly control the bio-tar component distribution and promote polymerization reactions, bio-carbon may have an insufficient pore structure and surface functional groups, similar to biochar. These issues seriously restrict the high-value utilization of bio-carbon. To further improve the quality of bio-carbon, researchers have proposed introducing additives to enhance the directional control of polymerization reactions. The modification regulation strategy of polymerization based on different additives is shown in Fig. 7. Biomass and its derivatives are effective additives for preparing high-performance bio-carbon while adding chemical activators and heteroatom dopants is an effective method for improving the pore structure and functional group characteristics of bio-carbon. Mochizuki and Tsubouchi (2022) investigated the reaction and product characteristics of the synergistic polymerization of lignocellulosic biomass and wood bio-tar to prepare bio-carbon. The results showed that adding a small amount of lignocellulosic biomass promoted the formation of polymeric bio-carbon and improved the conversion efficiency of wood tar. Lignocellulosic biomass decomposed during the reaction to produce intermediates such as glucose, which promoted bio-tar polymerization and conversion. The natural microstructure of lignocellulosic biomass promoted the formation of a carbon skeleton. Wu et al. (2020) used crab shells as hard templates, bio-tar as the raw material, and KOH as the activator to copolymerize and prepare porous bio-carbon with a specific surface area of 2489.62 $m^2\ g^{-1}$. The results showed abundant pores were formed for two reasons. Kitchen waste rich in carbonates is conducive to the formation of a carbon skeleton and generates volatile gas overflow during the reaction, thereby generating primary pores. Etching by KOH during high-temperature polymerization formed more micropores in bio-carbon. Luo et al. (2021) selected crayfish shells with similar raw material types and used NaOH to also prepare porous bio-carbon. In addition, based on the gas overflow mechanism during additive polymerization, Jia et al. (2023) introduced urea as a soft template and nitrogen doping agent and KOH as an activator to prepare bio-carbon. They observed a synergistic effect between impurity dopants and chemical activators. The gas overflow reaction of urea and etching by KOH synchronously formed a highly porous structure that provided a good template for bio-tar polymerization. Alkaline activators are conducive to the retention of nitrogen-containing groups and promote the modification effect of functional groups. This is why bio-carbon contains abundant pores and functional groups.

5 Potential applications of bio-carbon

Bio-carbon has similar physicochemical properties to biochar, and so they have similar applications. Because bio-carbon is a by-product of secondary reactions during biochar preparation, high-value application pathways can

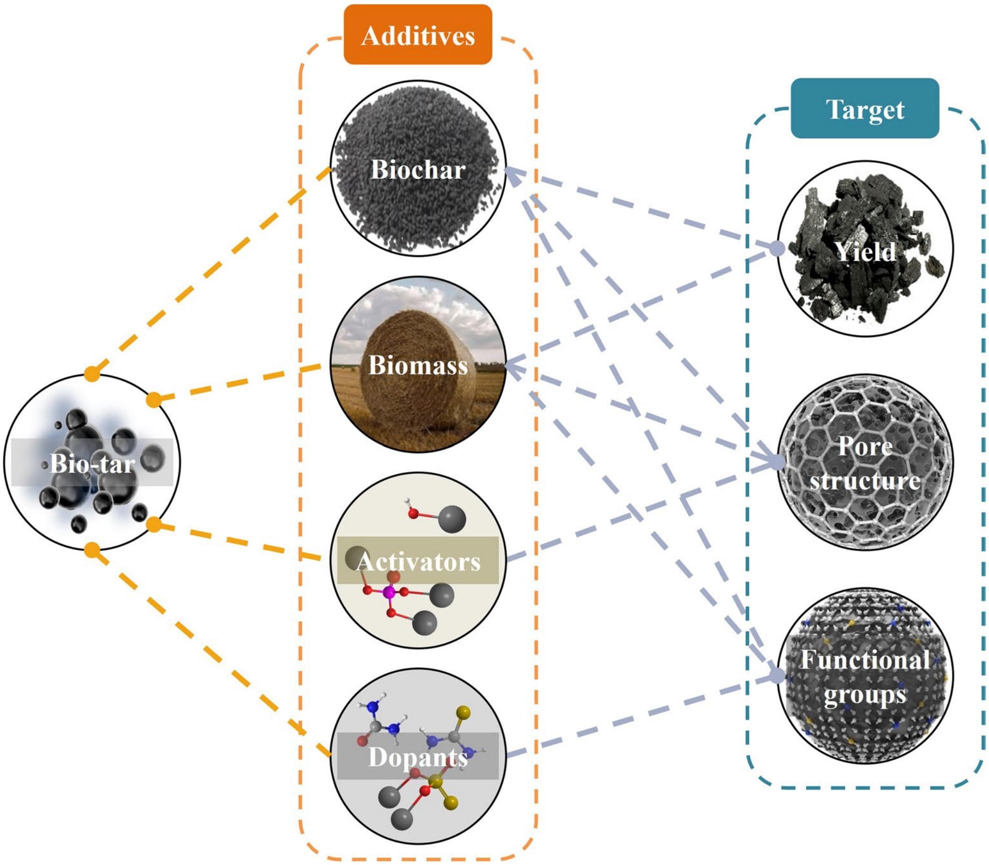


Fig. 7 Modification regulation strategy of polymerization

overcome the constraints of preparation costs, as shown in Table 3 and Fig. 8, including adsorbents, energy storage electrode materials, catalysts, and fuels.

5.1 Adsorbents

Similar to biochar, bio-carbon has a stable and disordered graphitic structure that gives it remarkable potential for preparing adsorbents (Cho et al. 2023). In the field of environmental remediation, it can be used to purify polluted water bodies and soil (McLaughlin et al. 2023; Mousavi-Avval et al. 2023). The rich pore structure and functional groups generated through activation, modification, and other means allow it to adsorb heavy metal ions and organic pollutants in water (Dissanayake et al. 2020). In industrial production, it can be applied to waste gas treatment by adsorbing harmful gas components in the air, playing an important role in creating a clean production environment (Savova et al. 2001; Sun et al. 2023). Zhu et al. (2022) prepared N/S dual-doped porous bio-carbon using bio-tar as the raw material and a one-step carbonization activation combined with in situ doping. The specific surface area reached 957.44 m^2 g^{-1}, the proportion of micropores exceeded 87%, and the CO_2 adsorption performance reached 2.21 mmol g^{-1} at 0 °C. Because bio-tar polymerization and carbonization involve bond breaking and reorganization, adding dopants can improve the functional group characteristics of bio-carbon, thereby enhancing its ability to chemically adsorb pollutants. However, bio-tar lacks some of the advantages of biomass, as shown in Table 4. The inherent ash structure and microstructure of biomass can be retained and functionalized in biochar, which promotes the adsorption of some pollutants. The ash structure forms specific functional groups that participate in the chemical adsorption of pollutants. The microscopic morphology is conducive to the construction of biochar with a porous structure, thereby forming a specific pore distribution suitable for physical adsorption. Although adsorbents prepared from bio-carbon are expected to be applied in a wider range of fields, the effects of pore structure and functional group modification need to be further enhanced. The synergistic effects of polymerization and modification processes need to be further explored. Although recent studies have begun exploring the utilization of bio-tar as a renewable carbon source for fabricating CO_2 adsorbents, a more comprehensive evaluation of

Table 3 Potential applications of bio-carbon

Raw material	Reaction temperature (℃)	Heating rate (℃ min^{-1})	Residence time (h)	Additive	Application	Effect	References
Bio-tar	800	10	1	N,N′-Diphenylthiourea and $C_7H_5KO_2$	Adsorbent	CO_2 adsorption performance reached 2.21 mmol·g^{-1} at 0 °C	(Zhu et al. 2022)
Bio-tar	800	5	1	Crayfish shell and NaOH	Electrode material	Capacitance of 351 F·g^{-1} at a current density of 0.5 A·g^{-1}	(Luo et al. 2021)
Corn straw bio-tar	800	10	1	Urea and KOH	Electrode material	Capacitance of 309.5 F·g^{-1} at a current density of 0.5 A·g^{-1}	(Jia et al. 2023)
Woody bio-tar	800	5	1	Crab shell and KOH	Electrode material	Capacitance of 338.5 F·g^{-1} at a current density of 0.5 A·g^{-1}	(Wu et al. 2020)
Rice husk bio-tar	240	–	20 min	–	Fuel	Calorific value reached 28.2 MJ·kg^{-1}	(Cheng et al. 2020)

this technology remains imperative. Furthermore, ensuring the regenerability of the derived materials emerges as a critical research challenge that requires urgent investigation. Addressing these fundamental aspects could significantly enhance the cyclic performance and economic viability of materials, thereby facilitating their industrial-scale applications in carbon capture systems.

5.2 Electrode materials

Due to continuous increases in energy demands and the urgent pursuit of sustainable energy technologies, electrode materials for energy storage are gradually becoming the focus of research (Zhang et al. 2023). In addition, the preparation of electrode materials is an important method to achieve high-value utilization of bio-carbon, but electrode materials have strict requirements in terms of the ash content and pore structure of bio-carbon (Frackowiak et al. 2006). The low ash and easy aggregation of bio-tar make it an ideal precursor for preparing high-performance electrode materials (Zhi et al. 2014). The unique polymerization reaction mechanism during the carbonization of bio-tar makes it easy to form pores due to the participation of activators. The resulting highly-developed pore structure helps overcome the problem of difficult pore formation in electrode materials prepared from biomass (Lota et al. 2005; Sun et al. 2024a, b). The synergistic formation of micropores and mesopores via aggregation and activation provides sufficient space for ion transport and storage, thus enabling efficient charge storage and release (Subramaniam et al. 2023). Compared with activated biochar, the larger specific surface area of activated bio-carbon promotes the formation of additional active sites that can fully contact the electrolyte, thus improving the electrochemical performance (Xue et al. 2023).

Supercapacitors are relatively new energy storage devices with high power densities and long cycle lifetimes. Researchers have studied the potential applications of bio-carbon as electrodes for supercapacitors. Luo et al. (2021) prepared porous carbon active material using bio-oil as the raw material, crayfish shell as the template, and NaOH as the activator. Its surface reached 3095 m^2 g^{-1}, its pore capacity reached 1.66 cm^3 g^{-1}, and it showed a capacitance of 351 F g^{-1} at a current density of 0.5 A g^{-1}. Jia et al. (2023) prepared nitrogen-doped porous carbon using corn straw bio-tar as the raw material, urea as the nitrogen source, and KOH as the activator through a one-step method. The specific surface area reached 1298.26 m^2 g^{-1}, and the specific capacitance reached 309.5 F g^{-1} at a current density of 0.5 A g^{-1}. After 10,000 cycles, the specific capacitance retention rate was 80.1%. Wu et al. (2020) prepared porous carbon using wood tar as the raw material and KOH as the activator via a natural biological template method. The resulting material showed a specific capacitance of 338.5 F g^{-1} at a current density of 0.5 A g^{-1}. As shown in Table 5, the energy storage characteristics of bio-carbon and biochar demonstrate comparable specific capacitance when bio-carbon is synthesized via polymerization of bio-tar. However,

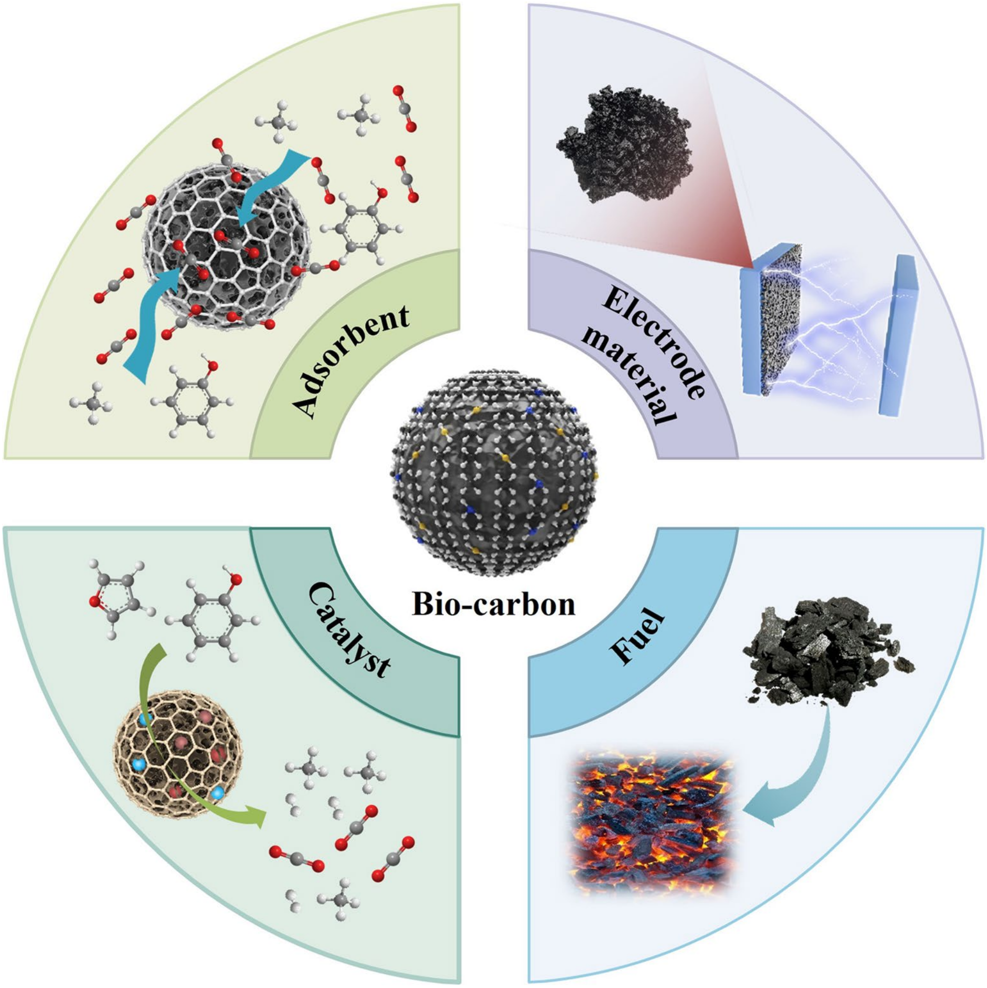


Fig. 8 Potential application of bio-carbon

Table 4 CO_2 adsorption performance of bio-carbon and biochar

Raw material	Doping element	Specific surface area (m^2 g^{-1})	Adsorption temperature (°C)	CO_2 uptake (mmol g^{-1})	References
Bio-tar	N, S	957.44	0	2.21	(Zhu et al. 2022)
Corn straw	N	465.80	25	2.40	(Sun et al. 2024a, b)
L-Glutamic acid	N, S	1213.00	25	3.54	(Shao et al. 2022)
Cornstalks	N, P	1136.31	25	3.10	(Yuan et al. 2022)
Cellulose	N	374.80	25	2.03	(Sun et al. 2023)

further improvement in cycling stability remains a critical focus for subsequent research to advance the practical application of bio-carbon-based energy storage systems. Future energy-storing electrode materials prepared from bio-carbon are expected to play a key role in many fields such as electric vehicles, portable electronic devices, and smart grids. This application will provide new ideas to solve energy storage problems and promote the widespread adoption of renewable energy. Although the introduction of template agents promotes bio-tar polymerization to prepare energy-storage electrode materials, further research is needed on how to further improve the electrochemical stability of bio-carbon, extend its service life, and achieve large-scale, low-cost production.

Table 5 Energy storage characteristics of bio-carbon and biochar

Raw material	Specific surface area ($m^2\ g^{-1}$)	Current density ($A\ g^{-1}$)	Specific capacitance ($F\ g^{-1}$)	Cycle characteristics	References
Bio-tar	3095.00	0.5	351.0	92.0% (5000 cycles)	(Luo et al. 2021)
Corn straw bio-tar	1298.26	0.5	309.5	80.1% (10,000 cycles)	(Jia et al. 2023)
Woody bio-tar	2489.62	0.5	338.5	95.0% (5000 cycles)	(Wu et al. 2020)
2-hydroxyethyl cellulose	1096.00	1.0	278.1	100.0% (10,000 cycles)	(Kim et al. 2022)
Rape pollen	374.80	0.5	390.0	92.9% (10,000 cycles)	(Liu et al. 2018)

5.3 Catalyst

Catalysts are another high-value utilization direction of bio-carbon. Carbon-based catalysts are widely used as multiphase catalysts in many reactions and processes (Lee et al. 2017), but the depletion of fossil fuels has prompted the search for alternative sources for preparing carbon-based catalysts (Rapagna et al. 1998). Biochar is a viable carbon source that plays an important role in replacing traditional carbon-based catalysts (Qian et al. 2015). Research has shown that biochar is inert to unnecessary reactions and is relatively stable during regeneration and harsh reaction conditions. Its adjustable surface area and mechanical properties allow biochar to be manufactured in various sizes and shapes of particles and polymers that can be adapted to different chemical reactors (Shen et al. 2015; Shen 2015). Biochar with a functionalized surface can be obtained through simple pyrolysis or gasification, but it shows a limited porosity and specific surface area, and almost no catalytic activity. The catalytic performance of biochar can be improved by adjusting its surface properties (surface doping and functional material loading) and constructing pores (in situ pore structure construction and post-activation pore structure construction) (Li et al. 2000). In theory, the bio-tar polymerization process can promote the loading of functional substances and the directional construction of pores, which is important for preparing bio-carbon materials with high catalytic performance. However, there is little research on the application of bio-carbon as a catalyst. The main reason is that the polymerization of bio-tar components is too complex, and it is highly difficult to synergistically control the pore structure and functional material loading (Shen and Yoshikawa 2013). In addition, existing research has shown that biochar-based catalysts are used for the catalytic upgrading of by-products such as bio-tar in the biorefinery process, but there are still issues with their low catalytic stability. This is mainly due to the coking and carbon deposition of bio-tar components during catalytic reactions. Due to the similarity between the bio-tar polymerization reaction and coking, the next stage of research is to use bio-tar polymerization to reduce the adverse effects caused by coking, thereby improving the catalytic activity and stability of biochar-based catalysts.

5.4 Fuels

The application of biochar-based fuels can potentially replace traditional fossil fuels to promote the development of renewable energy (Domínguez et al. 2006). Although biochar has a lower carbon content and higher ash content than coal-based fuels, its application potential as a fuel lies in its renewability and low cost. Carbonized biomass coal produced after biochar molding has a high stacking density and strength, making it easy to store and transport. It can potentially replace non-renewable energy sources such as natural gas and coal and be used as a new energy source for decentralized heating, especially in rural areas (Zhou et al. 2022). Bio-carbon has similar physicochemical properties and a lower ash content than biochar, making it valuable for the preparation of carbon-based fuels. The inherently low nitrogen and sulfur content in bio-tar results in bio-carbon polymerization products containing only trace levels of nitrogen and negligible sulfur impurities. This unique compositional profile significantly reduces nitrogen oxides (NO_x) and sulfur oxides (SO_x) emissions during combustion, thereby enhancing the environmental compatibility of bio-carbon as a sustainable fuel alternative compared to conventional carbon-based energy sources. Cheng et al. (2020) proposed a new process for preparing bio-coal using bio-oil fraction polymerization. The mass energy densities of the produced bio-coal reached 28.2 MJ kg^{-1}, which was the same as the combustion performance of commercial coal. The annual emission reductions from replacing the same amount of coal can reach 738 million tons of carbon dioxide equivalents. Although bio-carbon shows promising applications as a fuel, it has not yet achieved large-scale production, and its preparation costs present another barrier to its development for such applications.

6 Challenges and opportunities

Bio-tar is a renewable, low-ash, carbon-rich, and easily-polymerizable complex compound with important research value and application prospects for the preparation of bio-carbon via polymerization. Previous studies have shown that bio-carbon has promising application prospects for high-value utilization fields such as adsorption, energy storage, and catalysis, but the polymerization effect of bio-tar and the yield of bio-carbon require further improvements. The fundamental problem is the unclear interaction mechanism of complex components in bio-tar during the polymerization process. Although the introduction of furan compounds can improve the polymerization efficiency, some components are difficult to utilize during this process. This may require the introduction of a new research method combining computer simulation and experimentation to improve the analysis level of the changes throughout the entire polymerization reaction. This can help determine the optimal polymerization reaction conditions. For instance, constructing model compounds of bio-tar enables the prediction of polymerization reaction pathways through quantum chemical calculations, while machine learning-based predictive approaches optimize the process parameters for tar polymerization. These methodologies synergistically advance the rational design of bio-carbon with tailored functionalities, bridging molecular-level insights and industrial-scale manufacturability. Adding chemical activators and heteroatom dopants during the polymerization can also improve the pore structure and functional group properties of bio-carbon. However, the introduction of multiple substances further increases the reaction complexity. Collaboratively considering the complex interactions between polymerization, activation, and modification is necessary to achieve the targeted control of the physicochemical properties of bio-carbon. This article believes that the key issues in improving the yield and performance of bio-carbon should be addressed, and the next stage of research should involve optimizing the bio-carbon preparation process based on complex reaction interaction mechanisms.

In terms of the applications of bio-carbon, this article proposes a high-value utilization approach guided by high-performance carbon materials, which is the main method of solving the development of bio-tar polymerization technologies for preparing bio-carbon. Preliminary results have been achieved by the research involving energy-storage electrode materials and adsorbents. The next stage of research should focus on further optimizing the preparation process and promoting its large-scale applications. For catalytic applications, the next possible research direction is to use the mechanism of bio-tar polymerization to weaken the adverse effects caused by coking, thereby improving the quality of carbon-based catalysts. For emerging technologies and materials, evaluative research plays a pivotal role. Jia et al. (2023) conducted a techno-economic assessment using an actual pyrolysis carbonization project as a case study, demonstrating that processing 1 kg of bio-tar could yield a profit ranging from USD 1.64 to 2.38. Furthermore, Cheng et al. (2020) performed a life cycle assessment (LCA) to evaluate this technology from the perspective of biomass processing. Their findings revealed that utilizing bio-carbon as a fuel could reduce China's coal equivalent consumption by 14%. According to their calculations, the associated reduction in CO_2 emissions is projected to result in an additional economic benefit of USD 2.4 billion by 2030. In the next stage, the evaluation boundaries should be expanded, and the evaluation models improved. The economic and environmental benefits of the entire bio-tar polymerization process to prepare bio-carbon should be clarified to improve the attractiveness of bio-carbon in multiple fields. However, the different requirements for the characteristics of bio-carbon among different applications may present an obstacle, making it necessary to further improve and simplify the preparation process.

The technology for preparing bio-carbon through bio-tar polymerization has begun to take shape, and the resulting bio-carbon has shown good application prospects. To further improve the yield and quality of bio-carbon, additional in-depth research is necessary to determine the cross-linking mechanism between multiphase reactions such as bio-tar polymerization, activation, and modification. Further clarifying the conversion mechanism of key components of bio-tar during each reaction step and developing a process to prepare high-performance bio-carbon can promote the high-value utilization of bio-tar.

However, this study still exhibits several limitations:

i. While focusing comprehensively on bio-tar polymerization technologies for bio-carbon production, including polymerization mechanisms, pathways, and product applications, the in-depth analysis of individual process stages requires strengthening.
ii. Given that bio-carbon, as a novel material, exhibits distinct properties from conventional carbon materials—primarily attributed to the unique physicochemical characteristics of bio-tar—and considering the diverse requirements for tar-derived carbon properties across different applications, further systematic analysis and synthesis of research progress tailored to specific application scenarios are necessary.
iii. Although evaluative analyses hold critical significance for technology assessment, broader and

more robust evaluative research outcomes need to be developed and accumulated.

In future studies, targeted review research should address these issues to ensure comprehensive and profound insights. Investigations into polymerization pathways must advance with experimental progress by categorizing studies based on specific scenarios, processes, and feedstocks, thereby accurately identifying optimal process routes for distinct tar-based raw materials. Additionally, given the inherent toxicity of bio-tar, additional assessments of its ingress, egress, and exposure risks are imperative to ensure its safe and sustainable utilization. For product applications, scenario-specific categorization, clarification of key physicochemical properties, and enhanced traceability are essential to refine polymerization processes and support the development of novel high-performance materials.

7 Conclusions

This article reviews the research progress of bio-carbon preparation technologies through bio-tar polymerization and systematically summarizes and analyzes the bio-tar polymerization mechanism and potential applications of bio-carbon. This includes discussions on the formation process, distribution patterns, and polymerization reactions of the key components of bio-tar to determine the factors influencing the bio-tar polymerization process. This review also summarizes and analyzes current optimization strategies to clarify potential applications of the polymerization products. Clarifying the polymerization mechanism of key components and process control strategies is expected to promote the production of high-quality bio-carbon. The application prospects of bio-carbon in various fields such as adsorption, energy storage, catalysis, and energy have also been critically analyzed. From the above discussion, some important viewpoints can be summarized: (i) Oxygenated compounds play a crucial role in bio-tar polymerization, among which furan substances have the strongest effect. Active functional groups such as carbonyls and furan rings promote bond breaking and recombination during polymerization. (ii) It is important to adjust the polymerization reaction conditions while maintaining the retention of bio-tar components and reaction progress without exogenous additives to improve the bio-carbon yield. (iii) The introduction of chemical activators and heteroatom dopants significantly improves the yield and quality of bio-carbon. Clarifying the cross-linking mechanism between multiphase complex reactions is necessary for achieving the targeted regulation of bio-carbon. (iv) A high-value utilization approach guided by high-performance carbon materials is the key method of promoting the development of technology for preparing bio-carbon through bio-tar polymerization. The bio-tar polymerization technology for bio-carbon production still faces significant challenges before achieving industrial-scale application. In the next phase, priority should be given to research on process optimization strategies and product performance enhancement while advancing technical scale-up and conducting evaluative research to establish a comprehensive technological development framework. This review systematically summarizes recent progress in bio-tar polymerization technologies and provides a theoretical foundation for the efficient treatment of bio-tar and the development of advanced carbon materials.

Author contributions

Yuxuan Sun: investigation, methodology, formal analysis, writing-original draft. Jixiu Jia: conceptualization, supervision, writing-review & editing. Lili Huo: resources, supervision, writing-review & editing. Xinyi Zhang: writing-review & editing. Lixin Zhao: supervision, writing-review & editing. Ziyun Liu: writing-review & editing. Yanan Zhao: writing-review & editing. Zonglu Yao: supervision, project administration, writing-review & editing. The author(s) read and approved the final manuscript.

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Data availability

Data and materials will be made available on request.

Declarations

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported herein.

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