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Hydrothermal carbonization of rice husk for the production of nanoporous carbon materials: Recent advances and prospects for construction applications

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ABSTRACT

Rice husk is a high-volume agricultural waste that represents a promising feedstock for producing nanoporous carbon materials and value-added silicon-containing products. This review systematizes current understanding of the hydrothermal carbonization (HTC) of rice husk as an alternative to conventional thermochemical biomass-conversion methods. The fundamental mechanisms of pore-structure and surface-chemistry formation in hydrochar are examined, together with the main strategies of physical and chemical activation and the methods used to comprehensively characterize the resulting materials. Attention is given to the sorption properties of nanoporous carbon materials toward organic and inorganic pollutants in aqueous media and toward CO_2, as well as to the prospects for their application in the construction industry - in cement composites, geopolymers, asphalt binders, and self-sensing concretes. It is shown that hydrothermal carbonization of rice husk constitutes a versatile and environmentally sustainable platform for creating functional nanomaterials, although scaling up the technology and developing new construction applications remain promising directions for further research.

1. Introduction

The global transition toward low-carbon and circular models of materials production is driving researchers to turn increasingly to renewable lignocellulosic feedstocks as alternatives to conventional mineral and synthetic precursors. Rice husk occupies a special place among such feedstocks: it is a by-product of rice processing generated annually in volumes measured in tens of millions of tonnes and is characterized by a unique combination of organic (cellulose, hemicellulose, lignin) and inorganic (amorphous silica) constituents. The authors of [1] show that it is precisely this natural combination of silicon and carbon in biogenic form that makes rice husk a promising precursor for nanostructured materials with functional properties that are difficult to reproduce synthetically; this review systematizes the pathways for converting rice husk into heterogeneous catalysts, electrode materials, sorbents, and solar-grade silicon, confirming the multifunctional potential of this waste stream for a low-carbon economy.

Despite these evident prospects, rice husk remains a problematic agricultural waste. Work [2] notes that the lignocellulosic nature of rice husk, and in particular its high hemicellulose and lignin content, is responsible for its weak interaction with polymer matrices and complicates direct valorization without prior chemical or thermal treatment. An additional complicating factor is its high silica content: study [3] emphasizes that rice husk ash (RHA), generated upon its combustion, is a by-

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product that is difficult to dispose of, yet its high amorphous silica content is precisely what opens up opportunities for producing value-added materials, provided that efficient processing technologies are developed. Similarly, work [4], devoted to the synthesis of geopolymer materials from rice husk ash, confirms that despite the apparent environmental burden of this waste, its high amorphous silica content makes it a valuable feedstock for sustainable construction materials.

Among the existing thermochemical methods for biomass conversion - pyrolysis, gasification, and hydrothermal carbonization (HTC) HTC is regarded as one of the most promising approaches for processing wet feedstocks without prior drying. Review [5] provides a systematic comparison of biochar obtained by pyrolysis and hydrochar obtained by HTC, showing that despite the similar carbon skeleton of both materials, differences in synthesis conditions (the presence of subcritical water, lower process temperatures, autogenous pressure) lead to substantial differences in the pore structure, surface chemistry, and functional groups of the final products, which makes hydrochar a distinct class of carbon material rather than a mere analogue of biochar. A broader context for hydrothermal processes is presented in work [6], which analyzes feedstock flexibility, the range of obtainable products, and approaches to modeling hydrothermal biomass conversion within the concept of future biorefineries; the authors note that the variability of HTC process parameters allows the yield and properties of the solid, liquid, and gaseous products to be purposefully tuned according to the intended application.

The practical significance of co-hydrothermal carbonization of different biomass types is further confirmed in work [7], where, using co-HTC of sewage sludge as an example, it is shown that co-processing with higher-calorific biomass components makes it possible to correct the unsatisfactory fuel characteristics of hydrochar obtained from sludge alone - this approach demonstrates the fundamental possibility of purposefully controlling the properties of the final product by varying the composition of the initial feedstock. Work [8] emphasizes that rapid industrialization and urbanization are generating substantial volumes of wet biomass waste, for which HTC serves as a sustainable solution, yielding hydrochar with a high carbon content, a well-developed specific surface area, and a rich set of oxygen-containing functional groups, making it suitable, in particular, for water-treatment applications.

The functional potential of hydrochar as a sorption material is systematized in review [9], which analyzes how the properties of the initial biomass and the parameters of hydrothermal treatment determine the sorption efficiency of the resulting product toward a wide range of pollutants. Similar conclusions are drawn in review [10], which notes that hydrothermal carbonization offers a few inherent advantages over other thermochemical methods for processing biomass and organic waste, and that hydrochar itself can be used either directly or after modification as a biosorbent for wastewater treatment and CO_2 adsorption. A broader perspective on the role of biochar in general as an instrument of sustainable waste management and environmental remediation is presented in work [11], where biochar production from residual biomass is considered in the context of renewable energy generation and ecological remediation.

At the same time, several studies point to technological challenges specifically associated with the processing of silicon-containing biomass, to which rice husk belongs. Work [12] experimentally demonstrates that the inorganic component of biomass is not inert during activation: the interaction of silica with volatile substances and activating agents creates steric hindrance to activator access to the organic part of the feedstock's internal structure, so that removing SiO_2 by alkaline leaching prior to activation promotes more pronounced pore development and an increase in the specific surface area of the resulting activated carbon. A detailed analysis of the factors governing the efficiency of such leaching is presented in work [13], which, based on an experimental study of the effects of pH, acid type, temperature, treatment time, and the solid-to-liquid ratio, establishes the optimal conditions for obtaining high-purity biosilica; the authors also show that pre-leaching affects the character of rice husk's thermal decomposition and the subsequent oxidation of the resulting biochar. Taken together, these data indicate that the siliceous nature of rice husk, often perceived as a complicated factor in processing, can, with proper technological control, be turned into an additional advantage, enabling the production of bifunctional products - both a porous carbon material and high-purity biosilica. In addition to the traditional acid and alkaline methods of silica extraction, the use of microwave treatment of rice husk has been actively developing in recent years. This approach provides more intensive heating of the biomass, shortens the process duration, and yields high-purity silica suitable for the further synthesis of functional materials. These results confirm that rice husk is not only a promising source of carbon materials but also a valuable feedstock for silicon-containing products with high added value [14]. Further confirmation of the value of rice straw as a renewable feedstock is provided by work [15], which shows that microwave irradiation enables efficient extraction of cellulose from it, opening an additional route to valuable biopolymer components alongside silicon-containing and carbon products, consistent with the broader potential of cellulose-based sorbents for water remediation [16].

Expanding the range of activating agents and modification strategies also substantially increases the practical value of materials obtained from rice husk and

related biomass types. Review [17] systematizes the results of physical, chemical, and combined modification of activated carbon used to remove dyes and heavy metals from wastewater, showing that chemically modified sorbents generally exhibit higher sorption capacity compared with unmodified analogues, which makes the choice of activating agent and its application conditions one of the key factors in designing porous carbon materials for a specific purpose, in line with earlier findings on metal-ion sorption by waste-derived activated carbons from multicomponent aqueous solutions [18].

Beyond sorption and energy applications, carbon and silicon-containing materials based on rice husk and its ash show growing potential in the field of construction materials, which is directly linked to the decarbonization goals of the construction industry. Study [19] shows that using rice husk ash as a partial replacement for Portland cement in combination with multi-walled carbon nanotubes yields environmentally sustainable concrete with improved mechanical and service characteristics, which is regarded as one of the ways to reduce the environmental burden of the construction industry. A broader review of various admixtures in alkali-activated materials, considered as an alternative to Portland cement, is presented in work [20], which analyzes the influence of composition and activation conditions on hydration, microstructure, and surface-chemical processes in such systems.

Taken together, the data presented indicate that in recent years a substantial body of knowledge has accumulated both on the fundamental mechanisms of biomass hydrothermal carbonization and on individual applied aspects of obtaining and using porous carbon materials, including those based on rice husk. At the same time, existing studies are predominantly fragmentary in character: a significant portion of the work is devoted either to studying HTC and activation mechanisms on model or alternative biomass types without direct reference to rice husk, or to narrowly specialized sorption and energy applications of the resulting materials, whereas their potential as functional additives for construction composites - cement systems, geopolymers, asphalt binders, and materials for self-sensing structural elements - has been covered considerably less comprehensively and systematically. There is also no comprehensive analysis that consistently links the parameters of hydrothermal treatment and subsequent activation of rice husk with the structural and surface-chemical characteristics of the resulting nanoporous carbon materials and, further, with their service properties within construction composites.

The present review aims to fill this gap. Its purpose is to systematize and critically analyze current understanding of the hydrothermal carbonization of rice husk as a method for producing nanoporous carbon materials, and to assess the prospects for their application in the construction industry. To achieve this goal, the review sequentially addresses the following tasks: examining rice husk as a renewable lignocellulosic feedstock, including its composition, generation volumes, and disposal challenges; analyzing the fundamental mechanisms and process parameters of hydrothermal carbonization; systematizing chemical and physical activation strategies for the resulting hydrochar; summarizing current understanding of the structure, surface chemistry, and characterization methods of the resulting nanoporous carbon materials; and, finally, critically analyzing recent advances and prospects for using these materials in cement composites, geopolymers, asphalt binders, and self-sensing concretes, while identifying key scientific gaps and directions for future research.

2. Hydrothermal carbonization of rice husk: Fundamentals and process development

2.1. Rice husk as a renewable lignocellulosic precursor

As already noted in the introduction, rice husk is a lignocellulosic waste with a unique combination of organic and mineral constituents [1], yet the practical value of this feedstock is determined not only by its chemical composition but also by the extent to which various processing routes can unlock the potential of each component. This multifunctionality is illustrated by work [21], in which activated carbon obtained by hydrothermal treatment of rice husk was modified with cobalt and used as a catalytic support for the transesterification of waste vegetable oil into biodiesel; the authors achieved a feedstock conversion of 96.3% under response-surface-optimized conditions (75 °C, methanol-to-oil molar ratio of 1:9, 2 wt% catalyst), illustrating how a relatively simple hydrothermal modification of rice husk opens a route toward catalysts for energy applications, conceptually related to other carbon-supported metal catalyst systems, such as palladium on thermally expanded natural graphite [22].

Similar logic can be traced in studies devoted to obtaining electrode materials. In work [23], carbonized rice husk was activated with KOH, NaOH, and a mixture of the two, followed by a systematic comparison of electrochemical characteristics; the best cyclic stability (102.4% capacity retention after 10,000 cycles) was shown by the sample with mixed alkaline activation, while the NaOH-activated sample provided the maximum specific capacitance of 160.5 F/g - the authors conclude that electrochemical properties are governed by a combination of structural and chemical parameters rather than by a single dominant factor. A similar conclusion is drawn in work [24], where rice-husk-derived biochar, obtained by pyrolysis and subsequently activated with steam or CO_2, was used as a support for

nickel catalysts in CO_2 methanation; the catalyst on the CO_2-activated support exhibited stability over 20 h of testing and selectivity above 90%, which the authors attribute to a more developed porosity, higher crystallinity, and stronger interaction of nickel with the biochar surface. A further direction is disclosed in work [25], where a combination of hydrothermal treatment and high-temperature activation was used to purposefully tune the pore structure of rice-husk-derived carbon using a natural SiO_2 template, yielding a honeycomb-like structure with abundant mesopores; a supercapacitor cathode based on this material demonstrated a specific capacitance of 172.5 F/g and 97.7% capacitance retention after 12,000 cycles.

Attention should be paid to the silicon component of rice husk, which, given appropriate technological treatment, is transformed from a complicating factor into an independent resource. In work [26], the natural silica of rice husk was used as a source for synthesizing mesoporous silicate templates MCM-41 and SBA-15 by nanocasting, with subsequent production of their carbon replicas; the resulting materials had a specific surface area of 800–1400 m^2/g and demonstrated hydrogen adsorption of up to 3.6 wt% under cryogenic conditions, exceeding the performance of analogous carbon materials from other biomass sources. This confirms the conclusion already noted in works [12,13]: rice husk silica is not an inert impurity that complicates processing, but a potential independent precursor for functional nanostructured materials, which together justifies considering rice husk specifically as a bifunctional feedstock when designing hydrothermal carbonization technology, as discussed further below. This confirms the conclusion already noted in works [12,13]: rice husk silica is not an inert impurity that complicates processing, but a potential independent precursor for functional nanostructured materials, which together justifies considering rice husk specifically as a bifunctional feedstock when designing the hydrothermal carbonization technology discussed further below (Figure 1).

2.2. Fundamentals of hydrothermal carbonization

Fundamental understanding of the mechanism of hydrothermal carbonization of biomass, including rice husk, relies on the general patterns established for a wide range of feedstock types. As noted in review [8], the HTC process proceeds under subcritical water conditions and involves a sequence of hydrolysis, dehydration, decarboxylation, and condensation-polymerization reactions, as a result of which lignocellulosic biomass is converted into hydrochar - a material with a high carbon content, a well-developed surface, and a rich set of oxygen-containing functional groups; the authors also emphasize the economic significance of HTC in the context of the circular economy and sustainable development goals. A more detailed picture of the influence of specific process parameters is presented in work [27], where hydrothermal treatment of sawdust at varying temperature (200–260 °C) revealed a non-monotonic change in the yield of the liquid product - wood vinegar - and established that the chemical composition of the resulting products is governed by the temperature range at which different biomass components hydrolyze: hemicellulose converts predominantly at temperatures up to 200 °C, whereas cellulose and lignin convert in the range of 200–260 °C. The practical applicability of hydrothermal carbonization directly to rice husk has been confirmed by recent experimental studies. It has been shown that optimizing the parameters of hydrothermal treatment provides hydrochar with a high yield and a well-developed system of oxygen-containing functional groups, which are an important prerequisite for subsequent chemical activation and the formation of a nanoporous structure. These results further confirm the promise of rice husk as a renewable precursor for functional carbon materials of various purposes [28].

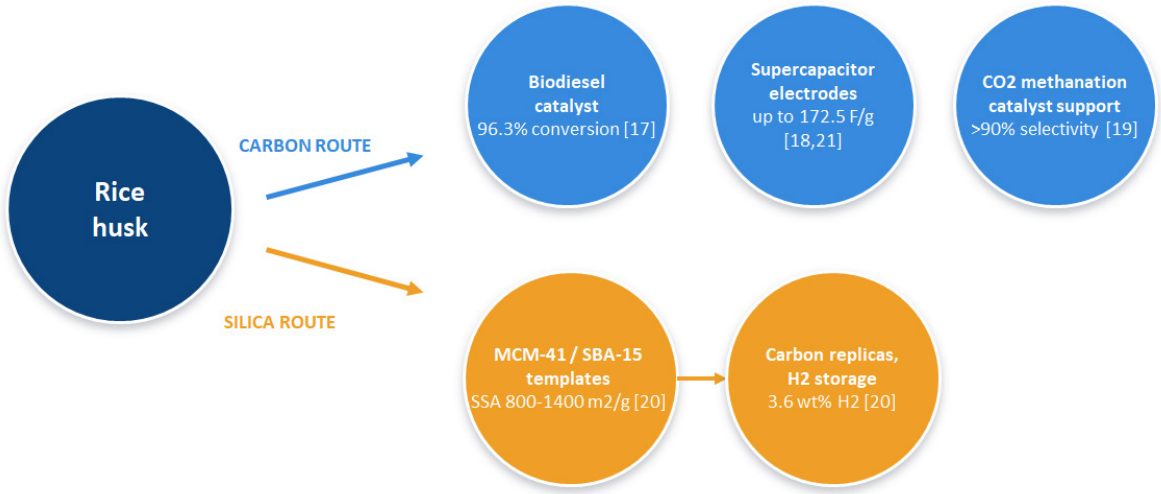

Fig. 1. Rice husk: two value-creation pathways from one precursor

A similar dependence of hydrochar structural transformations on feedstock composition is demonstrated in work [27] using residues of traditional Chinese medicine as an example: the authors found that a high hemicellulose content promotes maximum hydrochar yield at low HTC temperatures (160 °C), whereas increasing the temperature intensifies structural aromatization and de-hydroxylation, and a high lignin content promotes the formation of a graphite-like layered structure. The temperature dependences established in works [26] and [27] are summarized in Figure 2.

The influence of temperature and feedstock composition on the techno-economic performance of the process is also examined in detail in studies devoted to the co-hydrothermal processing of various wastes. In work [29], response surface methodology was applied to model the solid product yield and its carbon content as functions of process severity and initial solids content during HTC of sewage sludge; the authors showed that solids content has a stronger effect on yield than process severity, and that milder treatment regimens improve the subsequent dewaterability of the hydrochar. This direction is further developed in work [30], where the co-hydrothermal processing of food waste and agricultural biomass was investigated in terms of bio-oil yield and composition; it was established that the Maillard reaction between food-waste proteins and biomass decomposition products plays a key role in bio-oil formation, increasing its calorific value and lowering its oxygen content without substantially altering its elemental composition.

A broader technological context is provided by review works that systematize the family of hydrothermal processes. Review [6] analyzes the flexibility of hydrothermal processing across feedstock types - from municipal solid waste to microalgae - as well as current approaches to modeling transport phenomena in hydrothermal liquefaction reactors; the authors formulate a research roadmap combining theoretical and experimental modeling to accelerate the transition to next-generation biorefineries. Similarly, review [31] systematizes the mechanisms by which solvents and catalysts influence the hydrothermal liquefaction of biomass: it is shown that biphasic solvent systems increase the yield of platform furanic compounds, and the addition of sodium chloride substantially increases the yield of target products, while the choice between homogeneous and heterogeneous catalysts is determined by a trade-off between process selectivity and the practicality of catalyst regeneration. Finally, the applied potential of the resulting solid product for co-firing with coal is confirmed in work [7], which shows that co-HTC of sewage sludge with higher-calorific biomass makes it possible to correct the unsatisfactory fuel characteristics of hydrochar obtained from sludge alone, and that the elemental composition of the added biomass and the mixing ratio directly determine the final product quality.

Further examples of the technological versatility of hydrothermal processes are confirmed in studies devoted to fundamentally different feedstock types. Work [32] numerically models the hydrothermal conversion of municipal solid waste into a coal-like solid fuel at a pilot-scale facility, confirming the suitability of the technology for mixed municipal waste. Similarly, work [33] demonstrates the hydrothermal conversion of mango wood waste and sugarcane bagasse into biooil with a high calorific value, while work [34] demonstrates the catalytic hydrothermal conversion of polypropylene into short-chain olefins, which extends the concept of hydrothermal processes beyond biomass proper and illustrates the general potential of subcritical water as a reaction medium for the targeted depolymerization of diverse organic feedstocks.

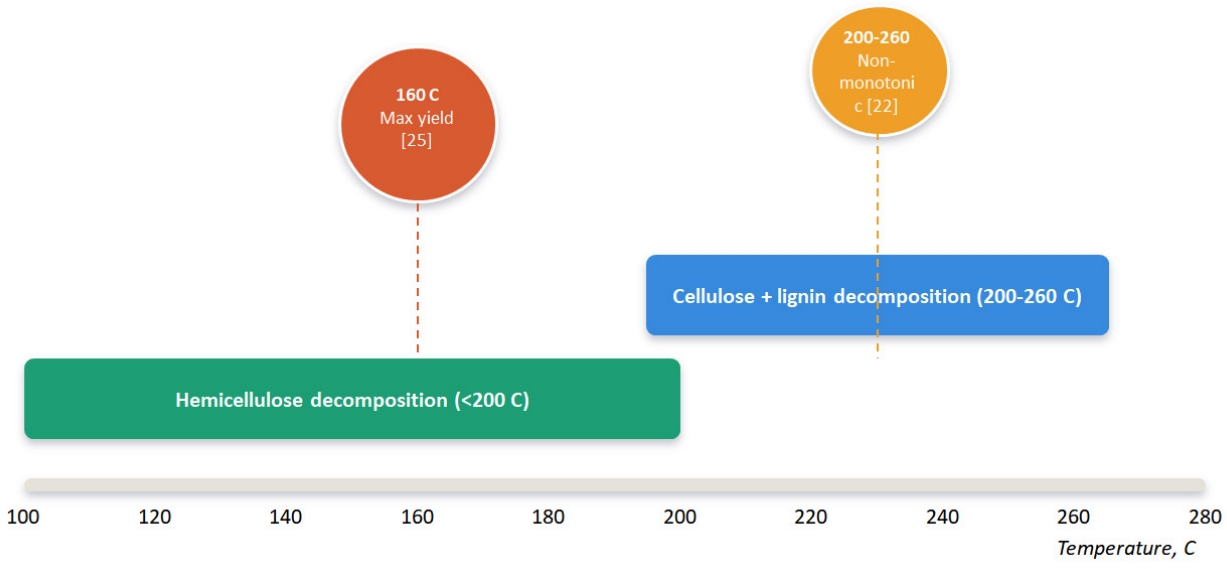

Fig. 2. Temperature-dependent decomposition of biomass components

Taken together, these data indicate that the parameters of hydrothermal carbonization - temperature, treatment duration, and feedstock composition and ratio - jointly determine the yield, elemental composition, and structural characteristics of hydrochar, providing a methodological basis for the purposeful design of rice husk processing that accounts for its specific lignocellulosic-siliceous composition, discussed in Section 2.1.

2.3. Modification and activation strategies

Converting hydrochar into a functional nanoporous carbon material depends critically on the subsequent activation stage, for which a wide range of chemical and physical agents has been described in the literature. A systematic comparison of the mechanisms of alkaline activators is presented in work [35], where coupling carbon activation with silicon separation from coal gasification slag using a mixed alkali (KOH:NaOH) revealed that the etching action of the alkali mixture widens the pore structure, increases the number of surface oxygen-containing groups, and forms graphitized defect sites, while simultaneously breaking stable Si–O–Si bonds and converting aluminosilicates into more reactive amorphous phases - that is, activation and silicon removal turn out to be interrelated processes, which directly echoes the role of SiO_2 in rice husk discussed above [12]. Work [36] proposes an alternative, less corrosive activation route - using urea and potassium citrate instead of conventional KOH - which yielded a material with a specific surface area of 1750 m^2/g and a specific capacitance of 310.1 F/g, demonstrating growing interest in environmentally friendly activating agents as alternatives to aggressive alkalis. The preference for milder salt activators such as K_2CO_3 or potassium citrate over aggressive hydroxides (KOH, NaOH) reflects a clear thermodynamic trade-off: carbonate and citrate salts decompose in situ to generate CO_2 and mildly alkaline intermediates, which etch the carbon skeleton gradually and at lower exothermicity, producing a narrower and more controllable micropore-size distribution but typically a lower ultimate specific surface area than hydroxide activation; concentrated KOH/NaOH, in contrast, drive a highly exothermic, thermodynamically favorable etching-and-intercalation reaction that maximizes pore volume and surface area at the cost of higher corrosivity, less selective pore widening, and greater equipment and neutralization costs. This trade-off is directly coupled to the fate of residual SiO_2 in rice-husk-derived carbons: under strongly alkaline hydroxide conditions, SiO_2 is thermodynamically driven toward dissolution as soluble silicates (Si-O-Si bond cleavage), which simultaneously frees additional pore volume and can be exploited for co-recovery of the silicon phase, whereas under milder carbonate/citrate activation, SiO_2 largely persists as a rigid inorganic scaffold that constrains pore widening but helps preserve the mesoporous framework - underscoring that the choice of activator governs not only the resulting pore architecture but also whether silicon removal and carbon activation proceed as coupled or largely independent processes.

A substantial portion of research is devoted to optimizing the conditions of physical and physicochemical activation for targeted gas separation and adsorption. In work [37], fibrous porous carbon from degreased cotton waste was activated with mild K_2CO_3, yielding a specific surface area of 1011 m^2/g and a maximum CO_2 adsorption capacity of 5.37 mmol/g while retaining 96% of its capacity after five adsorption-desorption cycles - the authors emphasize that it is specifically the narrow micropore-size distribution that determines the adsorption capacity. A similar physicochemical strategy is applied in work [38], where combined carbonization-activation of bamboo feedstock with H_3PO_4 and CO_2 provided a specific surface area of up to 2250 m^2/g and a methylene blue adsorption capacity of 759.15 mg/g, achieved through a combination of pore filling, electrostatic attraction, π–π stacking, and hydrogen bonding. Strategies for simultaneous co-activation with several agents are examined in works [39] and [40], where CO_2/NH_3 co-activation and synergistic KOH–K_2CO_3 activation, respectively, were applied for nitrogen doping of porous carbon; in both cases, combining activators provided a more developed pore structure and higher doping efficiency compared with the use of a single activator, confirming a general pattern: combined activation schemes are consistently more efficient than single-agent ones. A further direction in the development of porous carbon material technologies is the co-thermal processing of agricultural and technogenic waste. This approach makes it possible to obtain granular carbon sorbents with a well-developed pore structure and satisfactory mechanical properties, while simultaneously solving the problem of jointly disposing of several types of waste. The use of co-thermolysis is consistent with modern circular-economy principles and opens up new opportunities for the industrial production of highly efficient sorption materials [41].

Studies devoted directly to obtaining activated carbon from rice husk and straw using various binding agents for its subsequent granulation are of considerable practical interest. Thus, work [42] demonstrates the fundamental feasibility of converting rice husk and straw into activated carbon. This direction is further developed in work [43], where gelatin was used as a binding agent for the joint processing of rice and oil waste into granular activated carbon, while work [44] used polyvinyl acetate for a similar task - granulating activated carbon from rice husk and straw together with oil sludge - demonstrating the variability of binder systems applicable to this technological task. A comprehensive approach to the integrated processing of rice and oil waste into granular

activated carbon is summarized in work [45], which systematizes the conditions for obtaining a material with reproducible service characteristics. Particular attention should be given to studies in which activation is directly coupled with the formation of the material's functional purpose. Thus, work [40] shows that direct co-pyrolysis of agroforestry biomass with potassium oxalate allows simultaneous in-situ activation and yields ultrathin two-dimensional structures with a specific surface area of 1802 m^2/g, while work [46] demonstrates that a gel-salt co-regulation strategy—combining $ZnCl_2/K_2CO_3$ activation with gel confinement of a biopolymer precursor—provided a carbon yield of 34.2% with a specific surface area of 1792 m^2/g and a specific capacitance of 318.8 F/g.

A comparison of the specific surface areas of materials obtained using different activation strategies is presented in Figure 3. The specific character of rice husk as a feedstock for such processes is confirmed in works [2] and [3]: it is shown that pre-treatment of rice husk with alkali (KOH) removes hemicellulose more effectively than treatment with $KMnO_4$, shifting the pyrolysis activation energy within the range of 111.9–186.7 kJ/mol [2], while functionalizing rice husk ash through activation followed by sulfonation yields a bifunctional product - a catalytic material and high-purity silica simultaneously, with a silica yield of 84% and a purity of 96% [3]. Finally, the influence of hydrothermal treatment conditions on the subsequent suitability of rice husk hydrochar for activation is directly investigated in work [47], where recycling the HTC process water increased the hydrochar yield from 68.5% to 76.6% and the energy recovery efficiency from 72.2% to 89.7% through the accumulation of oxygen-containing functional groups, while simultaneously improving the sorption performance of the resulting product toward malachite green.

Thus, current practice in activating rice husk hydrochar and related lignocellulosic biomass shows a clear trend away from classical single-agent alkaline activation toward combined and less aggressive strategies, as well as toward synchronizing activation with the extraction of the silicon phase - an approach that is particularly well suited to the two-component (organic-mineral) nature of rice husk, providing a direct bridge to the discussion of the structure and characterization of the resulting nanoporous materials in the next chapter.

3. Structure, properties and characterization of nanoporous carbon materials

3.1. Formation mechanism of porous structure

The formation of the pore structure of nanoporous carbon materials results from a complex interplay of carbonization temperature, the nature and dosage of the activator, and the architecture of the initial carbon skeleton. A substantial body of current research is devoted specifically to controlling this interplay for materials used in electrochemical energy storage, which is of independent interest and simultaneously allows the established patterns to be extrapolated to rice-husk-derived porous materials. Thus, in work [48], nitrogen-doped hierarchical porous carbon was synthesized by single-step carbonization of agar with urea as the nitrogen source and $KHCO_3$ as the activator; the combination of a high content of nitrogen and oxygen functional groups with an interconnected hierarchical pore structure and a large specific surface area provided the electrode with a specific capacitance of 450 F/g.

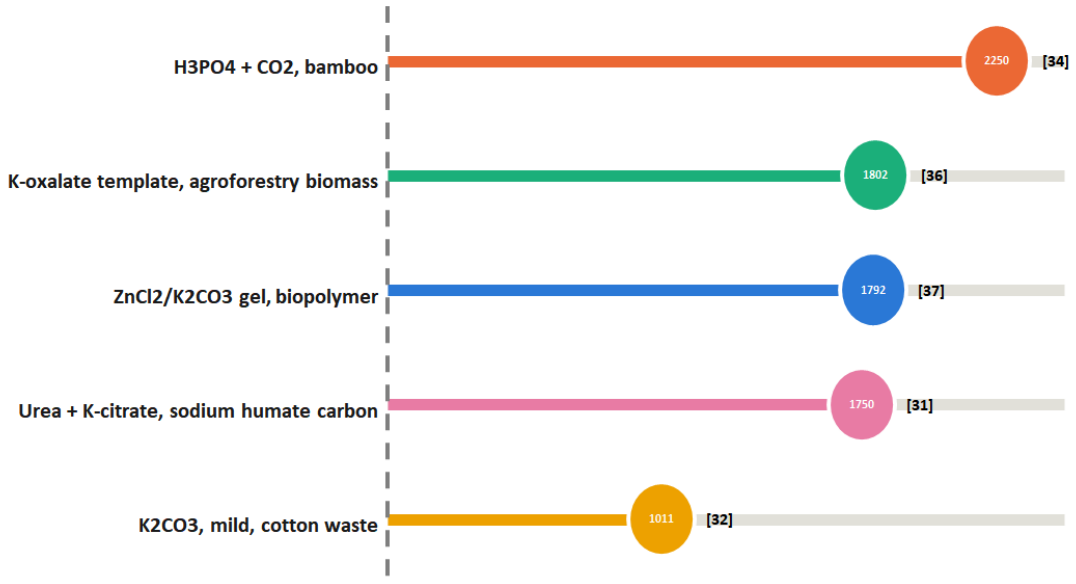

Fig. 3. Modification and activation strategies

A similar approach using natural templates is implemented in work [49], where algal bio-oil distillation residues were carbonized in the presence of nano-$CaCO_3$ and K_2CO_3, yielding a material with a record specific surface area of 2376.95 m^2/g; the authors separately showed that the pore size optimal for ion transport (2–5 nm) is determined by the ratio of templating to activating agent rather than by carbonization temperature alone.

The role of pore geometry and edge effects in pore structure formation is investigated in work [50], where hierarchical porous nanosheets of cobalt- and nitrogen-containing carbon with trimodal porosity (macro-, meso-, and micropores) were synthesized by a templating method using polystyrene; using density functional theory, the authors demonstrated that it is precisely the curvature of the carbon surface that promotes charge transfer and lowers the energy barrier of the catalytic reaction. A similar idea of controlling pore architecture through precursor selection is reflected in work [51], where hierarchical porous carbon was obtained by carbonizing rapeseed stalks followed by KOH activation, achieving a specific surface area of 846–1276 m^2/g, and in work [52], where sulfur-doped porous carbon was synthesized from sodium lignosulfonate using KOH, yielding a hierarchical pore structure with a specific surface area of 851.3 m^2/g and a pore volume of 0.53 cm^3/g, suitable for thallium(I) adsorption. Special attention should be given to work [53], in which dry processing of hierarchical porous carbon co-doped with nitrogen, oxygen, and sulfur, combined with vanadium nitride quantum dots, provided lithium-sulfur battery cathodes with stability over 1000 cycles and a degradation of only 0.0107% per cycle - this confirms that controlling the pore architecture at the stage of carbon-skeleton formation directly determines the electrochemical and sorption functionality of the final material.

The valorization of wastes containing aromatic and polycyclic structures as precursors for hierarchical porous carbon is demonstrated in works [54] and [55]. In the first, co-carbonization of bitumen asphaltenes with recycled cellulose acetate from cigarette butts yielded a material with a record specific surface area of 3613 m^2/g and a specific capacitance of 343.9 F/g, with the high evaporation rate of cellulose acetate promoting the pyrolysis and activation of asphaltenes and stimulating the formation of both micro- and mesopores. In the second work, pre-oxidation and pre-hydrothermal carbonization of coal tar with melamine followed by KOH activation produced a honeycomb-like three-dimensional structure (N-CTPAC) with a high specific capacity of 155.8 mAh/g and an energy density of 112.7 Wh/kg. Finally, the applied potential of hierarchical porosity for gas-separation membranes is demonstrated in work [56], where carbon molecular sieve membranes with a hierarchical pore structure provided a helium-recovery selectivity from high-pressure natural gas of 1427, while for temperature-swing adsorption of benzene, work [57] shows that intermediate pores of 1.5–2.0 nm optimally combine adsorption rate, desorption capacity, and space-utilization efficiency, providing an average adsorption capacity above 800 mg/g.

Taken together, these data point to a general pattern: the formation of the target hierarchical porosity is determined not by a single parameter but by the concerted action of carbonization temperature, the nature of the activator, and the structural organization of the precursor, which applies directly to rice husk as well, where the role of the natural silicon template discussed in Section 2.1 further complicates and simultaneously enriches the pore-formation mechanism.

3.2. Surface chemistry

The surface chemistry of nanoporous carbon materials - above all, the nature and density of oxygen-, nitrogen-, and sulfur-containing functional groups - determines not only their sorption but also their electrochemical and catalytic properties. The molecular-level interaction of water with biochar surface groups is investigated in work [58] using density functional theory: it is shown that water has a dual activating effect on biochar functional groups, enhancing charge transfer during the adsorption of volatile organic compounds while simultaneously lowering the energy barrier for their oxidative degradation via C–H and C–C bonds, opening up prospects for using biochar to purify wet flue gases. Competitive gas adsorption on functionalized carbon surfaces is examined in detail in work [59], where multiscale modeling shows that phosphorus-, sulfur-, and nitrogen-containing surface groups provide substantially higher selectivity for H_2/N_2, H_2/CO_2, and H_2/CH_4 separation compared with unmodified graphene - with the selectivity gain reaching 615% for the CO_2/H_2 system.

The influence of surface chemistry on the behavior of water in nanopores, using periodic mesoporous organosilicons as an example, is examined in work [60], which shows that hydrophilic and hydrophobic functional groups form fundamentally different water-adsorption profiles and adsorbed-layer thicknesses - a result that is methodologically significant for understanding moisture behavior in silicon-based porous systems and directly relevant to the two-component nature of rice husk. The role of graphene oxide functional groups in the adsorption of dyes and heavy-metal ions is systematized in review [61], which emphasizes that the production method and structural modification of graphene oxide determine its sorption efficiency toward a wide range of pollutants, while work [62], using functionalized carbon nanotubes as an example, shows that it is specifically the surface carboxyl groups that are responsible for the dominant contribution to electricity generation upon interaction

with water, providing the device with a spontaneous voltage above 200 mV even in natural seawater.

The applied significance of purposefully controlling surface chemistry for energy applications is confirmed in work [63], where activated carbon from date-pit waste, obtained by hydrothermal carbonization followed by sulfuric acid activation, demonstrated a specific capacitance of 179 F/g owing to a predominantly microporous framework enriched with oxygen-containing functional groups. The thermal stability of hydrogen-chemisorbing carbon active sites is studied by temperature-programmed desorption and reaction methods in work [64], which shows that these sites are deactivated in an inert atmosphere at pretreatment temperatures above 950 K, which is directly relevant to the design of thermally stable activated carbons.

A separate group of studies directly demonstrates the role of surface chemistry in rice-husk-based sorbents and related hydrochars. In work [65], steam-activated biochar from pre-desilicated rice husk, characterized by a highly developed specific surface area (1214 m^2/g) and a surface enriched with oxygen-containing groups, demonstrated a tetracycline hydrochloride sorption capacity of 591 mg/g, with a thermodynamically confirmed spontaneous endothermic sorption mechanism. Molecular dynamics simulation of Congo red adsorption on hydrochar in work [66] revealed that it is specifically the hydroxyl-enriched surface (O/C = 0.55) that provides a 33% higher maximum adsorption capacity compared with a carbon-enriched surface (O/C = 0.03), realized through van der Waals forces, π–π stacking, and hydrogen bonding. Finally, in work [67], hydrochar from olive pits, obtained by hydrothermal carbonization, was characterized by predominantly negatively charged surface sites (zeta potential of –19.4 mV) and demonstrated a physisorption-based, spontaneous, and entropy-driven mechanism for methylene blue removal.

Taken together, these data confirm the thesis already formulated in the Introduction: the surface chemistry of nanoporous carbon is a controllable parameter, and its purposeful regulation - through the choice of activator, carbonization conditions, and, in the case of rice husk, the degree of preliminary desilication - directly determines the functional characteristics of the final material.

3.3. Morphology and pore development

The morphology and pattern of pore development are largely determined by the thermal history of the initial feedstock - in particular, by the presence and parameters of a pre-carbonization stage. Work [68] systematically shows that pre-carbonizing sawdust, cellulose, and lignin removes a significant portion of aliphatic structures, hindering subsequent pore development during activation with $K_2C_2O_4$, CO_2, or H_2O, whereas $ZnCl_2$ and H_3PO_4 as activators provide a more developed pore structure specifically during direct activation of biomass without pre-carbonization, catalyzing the dehydration of aliphatic fragments; the authors also show, based on life-cycle analysis, that direct activation is characterized by a lower environmental impact. A similar methodology is applied in work [69] to garlic-peel waste: varying the particle size and carbonization temperature during hydrothermal pretreatment followed by K_2CO_3 and urea activation yielded porous carbons with a specific surface area of 2000–2700 m^2/g and high CO_2 adsorption (4.9–5.9 mmol/g).

A systematization of mechanisms for the purposeful control of pore architecture is presented in work [70], where, using coconut shell as an example, it is shown that combining hydrothermal carbonization at 240 °C with physical activation makes it possible to purposefully obtain activated carbons with a widely variable meso-/macroporosity fraction (18–77%) at a comparable specific surface area (~450 m^2/g) - that is, specific surface area and pore hierarchy can be regulated as independent parameters. The influence of pretreatment and activation conditions on the pore structure of coal-based carbons is examined in detail in works [71] and [72]: the first shows that single-step activation for 120 minutes provides a specific surface area of 1038.1 m^2/g and a hierarchical-pore fraction of 50.7%, while the second shows that steam activation at 750 °C is most favorable for developing mesoporous structure, and that the fractal dimension of the micropore surface correlates positively with the micropore volume fraction.

Control of porous-carbon particle morphology by soft-templating methods is examined in works [73] and [74]. In the first, a modified Stöber method yielded mesoporous carbon spheres with a tunable pore size from 2.25 to 8 nm by varying the heating rate and acid treatment, which is promising for applications in adsorption, encapsulation, and delivery. In the second, an HCl-concentration-controlled hydrothermal templating strategy yielded ordered mesoporous carbons from liquefied wood with morphology ranging from platelets to gyroids and spheres, with the most ordered p6mm mesostructure, synthesized at an optimal HCl concentration of 1.61 M, showing enhanced electrochemical performance.

Taken together, these studies confirm that morphology and pore development are controllable process parameters, for which the sequence of thermal-treatment stages and the nature of the templating or activating agent both play a determining role - a conclusion directly applicable to rice husk, where the embedded natural silicon template can perform a function analogous to the synthetic templates used in the studies discussed above. Comparative specific-surface-area values for materials obtained by different precursors and activation strategies, discussed in Sections 3.1–3.3, are summarized in Figure 4.

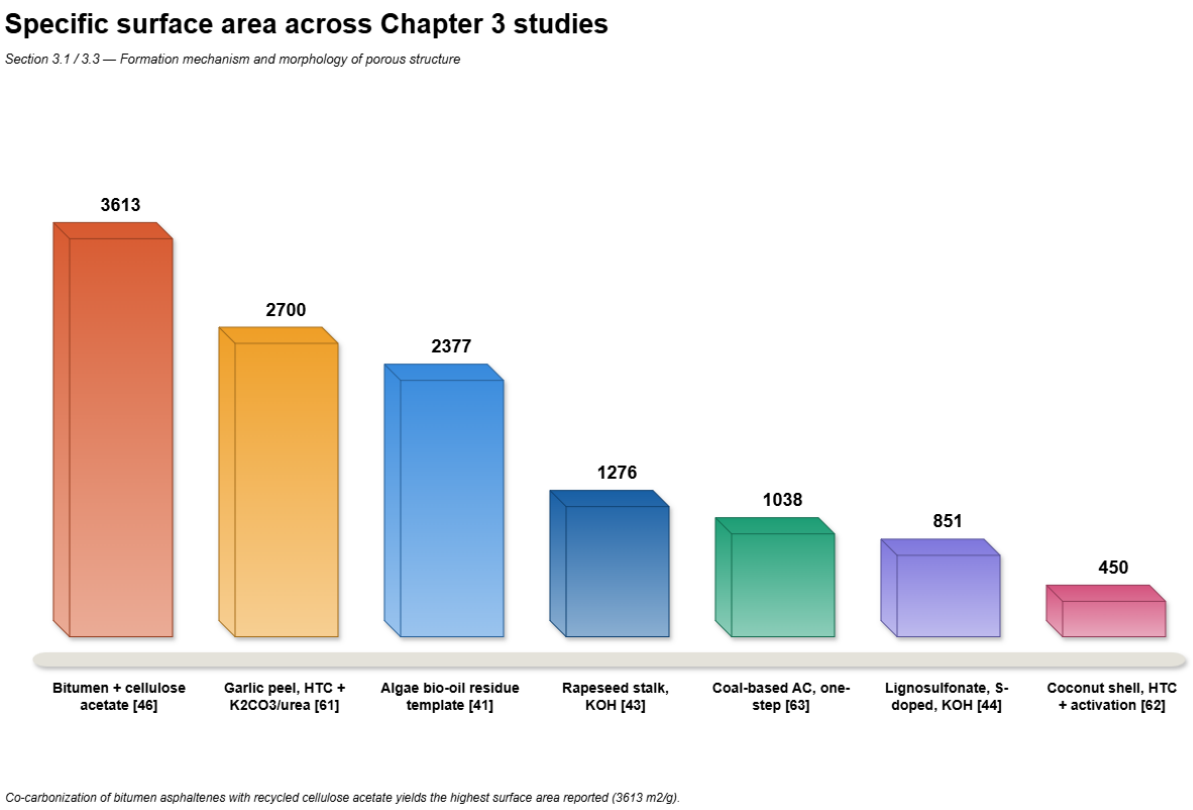

Fig. 4. Formation mechanism and morphology of porous structure

3.4. Characterization techniques

For a reliable interpretation of the structural and surface-chemical characteristics of nanoporous carbon materials, the accuracy of the characterization methods employed is of fundamental importance, above all the BET (Brunauer–Emmett–Teller) method, which remains the basic tool for determining specific surface area. An important methodological caveat is provided by the large-scale interlaboratory study [75], in which 18 experimental adsorption isotherms were distributed to 61 laboratories for BET area calculation; the results showed considerable scatter in the obtained values, casting doubt on the reproducibility of the method and prompting the development of specialized software (BETSI) for the unambiguous determination of BET area based on Rouquerol criteria. A similar methodological issue is raised in work [76], which proposes a krypton adsorption method for measuring the specific surface area of nanoparticles collected on filters, providing a quantification limit of 0.05 m^2 with an uncertainty of 15% - a significant improvement for materials with small sample masses.

The practical significance of choosing an appropriate surface-area determination method for a specific application is demonstrated in work [77], which, comparing four methods for determining the surface area of graphite granules for microbial electrodes, shows that the BET method systematically overestimates the microbiologically accessible area compared with profilometry - directly relevant when assessing the functional, rather than merely formal, specific surface area of carbon materials. It should also be emphasized that standard N_2 physisorption at 77 K, while forming the basis of the BET method, has intrinsic limitations for characterizing ultra-narrow micropores (<0.7 nm): at cryogenic temperature, N_2 molecules diffuse slowly into such constrictions, which can lead to incomplete pore filling within practical equilibration times and, consequently, to an underestimation of the true micropore volume and surface area of highly microporous hydrochars. CO_2 adsorption at 273 K is therefore increasingly used as a complementary method, since the higher measurement temperature affords CO_2 molecules sufficient kinetic energy to access and equilibrate within ultra-narrow micropores inaccessible to N2 at 77 K, providing a more reliable estimate of narrow-micropore volume and a valuable cross-check on BET-derived surface areas for rice-husk-derived nanoporous carbons.

In-situ spectroscopic methods are becoming increasingly important for understanding the dynamics of surface processes in real time. In work [78], the combination of in-situ Raman and FTIR spectroscopy made it possible to simultaneously track changes in the intramolecular vibrations of water confined within the MXene structure and the surface terminal groups during electrochemical processes, allowing the behavior of hydrophilic and hydrophobic electrode materials to be distinguished. A similar methodological approach is applied in work [79], where in-situ FTIR spectroscopy

was used to monitor the electrochemical reduction of CO_2, making it possible to identify the active sites and intermediate species of the catalytic reaction in real time. High-resolution in-situ electron microscopy is reviewed in works [80] and [81]: the first systematizes the capabilities of in-situ transmission electron microscopy for studying interfacial nanostructures in electrochemical energy-storage systems - from atomic-scale imaging to strain mapping; the second analyzes graphene liquid cells for observing nanoscale dynamic processes in the liquid phase, including crystallization and phase transformations at the atomic level.

Diffraction and spectroscopic methods for structure determination are also represented in literature by a number of methodologically significant works. Work [82] proposes the first equivariant deep-learning generative model, XtalNet, for end-to-end crystal structure prediction from powder X-ray diffraction, achieving a prediction accuracy of up to 90.2% for complex metal-organic frameworks, while review [83] systematizes the advantages of synchrotron radiation for zeolite X-ray diffraction - enhanced resolution and the ability to track structural evolution during synthesis and catalytic processes. Thermogravimetric analysis as a tool for assessing thermal stability and decomposition kinetics is confirmed in works [84] and [85]: the first, using co-incineration of municipal waste, sewage sludge, and soil as an example, shows that adding 10% municipal waste significantly improves co-incineration performance, and the developed neural-network model predicts thermal decomposition with an accuracy of $R^2 = 0.9999$; the second demonstrates a reduction in the activation energy of bamboo biochar (121.22 kJ/mol) compared with the initial biomass (183.63 kJ/mol), indicating improved energy efficiency after pyrolysis.

Finally, the comprehensive application of combined structural and spectroscopic methods to multifunctional carbon materials is illustrated by work [86], in which a Cu-doped cellulose-derived carbon aerogel from Nypa fruticans shells was characterized by SEM, EDS, XRD, FTIR, nitrogen adsorption, Raman, and X-ray photoelectron spectroscopy, confirming the material's hierarchical pore structure and explaining its simultaneous functionality as a sorbent, a supercapacitor electrode material, and an electrochemical vitamin C sensor.

Taken together, the characterization methods discussed form the methodological basis necessary for a reliable interpretation of the structure and functional properties of rice-husk-derived nanoporous carbon materials discussed in this review.

3.5. Factors affecting material performance

In addition to the carbonization temperature, activator nature, and surface chemistry already discussed, the set of parameters governing the service characteristics of nanoporous carbon materials also includes the conditions of the activation process itself and the specifics of the target application.

The influence of the type and dosage of the chemical activator on CO_2 sorption capacity is systematically investigated in work [87], where activated carbons obtained by cellulose pyrolysis were treated with KOH and KNO_3 at various temperatures; it is shown that carbon activated exclusively with KOH exhibits the highest CO_2 adsorption capacity at 1 bar, whereas the maximum capacity at saturation pressure is achieved with a higher KNO_3 ratio—that is, the optimal activator depends on the target pressure range.

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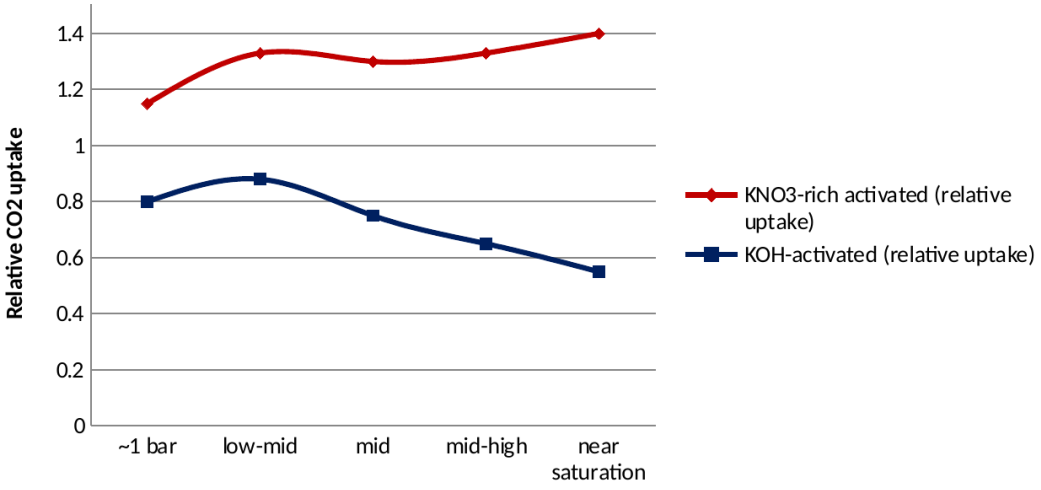

Fig. 5. Optimal CO_2 activator depends on the target pressure regime.

The importance of precisely tuning process parameters for a specific sorption task is further confirmed in work [88], where adsorption of octocrylene - an emerging pollutant - on $ZnCl_2$-activated biochar from spent coffee grounds achieved a removal efficiency of about 100% with complete elimination of the phytotoxicity of the sorbed solution, as confirmed by a bioassay using Allium cepa roots.

Synergistic effects of co-processing several biomass types on the service characteristics of hydrochar are quantitatively characterized in work [89], where co-hydrothermal carbonization of digested sewage sludge and sugarcane bagasse demonstrated a positive synergistic effect on lead adsorption at elevated sludge-to-bagasse ratios, with the experimental adsorption capacity increasing from 105 to 140 mg/g relative to the calculated value - this result is methodologically significant, as it confirms the nonlinear, synergistic character of feedstock composition's influence on the resulting sorption characteristics, directly echoing the co-carbonization studies discussed in Section 2.2 [7,30].

In addition to sorption functionality, the service characteristics of carbon nanomaterials are substantially determined by their thermal conductivity, which becomes especially important when used in composite and energy-storage systems that potentially intersect with the construction applications considered in the next chapter. Work [90] proposes a phase-transition-induced exfoliation strategy for producing flexible composites with a thermal conductivity of 4.54 $W \cdot m^{-1} \cdot K^{-1}$ while retaining a high phase-transition enthalpy, while work [91] achieves a thermal conductivity of 82.4 $W \cdot m^{-1} \cdot K^{-1}$ for graphene-fiber-based thermal interface materials while retaining mechanical elasticity through synergistic alignment under combined mechanical and electric fields. The modification of microencapsulated phase-change materials to suppress supercooling and enhance thermal conductivity is systematized in review [92], and the specifics of aramid-based aromatic nanofibrils as highly thermally conductive film composites are reviewed in [93], which emphasizes the role of hydrogen bonds in forming a rigid molecular network. Finally, the significance of processing parameters for the mechanical characteristics of agricultural-waste-based composites is confirmed in work [94], where optimizing the parameters of selective laser sintering of a peanut-shell/polyethersulfone composite (laser power, preheating temperature, scanning speed) substantially improved the mechanical strength and dimensional accuracy of the resulting parts, which is directly relevant when considering the prospects for additive manufacturing of biomass-based construction elements.

Summarizing the material presented in Sections 2.1–2.5, it can be concluded that the structural, surface-chemical, and service characteristics of nanoporous carbon materials are shaped by the multifactorial, often nonlinear interaction of temperature, activator nature and dosage, feedstock composition, and the sequence of thermal-treatment stages, while reliable characterization of these materials requires the combined use of several complementary methods. It is precisely this methodological foundation that sets the stage for turning to the practical achievements in the application of rice-husk-derived nanoporous carbon materials, the subject of the next chapter of this review.

4. Recent advances and construction applications

4.1. Adsorption properties

Before turning to the construction applications of nanoporous carbon materials, it is worthwhile to systematize the remaining body of research on their sorption functionality, since the ability to effectively bind a wide range of pollutants serves as the connecting link between the fundamental understanding of pore structure (Chapter 2) and the applied challenges of sustainable construction discussed below - particularly since many of the biomass-based sorbents considered below are structurally and technologically related to the materials used as functional additives in cement and geopolymer systems.

A significant portion of research is devoted to the removal of emerging organic pollutants - pharmaceuticals, personal-care products, and industrial dyes. In work [95], nanoporous carbon sorbents obtained by thermal treatment of municipal and plant waste were used to remove triclosan from aqueous solution; the authors established that the determining parameters of sorption efficiency are pore texture, the surface area accessible to triclosan molecules, and the chemical nature of the sorbent surface, confirming the relationship between surface chemistry and functional efficiency already noted in Section 2.2. A methodologically significant contribution to understanding the dynamics of sorption processes is made by work [96], which compares five models - from instantaneous adsorption to anomalous diffusion described by fractional-order differential equations - for describing butanol adsorption breakthrough curves on activated carbon; it is shown that model accuracy depends substantially on the adsorbent type, which is of practical significance for designing industrial adsorption columns. It should be noted that the inorganic component of rice husk is of interest not only as a source of amorphous silica but also as a feedstock for producing calcium silicate materials. Calcium silicates obtained from rice husk exhibit high sorption characteristics and can be regarded as promising materials for environmental and construction purposes. Thus, the comprehensive processing of rice husk makes it possible to simultaneously obtain both carbon and silicate functional materials, substantially increasing the efficiency of raw biomass utilization [97].

Of particular interest for this review is work [98], which directly addresses carbonized rice husk: the authors showed that regenerating the spent sorbent by a cold-plasma method makes it possible to maintain methylene blue removal efficiency at about 70% of the original level after five successive regeneration cycles - substantially higher than sequential adsorption without plasma treatment (9–13%) - while the energy expenditure for plasma regeneration was approximately 6.4 times lower than that for carbonizing a fresh batch of rice husk. This result is of direct practical significance for the life-cycle economics of rice-husk-based sorbents, as it demonstrates a path toward repeated use of the material without complete loss of functionality. A similar resource-conservation logic is seen in work [99], where hydrothermal carbon obtained from sweet chestnut bur waste was used to remove per- and polyfluoroalkyl substances (PFAS) from water, demonstrating an equilibrium sorption capacity of 1029.5 mg/g at a point of zero charge within the pH range 3.8–4.8.

A few studies are devoted to the purposeful functionalization of activated carbon with composite and heterostructured modifiers to enhance sorption selectivity. In work [100], bimetallic metal-organic framework derivatives (ZrO_2/Fe_3O_4) anchored on wood-derived activated carbon provided rapid attainment of sorption equilibrium (15 min) and a capacity of 229.7 mg/g toward the antibiotic sulfamethoxazole through an increase in pore-structure complexity and the number of active sites. The valorization of other agricultural wastes as activated-carbon precursors is confirmed in works [101-103]: bio-activated carbon from cocoa bean shells [99], with a specific surface area of 1661 m^2/g, achieved over 90% removal of a reactive dye within three minutes; KOH-modified activated carbon from Croton caudatus biomass [103] demonstrated an adsorption capacity of 53.6 mg/g toward 2-chlorophenol, with the dominant contribution from carboxyl functional groups confirmed by density functional theory calculations; and phosphoric-acid-modified activated carbon from murumuru seeds [102] showed differentiated removal efficiencies for various pharmaceutical and industrial pollutants - from 56% for phenol to 97% for diethyl phthalate - highlighting the need to tailor the sorbent to the specific target pollutant rather than relying on a universal solution.

An overview of this research direction is presented in review works [104] and [105]. The first systematizes the mechanisms of heavy-metal adsorption by biochar, with an emphasis on the role of pore-size distribution, surface functional groups, and pyrolysis temperature, and also examines the synergistic effects of combining biochar with anaerobic digestion and membrane technologies, a direction complemented by recently developed colour-changing sorption materials for effective heavy-metal removal from wastewater [106]. The second analyzes the potential of algae-derived biochar for the environmental remediation of a broad spectrum of pollutants - from heavy metals to microplastics - highlighting its soil-improvement function as a separate, sustainable application direction. Finally, the use of KOH-modified biochar from oil-palm shells for amoxicillin removal is examined in work [107], where optimization was carried out using Box–Behnken response surface methodology combined with density functional theory calculations to clarify the sorption mechanism - a methodological approach analogous to that previously applied in work [3] for rice husk, underscoring the commonality of the experimental-theoretical methodology for optimizing sorbents based on different biomass types.

Beyond the sorption of aqueous pollutants, rice-farming waste is also considered a promising feedstock for producing sorbents intended for capturing carbon dioxide at elevated temperatures: work [108] shows that lithium-containing sorbents synthesized from rice waste possess a high CO_2 capacity under high-temperature capture conditions, extending the scope of application of rice-waste-derived products beyond water purification. The practical significance of such sorption materials is also confirmed at the regional level: in work [109], a sorbent obtained from rice straw and husk of the Kyzylorda region was successfully applied for wastewater treatment as part of an educational laboratory exercise, demonstrating the potential for integrating developments in rice-waste processing into educational and environmental practice. The body of work reviewed demonstrates that nanoporous carbon materials from various lignocellulosic biomass types, including rice husk, represent a mature and well-studied platform for the sorption of a wide range of aqueous pollutants; at the same time, this very maturity of the sorption research direction, set against the relatively limited number of studies on construction applications, underscores the need for a more active transfer of the accumulated knowledge on the structure and functionality of porous carbon materials into the field of cement and geopolymer composites, to which we now turn.

4.2. Cement-based composites

The use of carbon nanomaterials and rice husk ash as a partial replacement for Portland cement or as a functional additive represents one of the most dynamically developing directions for decarbonizing the construction industry, which accounts for a substantial share of global CO_2 emissions [110]. Direct integration of biochar into a cement matrix combined with accelerated carbonation curing (ACC) is investigated in work [111]: biochar obtained by pyrolysis of corn stover at 500 °C provided the maximum CO_2 uptake by the cement mortar (a 31.6% increase compared with biochar obtained at 300 and 700 °C), with biochar porosity - rather than the chemisorption effect of its oxygen-containing functional

groups - playing the determining role in carbonation intensity (Figure 6). The problem of strength reduction at high biochar content in the cement matrix is addressed in work [112] by modifying biochar with ground shell ash: mechanochemical treatment increased the compressive strength of a composite containing 30 wt% modified biochar by 58.2% through densification of the interfacial transition zone (ITZ) between aggregate and matrix and an increased proportion of dense C-S-H gel.

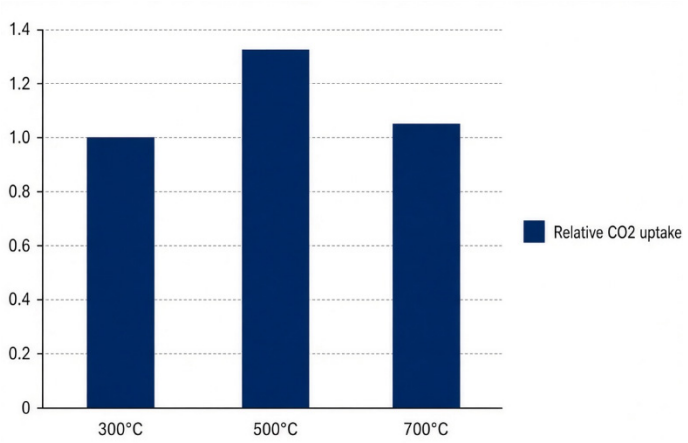

Fig. 6. Biochar pyrolysis temperature: an optimum for CO_2 uptake in cement

Carbon nanotubes (CNTs) represent the second most important direction in the nano-engineering of cement composites and are especially widely represented in the literature base under consideration. Work [105] shows that a CNT dosage of 0.05 wt% of cement mass, combined with an optimal dispersion technique (mixing with water and manual agitation), improves the mechanical and physical properties of mortar with reduced cement content, whereas exceeding a dosage of 0.10% leads to a deterioration in performance - this non-monotonic dependence is consistently confirmed in other studies in this direction. Thus, work [113] establishes that the reinforcing effect of carbon nanotubes on the aggregate-matrix interfacial transition zone depends quadratically on the aggregate's particle-size distribution (Talbot index), with an optimum at an index value of 0.8, providing a 30% reduction in ITZ width and a 20.7–35.6% improvement in mechanical characteristics. The influence of CNTs on the chloride-diffusion resistance of ultra-high-performance concrete is examined in work [114], which shows a non-monotonic change in compressive strength as CNT content increases from 0.025 to 0.075 wt%, with the chloride diffusion coefficient remaining below the regulatory limit for all mixes. The synergistic effect of CNTs together with nano-SiO_2 in lightweight cement mortar based on fly-ash cenospheres is confirmed in work [115], and the influence of multi-walled CNTs on internally cured concrete with pre-wetted lightweight aggregate is examined in work [116], where a positive effect was observed at CNT dosages below 0.25 wt%. Finally, work [117], using metakaolin-based cement binders as an example, shows that adding just 0.1 wt% CNTs increases the flexural strength and Young's modulus by 88% and 107%, respectively, through a reduction in the Ca/Si ratio of the C-S-H gel in the transition zone and an increased degree of silicate-chain polymerization. A comprehensive techno-economic and environmental assessment of nano-engineered cement composites, combining the effects discussed above, is presented in work [118]: nano-engineered concrete for marine infrastructure demonstrated a 62.8% reduction in the chloride diffusion coefficient relative to the control mix, together with an 18.1–27.8% reduction in production cost and a 14.4–22.2% reduction in CO_2 emissions—this result is methodologically important, as it confirms the compatibility of the goals of improving durability and reducing the carbon footprint of cement composites, directly aligning with the overarching aim of this review. Specifically with regard to rice husk ash, already considered as a key feedstock in Sections 2.1 and 2.3, the previously mentioned work [17] demonstrated that the joint introduction of 15% rice husk ash and 0.1% multi-walled carbon nanotubes significantly improves concrete durability under sulfate and acid attack (a 50.9–61.7% reduction in mass loss and a 3.08–9.23% improvement in drying-shrinkage resistance), confirming the compatibility of rice husk ash with carbon nanoadditives as a unified strategy for enhancing the durability of cement composites.

4.3. Geopolymers

Alkali-activated materials (AAMs), including geopolymers, are regarded as one of the most promising alternative binders owing to their low carbon footprint compared with Portland cement [19]. The role of nanoscale modifiers in shaping geopolymer microstructure has been studied in detail using silica nanoparticles as an example. Work [119] shows that introducing nano-SiO_2 into a water-glass-based alkaline activator during the activation of fly ash and granulated blast-furnace slag increases compressive strength from 40 to 55 MPa at an optimal modified polycarboxylate dosage of 1%, which is attributed to the nucleating effect of nano-SiO_2 and the formation of a more compact gel microstructure with fewer pores. A similar positive, but nonlinear, effect of nano-SiO_2 on the early strength of alkali-activated composites based on high-fluidity slag and desulfurization gypsum is confirmed in work [120], where exceeding a nano-SiO_2 content of 3% when using seawater as the mixing water led to a reduction in 7-day strength - a pattern that directly echoes the 'optimal dosage' effect noted above for CNTs in cement systems [105]. Alongside silica production, a promising direction is the synthesis of aluminosilicate materials from rice husk. In recent years, it has been shown to be possible to

obtain sodium aluminosilicates with high chemical stability and sorption activity. Such materials can be used as components of geopolymer systems and alkali-activated binders, further expanding the directions for the comprehensive processing of rice husk [121].

The functionalization of geopolymer systems with graphene oxide and electrolytic copper powder is examined in work [122]: it is shown that dissolved Cu^{2+} ions affect the Al–O bonds in the geopolymer framework, while the joint introduction of graphene oxide promotes the formation of highly cross-linked gel networks and a reduction in overall porosity, while simultaneously increasing the material's thermal conductivity - this result opens up prospects for using modified geopolymers as thermal-energy-storage materials. The expansion of the alkali-activated binder family with mineral modifiers of a different nature is demonstrated in work [123], where introducing mesoporous tungsten oxide into a slag-bentonite geopolymer under optimized hydrothermal curing conditions (8 wt% NaOH, 3 bar, 4 h) provided a compressive strength of 53.6 MPa while simultaneously imparting radiation-shielding functionality - illustrating that geopolymer systems can integrate functionalities extending beyond purely mechanical characteristics.

Reinforcement of alkali-activated matrices with carbon nanotubes is examined in work [124], where introducing multi-walled CNTs into a fly-ash-lime binder system at an optimal dosage of about 0.3 wt% provided a compressive-strength increase of up to 14% and a flexural-strength increase of up to 28%, along with minimal strength loss under acid and sulfate attack - this result directly aligns with earlier observations of the positive effect of CNTs on cement systems [110–115], confirming the universality of this reinforcing effect regardless of the type of alkaline matrix. A comprehensive review of the influence of various admixtures on the rheology, hydration, and microstructure of AAMs is presented in work [19], which separately notes that reduced plasticizer solubility and adsorption is a key reason for their ineffectiveness in certain mixes, underscoring the need for individually tailored modifiers for each specific alkali-activated system. Specifically in the context of rice husk and other agricultural waste, the geopolymer direction shows particularly active development.

The previously discussed work [4] showed that geopolymer brick containing up to 40% rice husk ash meets ASTM compressive-strength standards and demonstrates improved acid resistance compared with conventional cement mixes, with the formation of stable mullite and albite phases.

This direction is further developed toward the simultaneous use of several aluminosilicate feedstocks in work [125], where geopolymer concrete based on sugarcane bagasse ash, rice husk ash, and cow-dung ash, reinforced with basalt fiber, demonstrated a parabolic dependence of performance on fiber content, with an optimum at about 1% providing a 24% increase in compressive strength and a 32% increase in flexural strength. The combined use of rice husk ash together with other agricultural and marine wastes (peanut shell ash, coconut shell ash, bamboo leaf ash, seashell ash) is examined in work [126], where an optimal mix with partial replacement of 20% Portland cement by such a blend of ashes provided a CO_2 emission reduction of up to 15% while maintaining strength characteristics sufficient for non-structural applications. Finally, a specific aspect of the durability of geopolymer systems based on recycled aggregate - carbonation resistance - is investigated in work [127], where introducing nano-SiO_2 into geopolymer concrete based on recycled concrete powder, fly ash, and granulated blast-furnace slag substantially slowed carbonation depth and improved the microstructure through the formation of additional geopolymer gels. Considering works [4,19,119-124], and [128] (mentioned below in the context of future prospects) together, it can be concluded that the geopolymer application of rice husk ash and related agricultural wastes is a mature and actively developing field, in which nanoscale modification (SiO_2, CNTs, graphene oxide) serves as an effective tool for further enhancing mechanical and service characteristics - a direction that, to date, is considerably ahead, in terms of the degree of study, of the asphalt-binder direction discussed next.

4.4. Asphalt

The application of carbon nanomaterials in asphalt binders is considerably less thoroughly represented in the literature base under consideration compared with cement and geopolymer systems, which in itself points to an evident scientific gap and, at the same time, to the promise of this direction for future research. In work [129], graphene oxide is used to enhance the performance of aged asphalt regenerated with bio-oil extracted from reclaimed asphalt pavement (RAP); response surface methodology was used to optimize the binder composition (0.8% graphene oxide, 7.3% bio-oil, 30% original asphalt) (Figure 7), and molecular dynamics simulation showed that the interaction energy between graphene oxide and the asphalt binder is determined by the density of graphene oxide's surface functional groups - a methodological conclusion directly echoing the role of surface chemistry previously discussed for sorption and cement systems (Sections 2.2, 3.2). A complementary result is obtained in work [130], where graphene oxide was used as an additive for cold-mixed epoxy asphalt (CEA) binder: it is shown that graphene oxide's functional groups react with the asphalt's epoxy resin, improving their compatibility, while an optimal graphene oxide content of 0.1 wt% provided the best thermal stability with a moderate decrease in glass transition temperature (from 51.4 to 47.1 °C).

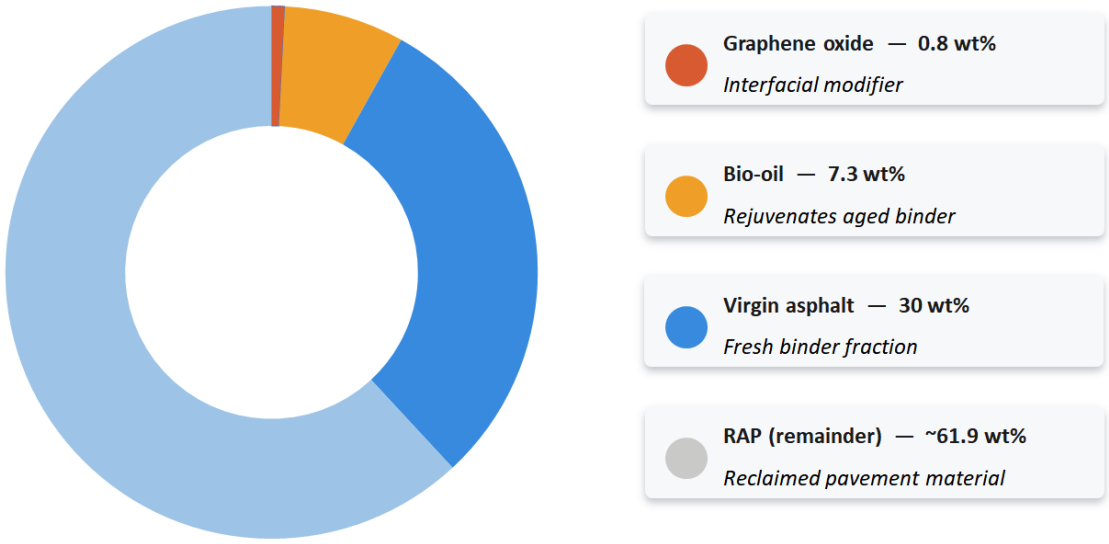

Fig. 7. RSM-optimized formulation for GO-modified RAP asphalt binder

The absence, in the literature reviewed, of studies directly addressing the use of activated carbon or hydrochar from rice husk in asphalt binders represents a significant scientific gap: despite the functionality of rice-husk-derived porous carbon materials as sorbents and structural modifiers, confirmed in Sections 2.1–2.5, their potential as a filler or modifier for bituminous systems - by analogy with the demonstrated effectiveness of graphene oxide [129,130] - remains practically unexplored and deserves targeted investigation in future work.

4.5. Self-sensing concrete

In contrast to the directions discussed above, the literature base collected contains no studies directly devoted to the use of rice-husk-derived nanoporous carbon materials in self-sensing (piezoresistive) concretes - structural materials capable of built-in monitoring of their own stress-strain state through changes in electrical resistance under load. At the same time, the body of results presented in Section 3.2 provides a methodological foundation for developing this direction: the demonstrated ability of carbon nanotubes to form extended conductive networks within a cement matrix [105,111–115], together with the confirmed ability of graphene oxide to modify the electrical and thermal conductivity of geopolymer systems [119], indicates the fundamental compatibility of biomass-derived carbon nanomaterials with the task of creating electrically conductive cement and geopolymer composites. Achieving self-sensing functionality in practice depends on exceeding the percolation threshold - the critical filler concentration at which discrete conductive particles first connect into a continuous, sample-spanning network that lowers the composite's electrical resistivity by several orders of magnitude; below this threshold the insulating cement or geopolymer matrix dominates charge transport, whereas above it inter-particle contact and electron tunneling across nanoscale gaps between adjacent carbon domains enable current flow, so that any application of rice-husk-derived porous carbon in self-sensing composites will require dedicated dosage-optimization studies to identify the percolation threshold specific to its particle morphology and dispersion state within the matrix. The absence of direct experimental data specifically for rice-husk-derived porous carbon materials in the context of self-sensing properties should be viewed not as evidence that this direction lacks promise, but as a rationale for targeted future research into the electrical conductivity and piezoresistive response of composites based on activated rice husk hydrochar - this gap is explicitly formulated as one of the directions for future research in Section 3.6.

4.6. Future perspectives

Summarizing the material of Chapters 2 and 3, it can be concluded that hydrothermal carbonization of rice husk combined with subsequent chemical or physical activation [1–3,12,13] makes it possible to obtain nanoporous carbon materials with widely variable structure and functionality, confirmed both in sorption [10,12,63–67,95–105] and in construction applications [4,17,107,110–126]. At the same time, an analysis of the distribution of literature across the sections of this review reveals a pronounced imbalance: the overwhelming majority of studies focus on sorption and energy applications (supercapacitors, batteries), whereas construction applications - with the exception of the geopolymer direction - have been studied considerably less intensively, and asphalt applications (Section 3.4) and, especially, self-sensing applications (Section 3.5) represent practically unexplored niches.

In the context of the transition to carbon neutrality and the circular economy, the data presented in works [1] and [116] point to two complementary directions for technology development: first, further improvement of the HTC and activation process itself toward less energy-intensive and less aggressive chemical reagents - enzymatic treatment, microwave- and ultrasound-assisted conversion, and environmentally friendly activators [1] - which directly aligns with the trend, noted in works [35], [36], and [37], of replacing conventional KOH with less corrosive alternatives; second, the demonstration in work [125] of the feasibility of creating clinker-free alkali-activated binders based on carbide slag and rice husk ash points to a realistic path toward the complete elimination of Portland cement from construction materials while maintaining acceptable mechanical characteristics (about 16 MPa) for non-structural applications (Figure 8).

The economic and infrastructural scalability of the technology remains a key unresolved issue: as noted in work [1], most existing methods for processing rice husk are characterized by high energy consumption and the use of aggressive chemical reagents, which limits their industrial scale-up, while the demonstration of economic and environmental efficiency in work [116] - an 18–28% reduction in production cost and a 14–22% reduction in CO2 emissions - remains, for now, a singular, though illustrative, example of compatibility between the goals of improved durability, reduced carbon footprint, and economic feasibility at a scale approaching industrial production. Thus, future research in this field should be usefully concentrated on the following directions: (1) systematic comparison of the sorption, structural, and electrochemical characteristics of activated rice husk hydrochar with analogous materials from other biomass types within a unified methodological protocol; (2) targeted investigation of the use of rice-husk-derived carbon materials in asphalt binders, by analogy with the already confirmed effectiveness of graphene oxide [131,132]; (3) experimental study of the electrically conductive and piezoresistive properties of cement and geopolymer composites containing activated rice husk hydrochar, to assess their applicability in self-sensing structures; and (4) large-scale techno-economic and life-cycle analysis of the production of such materials, necessary for the transition from laboratory demonstrations to industrial implementation in the construction sector.

5. Conclusion

Hydrothermal carbonization is currently regarded as one of the most promising thermochemical methods for processing rice husk, owing to its ability to efficiently convert wet lignocellulosic biomass without prior energy-intensive drying, while simultaneously producing carbon-rich hydrochar whose properties can be purposefully tuned by adjusting process parameters. The analysis presented in this review shows that the structure, porosity, surface chemistry, and service characteristics of nanoporous carbon materials are determined by the combined influence of hydrothermal carbonization conditions, subsequent activation methods, feedstock composition, and the high content of biogenic silica in rice husk. Comprehensive control of these parameters makes it possible to obtain materials with a well-developed specific surface area, a hierarchical pore structure, and abundant oxygen-containing functional groups, providing high sorption, catalytic, and electrochemical properties. The literature analysis performed indicates that rice husk should be regarded as a bifunctional renewable feedstock, enabling the simultaneous production of both nanoporous carbon materials and a broad range of value-added silicon-containing products.

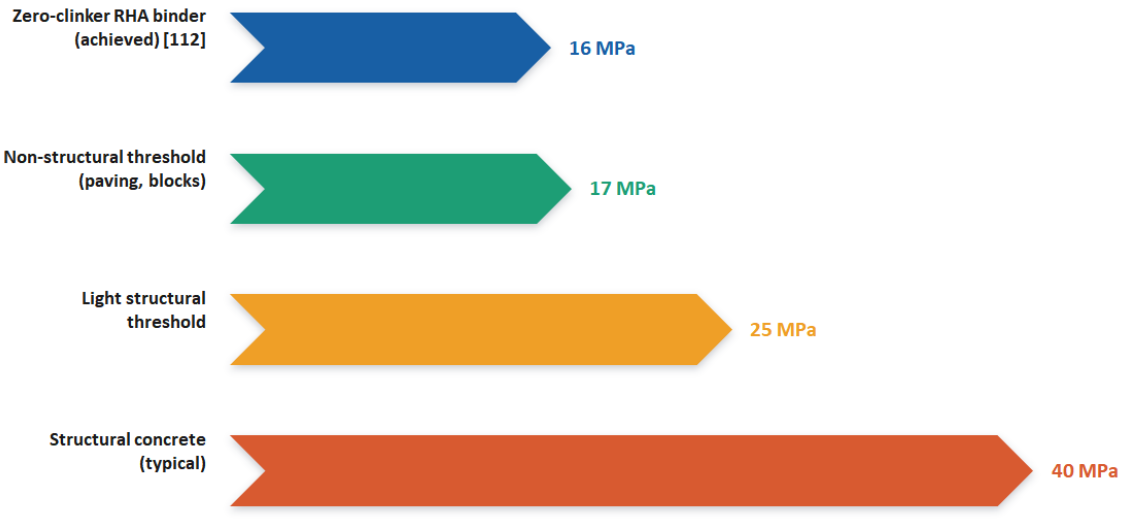

Fig. 8. Where a 16 MPa clinker-free binder fits

In addition to the traditional production of sorbents and electrode materials, research devoted to the synthesis of high-purity silica, calcium silicates, sodium aluminosilicates, and other functional materials has been actively developing in recent years, substantially increasing the efficiency of comprehensive biomass processing and aligning with modern circular-economy principles. The review shows that the most mature application direction for rice-husk-derived nanoporous carbon materials remains water and gas purification, where these materials demonstrate high efficiency in removing dyes, heavy metals, pharmaceuticals, and other pollutants. Significant progress has also been achieved in the fields of electrochemical energy storage, catalysis, and gas storage. In the construction industry, the most actively developing research concerns the use of carbon materials and rice husk ash in cement composites and geopolymer systems, where they contribute to increased strength, durability, resistance to aggressive environments, and a reduced carbon footprint of construction materials. At the same time, the use of rice-husk-derived hydrochar and activated carbon in asphalt binders and self-sensing cement composites remains insufficiently studied, despite the presence of objective prerequisites for their successful use. A critical analysis of the published studies makes it possible to identify a number of unresolved scientific and technological challenges hindering the widespread industrial adoption of the materials under consideration. Most available work has been carried out under laboratory conditions, whereas questions of process scale-up, techno-economic efficiency, life-cycle assessment, and material durability under real service conditions have been studied considerably less thoroughly. Furthermore, the absence of unified methodological approaches to hydrothermal carbonization, activation, and material characterization substantially complicates the correct comparison of results across different studies. Future research should usefully focus on developing environmentally friendly activation methods, reducing the consumption of aggressive chemical reagents, improving technologies for the comprehensive processing of rice husk within the biorefinery concept, and scaling up the processes for producing nanoporous carbon materials. Of particular scientific and practical interest is the development of new construction materials using rice-husk-derived carbon materials, including low-carbon cement composites, alkali-activated binders, modified asphalt materials, and self-sensing concretes. At the same time, integrating hydrothermal carbonization processes with the extraction of silicon-containing products will substantially increase the economic efficiency and environmental sustainability of comprehensive rice husk processing. Thus, the results of this review confirm that hydrothermal carbonization is one of the most versatile and promising technologies for producing functional nanoporous carbon materials from rice husk. Further improvement of process technologies, the development of material modification methods, and the expansion of application directions - above all in the construction industry - will contribute to the creation of new low-carbon materials, the efficient utilization of agricultural waste, and the practical implementation of circular bioeconomy principles.

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