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### UNLOCKING SUSTAINABILITY: A COMPREHENSIVE REVIEW OF UP-RECYCLING BIOMASS WASTE INTO BIOCHAR FOR ENVIRONMENTAL SOLUTIONS

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Abstract. From the perspective of converting waste into valuable products and reducing environmental pollution, the up-recycling of biomass waste into carbon-rich materials is attracting widespread attention. This literature review presents the possibilities of using the solid product of one-stage carbonization (char) of plant-origin waste biomass. Several applications are discussed, including the production of sorbents, energy storage materials, catalyst carriers, and agricultural applications.

**Keywords:** carbonization; char; sorbent; catalyst; agriculture.

### 1. Introduction

Research on char (also known as biochar) is a current trend due to its vast applicability in various fields and has gained widespread attention due to its unique physicochemical properties and surface structure. In terms of the proposed review, biomass char is defined as the carbonaceous product of waste plant-origin biomass thermal decomposition conducted in the absence of oxygen or other oxidizing agent. Clarification of the char definition used in this work seems to be justified, especially since in many works, the term char/biochar refers to both thermal and thermochemical conversion products<sup>1</sup>.

The continuous emission of untreated effluents and human-generated air pollution are significant challenges that strongly influence the ecosystem. Efforts are being focused on finding eco-friendly, cost-effective strategies to remediate various pollutants. These efforts include adsorption processes. Obtaining an effective sorbent in a single-stage waste conversion seems to be an interesting and economically justified direction of research. Due to the above, this review presents the latest literature reports on the processes of pollutant removal from both water and air. Moreover, char was studied for energy storage applications mainly as an electrode material for electrochemical devices, but also for material-based storage of hydrogen and natural gas. Several reviews were published in recent years summarizing those results<sup>2-5</sup>. However, their authors adopted a different definition of char than that used in this review. An interesting aspect is also the attempt to use char as a catalyst/catalyst support, as in the case of bioprocesses, and the conventional catalytic processes, such as syngas production. The last direction in which potential is intensively developed in the industrial use of char is its use in agricultural processes, where high carbon content, sorption potential of the selected compounds from the soil, and sufficient surface area to use char as a nutrient carrier can be evaluated.

This review is aimed to present the most recent results on the plant origin char properties and its features for application in several processes of industrial potential.

# 2. Sorbents for Water and Air Purification

### 2.1. Water Purification

The last decade mainly emphasized novel feedstocks and activation methods to increase biochar's surface area, porosity, and pore volume. The modification of carbonaceous materials that increases the pore volume of the adsorbent and the char functionalization methods will need to be further researched and optimized to achieve the highest adsorption capacity. The most popular method for studying adsorption as a method of water purification is to work on dyes and ions. Almost all of the dye adsorption studies used only aqueous solutions of dyes instead of real dyehouse effluent. The authors

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analyzed the initial concentration of the dye, the effect of solution pH, and contact time in the batch adsorption

process from solutions applying different adsorbent concentrations (Table 1).

|                                | Dye | Pyrolysis conditions |            | So                   | orption parameter                | Comption.                                    | SSA                  |                    |      |
|--------------------------------|-----|----------------------|------------|----------------------|----------------------------------|--|----------------------|--------------------|------|
| Source of char                 |     | Temp.,<br>°C         | Time,<br>h | Contact<br>time, h   | Adsorbent dose, $g \cdot L^{-1}$ | Initial dye<br>conc.,<br>mg·dm <sup>-3</sup> | efficiency, %        | $m^2 \cdot g^{-1}$ | Ref. |
| Coffee                         | MB  | 700                  | 1          | 20                   | 50                               | 50   | 90                   | n/a                | 6    |
| grains                         | MB  | 500                  | 2          | 1                    | 2-5                              | 50   | 90                   | 2.62               | 7    |
|                                | MD  | 280                  | 0.2        | 2                    | 2.5                              | 100  | 96                   | n/a                | -    |
| Coffee                         | MB  | 400                  | 0.2        | 2                    |                                  | 100  | 98                   | 3.0                |      |
| collee                         |     | 280                  |            |                      |                                  |  | 98                   | 2.3                | -    |
| SILVEISKIII                    | МО  | 400                  | 0.2        | 2                    | 2.5                              | 100  | 40                   | 3.6                | -    |
|                                | _   | 500                  |            |                      |                                  |  | 36                   | 2.3                | 8    |
| Almond<br>shells               | MB  | 700                  | 1          | 20                   | 50                               | 50   | 89                   | n/a                | 6    |
| Almond                         | MB  | 600                  | 3          | 1                    | 0.6                              | 50   | 91.7                 |                    |      |
|                                |     | 700                  |            |                      |                                  |  | 96.2                 | n/a                |      |
| SKIII                          |     | 900                  |            |                      |                                  |  | 98.5                 |                    | 9    |
| Grape wine sticks              | MB  | 700                  | 1          | 20                   | 50                               | 50   | 99.6                 | n/a                | 6    |
| Banana                         | MG  | 500*<br>900*         | 0          | 0.2–8                | 0.2–2.0                          | 200  | 1790.3**<br>2297 8** | n/a                | 10   |
| Watermelon                     | MB  | 550                  | 2          | 2                    | 0.4–4                            | 50–500                                       | 76-82                | 45.64              | 11   |
| Sunflower<br>shells            | MB  | 700                  | 1          | 20                   | 50                               | 50   | 99.6                 | n/a                | 6    |
| Corncob                        | MB  | 700                  | 1          | 0.1–2h               | 0.3-1.2                          | 7–15   | 97.5–99              | 435.15             | 12   |
| Calophyllum                    | AY  | 500                  | 0.5        | 3                    | 4                                | 10-100                                       | 22.3±6.0             | n/a                | 13   |
| <i>inophyllum</i><br>seed husk | MG  | 500                  | 0.5        | 3                    | 4                                | 10–100                                       | 90.8±4               | n/a                | 13   |
|                                | BFR | 400                  | 2          | up to<br>equilibrium | 1–10                             | 50   | 80.9-82.6            | n/a                | 14   |
| Leaf waste                     | MB  | 400                  | 2          | up to<br>equilibrium | 1–10                             | 50   | 75.2–75.4            | n/a                | 14   |
|                                | CV  | 400                  | 2          | up to<br>equilibrium | 1–10                             | 50   | 73.2                 | n/a                | 14   |

**Table 1.** Biochar water purification from dyes. MB – methylene blue; MG – malachite green; AY – alizarin yellow; MO – methyl orange; BFR – basic fuchsin red, CV – crystal violet

\* Microwave pyrolysis (1500 W).

\*\* Adsorption capacity,  $mg \cdot g^{-1}$ .

The indicated method of analyzing newly obtained materials as adsorbents of dyes from water is important due to the need to characterize the basic properties and limitations of the newly obtained sorbents, but it will require significant modification before implementation in industrial conditions. Actual dye effluents contain salt, starch, and various dyeing auxiliaries other than the dyes. Those admixtures may compete with dye molecules in the adsorption process<sup>15</sup>. Moreover, laboratory tests are limited to static adsorption testing (batch adsorption). In

industrial conditions, the most common method of purification under the conditions of the adsorption process is dynamic adsorption, which has not been published for the last 4 years (2020–2023). The latest results regarding the sorption of dyes from water are summarized in Table 1. Analyzing the obtained results, it can be noticed that even one step, thermal treatment of biomass leads to effective adsorbents. The obtained materials are characterized by a wide range of SSA values:  $2.3^{8}$ –435.15 m<sup>2</sup> · g<sup>-1</sup>.<sup>12</sup> While SSA, as an elemental composition (carbon content

in the range of  $32.1^{14}$ –78.05 % <sup>12</sup>) depends on the source of adsorbent as well as pyrolysis/ carbonization temperature (investigated from 280 to 700 °C), and residence time at the final temperature, which was tested in a wide range from 0 to 3 hours (Table 1). The research results of the adsorption process analysis allow to conclude that one-stage conversion of waste biomass leads to obtaining effective adsorbents, capable of removing significant amounts of dyes (initial concentration

in the range of 10–500 mg  $\cdot$  dm<sup>-3</sup>).

Similar observations, as in the case of dves, can be noted in the case of ions sorption processes from water solutions (Table 2). Artificial ion solutions with a range of  $0.05-500 \text{ mg} \cdot \text{dm}^{-3}$  concentrations were effectively purified by sorbents characterized by a large surface size discrepancy (straw-based char, 2.1 m<sup>2</sup> g<sup>-1 16</sup> – walnut shellbased char, 456.9 m<sup>2</sup>  $\cdot$  g<sup>-1</sup> <sup>17</sup>). Biochars were observed to be very good adsorbents, especially when pH of the water solutions was adjusted in the experiment<sup>18,19</sup>. Negatively charged anions and positively charged cations will be preferably adsorbed when the surface of the adsorbent applied will be characterized by an opposite charge to the absorbed ion. Therefore, the pH modification of adsorbate solution and adsorbent surface functionalization are used through chemical modification of chemical groups present on the sorbent surface. Modifying the pH value of solutions

from which ions are adsorbed is a good solution, but primarily for laboratory conditions. When trying to use sorbents for industrial purposes, it is believed that chemical functionalization is more justified, which was also observed by other authors<sup>20–22</sup>.

Analyzing the data in Tables 1, 2, it can be seen that despite a significant number of literature data, the correlations between the obtained results are still unclear. The authors of the publications (correctly) use locally available waste biomass raw material. The carbonization temperature is most often selected based on the course of the thermogravimetric analysis curve or, which is quite common, an appropriately higher temperature that is a preparation stage of the raw material for activation processes into activated carbon. Water purification processes, both from organic compounds and ions, are influenced primarily by the chemical nature of the surface that binds or repels ions and dissociated compounds, as well as the size of the surface on which adsorption processes take place. Building a correlation between the nature of the surface and carbonization parameters is therefore crucial in further research on the use of biochar as a sorbent for water purification. It would be worth standardizing the methodology for analyzing the properties of biochars as potential sorbents, especially since this is currently an intensive direction in the development of waste biomass management.

Table 2. Removal of ions from water by biochar derived from different feedstocks

|                    |         | Pyrol<br>condit | ysis<br>ions | S                  | orption paramete                 | a .:   | SSA  |                    |      |
|--------------------|---------|-----------------|--------------|--------------------|----------------------------------|--|--|--------------------|------|
| biochar            | Ion     | Temp.,<br>°C    | Time,<br>h   | Contact<br>time, h | Adsorbent dose, $g \cdot L^{-1}$ | Initial ion<br>conc.,<br>mg·dm <sup>-3</sup> | Sorption efficiency,<br>%                            | $m^2 \cdot g^{-1}$ | Ref. |
| 1                  | 2       | 3               | 4            | 5                  | 6                                | 7  | 8  | 9                  | 10   |
| Watermelon<br>peel | Cr(VI)  | 600             | 3            | 8                  | 0.1–4                            | 150  | 89.4   | 78.88              | 23   |
|                    |         | 350             |              |                    |                                  |  | 15   | n/a                | 24   |
| Pomelo peel        | As(III) | 550<br>650      | 3            | 24                 | 1                                | 0.05–20                                      | 15   | n/a                |      |
|                    |         |                 |              |                    |                                  |  | 18   | n/a                |      |
|                    |         | 350             | 350          |                    |                                  |  | 10   | n/a                |      |
| Pomelo peel        | As(V)   | 550 3           | 24           | 1                  | 0.05–20                          | 10   | n/a  |                    |      |
|                    |         | 650             |              |                    |                                  |  | 13   | n/a                |      |
|                    |         | (II) 550        |              | 0.5–4 6.25–25 20   |                                  | 99.7 (12.5 g $\cdot$ L <sup>-1</sup> ,       |  |                    |      |
|                    | Zn(II)  |                 | 0            |                    | 6.25–25                          | 20–320                                       | initial 20 mg $\cdot$ dm <sup>-3</sup> )             | 434.5              | 25   |
| Rice husk          |         |                 |              |                    |                                  |  | $5(125 \text{ g} \cdot \text{L}^{-1}\text{initial})$ |                    | 23   |
|                    |         |                 |              |                    |                                  |  | 5 (12.5 g·L iiitiai                                  |                    |      |
|                    |         |                 |              |                    |                                  |  | $320 \text{ mg} \cdot \text{dm}^{-3}$                |                    |      |
| Walnut shell       |         | 400             |              | ~                  |                                  |  | n/a  | 6.3                |      |
|                    |         | 500             | 500<br>600   |                    |                                  | 15 45  | n/a  | 7.7                |      |
|                    | Dh(II)  | 600             |              |                    | 1 2                              |  | n/a  | 39.2               | 17   |
|                    | Pb(11)  | 700             | 5            | 5 1-3              | 15-45                            | 83   |  |                    |      |
|                    |         |                 |              |                    |                                  | $(3 \text{ g} \cdot \text{L}^{-1})$ ,        | 256.9  |                    |      |
|                    |         |                 |              |                    |                                  |  | initial 15 mg ⋅ dm <sup>-3</sup> )                   |                    |      |

| 1              | 2                          | 3          | 4       | 5       | 6       | 7   | 8  | 9     | 10 |
|----------------|----------------------------|------------|---------|---------|---------|---|--|-------|----|
|                |                            | 400        |         |         |         | -   | n/a                                      | 6.3   |    |
|                |                            | 500        |         |         | 1–3     |   | n/a                                      | 7.7   |    |
|                | C (II)                     | 600        |         | ~       |         | 15 45                                     | n/a                                      | 39.2  | 26 |
| Walnut shell   | Cu(II)                     |            | 2       | 5       |         | 15–45                                     | 86                                       |       | 20 |
|                |                            | 700        |         |         |         |   | $(3 \text{ g} \cdot \text{L}^{-1})$      | 256.9 | I  |
|                |                            |            |         |         |         |   | initial 15 mg·dm <sup>-3</sup> )         |       |    |
|                |                            | 400        |         |         |         |   | n/a                                      | 5.6   |    |
| Hazalnut shall |                            | 500        | 500 ,   | 5       | 1.2     | 15 45                                     | 78 (3 g·L <sup>-1</sup> ,                | 124.3 | 17 |
| Hazemut shen   | PD(11)                     |            | 1       | 5       | 1-5     | 15-45                                     | initial 15 mg·dm <sup>-3</sup> )         |       |    |
|                |                            | 600        |         |         |         |   | n/a                                      | 81.5  |    |
|                |                            | 700        |         |         |         |   | n/a                                      | 52.9  |    |
|                | Cu(II)                     | 400        |         |         |         | 15–45                                     | n/a                                      | 5.6   |    |
|                |                            |            |         | 2 5     | 1–3     |   | 82                                       | 124.3 |    |
| Hazelnut shell |                            | 500        | 2       |         |         |   | $(3 \text{ g} \cdot \text{L}^{-1})$      |       | 26 |
|                |                            |            |         |         |         |   | initial 15 mg·dm <sup>-3</sup> )         |       |    |
|                |                            | 600        | 600     |         |         |   | n/a                                      | 81.5  |    |
|                | Cu(II)                     |            |         |         |         |   | 9.3*                                     |       |    |
| Peanut shell   | Mn(II)<br>Pb(II)<br>Zn(II) | Mn(II) 600 | 1       | 8       | 5       | 10 500                                    | 20.9*                                    | 377.2 | 27 |
| i canat shen   |                            | 000        | 1       | 0       | 5       | 10 500                                    | 74.5*                                    |       |    |
|                |                            |            |         |         |         |   | 15.0*                                    |       |    |
| Bamboo         | Zn(II)                     | Zn(II) 550 |         |         | 6 25_25 | 20, 320                                   | 99.9 (12.5 g $\cdot$ L <sup>-1</sup> ,   |       |    |
|                |                            |            | 0 0.5–4 | 0.5_1   |         |   | initial 20 mg $\cdot$ dm <sup>-3</sup> ) | 3 29  | 25 |
|                |                            |            |         | 0.25-25 | 20-320  | $40 (12.5 \text{ g} \cdot \text{L}^{-1})$ | 5.27                                     |       |    |
|                |                            |            |         |         |         |   | initial 320 mg·dm <sup>-3</sup> )        |       |    |
| <u>S</u> 4     | <b>7</b> (II)              | 800        |         | 0.5     | 0.5     | 1.4                                       | 16                                       | 2.1   | 16 |
| Straw          | Zn(II)                     | 800        | n/a     | 0.5     | 0.5     | 1-4                                       | (initial 4 mg $\cdot$ dm <sup>-3</sup> ) |       |    |

#### Continuation of **Table 2**

\* Adsorption capacity,  $mg \cdot g^{-1}$ .

### 2.2. Air Purification

Thanks to their structure and specific functional groups on their surface, waste biomass-derived biochars are promising adsorbents that can be used in various air purification processes. According to the reports, these processes include removing volatile organic compounds (VOCs), acidic gases, and odorants such as SO<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub>, and greenhouse gases, such as CO<sub>2</sub> and N<sub>2</sub>O. In most cases, however, biochars are activated chemically or physically to improve textural properties and thus, their adsorption capability. The activation process generates additional costs and, in the case of chemical activation, extra waste that must be managed. This increases the final cost of the materials obtained and brings it closer to the cost of traditional activated carbons. For this reason, the authors of this review decided to focus on non-activated biochars.

The main application areas of this type of biochar, which consist of the removal of volatile organic

compounds, the capture of ambient carbon dioxide from the air, and the biogas upgrading are summarized in Table 3.

VOCs contribute to photochemical smog, the greenhouse effect, and ozone layer depletion. Therefore, it is necessary to limit their emissions. The most recent reports focus on removing acetone, benzene, and toluene as representatives of VOCs.

Švábová *et al.*<sup>28</sup> describe using biochars obtained from walnut shells and apricot pits in acetone adsorption. Despite having a lower surface area than air-activated biochars, non-activated materials were characterized by a similar acetone sorption capacity (c. a. 100 mg·dm<sup>-1</sup>; Table 3), which is explained by a mixed physicalchemical sorption mechanism on non-activated biochars. The lack of surface area, which contributes to physisorption, was compensated by the presence of oxygen functional groups involved in the chemisorption process.

Similar results of acetone sorption on unmodified biochars prepared from corn stalks, rice husk, and pinewood sawdust were obtained by Zhuang *et al.*<sup>29</sup>. The

sorption capacity was related to the feedstock type and the biochar production temperature. The pinewood sawdust pyrolyzed at 700 °C was found to adsorb the highest amount of acetone (about 200 mg·dm<sup>-1</sup>, Table 3) among other unmodified biochars. Furthermore, using a ball mill, they increased the external surface of the biochars and the share of acidic functional groups, which increased the sorption capacity from 1.2 to 3.2 times. In the study, Zhuang also tested the possibility of toluene removal by

biochars. The presented results show similar relationships to those discussed earlier. Still, the sorption capacity of toluene was much smaller and did not exceed 136 mg of toluene per gram of ball-milled biochar. The lower sorption capacity of toluene resulted from its hydrophobic nature and, consequently, from a more negligible interaction with acidic surface groups than in the case of hydrophilic compounds such as acetone.

| Table 3. Rem | oval of air pollutant | s using biochars fr | rom different feedstocks. | MEK - methyl ethyl ketone |
|--------------|-----------------------|---------------------|---------------------------|---------------------------|
|--------------|-----------------------|---------------------|---------------------------|---------------------------|

|  |                              |                           | Comption                                   |      |
|--|------------------------------|---------------------------|--|------|
| Source of biochar  | Pyrolysis<br>temperature, °C | Adsorbate                 | capacity, $mg \cdot g^{-1}$                | Ref. |
| Walnut shell, apricot pit  | 500, 600, 700                | acetone                   | 100.6±19                                   | 28   |
| Corn stalk, rice husk, pinewood sawdust  | 300, 500, 700                | acetone<br>toluene        | 59–304 <sup>*</sup><br>20–136 <sup>*</sup> | 29   |
| n/a  | n/a                          | formaldehyde              | 0.056-0.106                                | 30   |
| <i>Miscanthus</i> straw pellets, oil seed rape straw pellets, rice husk, sewage sludge, soft wood pellets, wheat straw pellets | 550, 700                     | benzene<br>MEK            | 0.05–2.9<br>0.67–43                        | 31   |
| Mixed-wood sawdust   | 400, 500                     | carbon dioxide            | 51.05-139.95                               | 32   |
| Mixture of food and wood wastes  | n/a                          | carbon dioxide            | 39.4–79.9                                  | 33   |
| Plantain peelings  | 600                          | hydrogen<br>sulfide       | 0.02–2.09**                                | 34   |
| Sugarcane bagasse  | 255                          | carbon dioxide<br>methane | n/a  | 35   |
| Wood biomas  | 200-300                      | carbon dioxide            | 8-10                                       | 36   |

<sup>\*</sup> Ball milled chars.

\*\* Wetted biochar.

Biochar of unknown origin was also compared to the activated carbon in the formaldehyde removal process<sup>30</sup>. Despite the similar price of biochar and activated carbon, which was 1.26 and 1.19 USD/kg, respectively, the economic analysis showed lower profitability in the case of biochar, which was caused by a lower total formaldehyde sorption capacity in the range of  $0.056-0.106 \text{ mg} \cdot \text{dm}^{-1}$  and a shorter replacement cycle (max. 18 min.) in comparison to  $0.654-1.541 \text{ mg} \cdot \text{dm}^{-1}$ sorption capacity and 269.5 min. of maximum replacement cycle for activated carbon.

Extensive research on the benzene adsorption and methyl ethyl ketone (MEK) on biochars from savage sludge, rice husk and pellets of softwood, Miscanthus straw, oil seed rape straw, and wheat straw was carried out by Vikrant *et al.*<sup>31</sup> (Table 3). Authors demonstrated that the adsorption of non-polar compounds such as benzene is affected mainly by the surface area of biochar and, to a small degree, by its surface chemical properties. On the other hand, the performance of polar compound removal was dependent not only on textural properties and the

volatile matter content of the adsorbent but also on the type of feedstock used for biochar production. The removal of MEK on the tested biochars was comparable with other adsorbents, such as activated carbons, zeolites, and metal-organic frameworks (MOFs). The authors recommended using modified or produced from different feedstock biochars for less polar organic compounds, consistent with other literature reports<sup>37–39</sup>.

The direct air capture of ambient carbon dioxide by biochar obtained from mixed-wood sawdust was reported by Kua *et al.*<sup>32</sup>. The results show a significant influence of temperature and biochar preparation method on the biochar's performance in CO<sub>2</sub> adsorption. Biochars obtained in the controlled environment using TGA at 400 and 500 °C were characterized by 51 and 140 mg·dm<sup>-1</sup> sorption capacities, respectively. In comparison, the sorption capacity of biochars prepared in the furnace was only about 7 mg·dm<sup>-1</sup>. There was no significant relationship between the initial carbon dioxide concentration and the amount of CO<sub>2</sub> removed during the process. The authors draw attention to the negative effects of indoor particulate matter, which can contaminate adsorbent, contributing to the reduction of the carbon capture capability of biochar.

Biochars obtained from mixtures of food and wood wastes by the gasification process were tested for carbon dioxide adsorption at room temperature<sup>33</sup>. The results indicate that the increase of food waste content in the feedstock has a negative impact on  $CO_2$  sorption capacity, which decreases from 79.9 to 39.4 mg·dm<sup>-1</sup> for biochars containing 20 and 40 wt. % food waste, respectively. It is explained by a higher percentage of heteroatoms (*i.e.*, N and S) on the surface of the first biochar.

### 2.3. Biogas Purification

The possibility of biogas purification from hydrogen sulfide using biochars obtained from Musa Paradisiaca peelings was presented by Gbangbo et al.<sup>34</sup>. Prepared at 600 °C, biochars were used in the adsorption test in a nonmodified form and with the addition of water (25-100 wt. %). The results show that the water content plays a significant role in the H<sub>2</sub>S removal. The sorption capacity increases from 0.02 to 2.09  $mg \cdot dm^{-1}$  while saturation time increases from 114 seconds to 191 minutes for dry and 75 % water content biochar, respectively. The authors explain this phenomenon by the dissolution of hydrogen sulfide bonded to the surface of the adsorbent in the aqueous film covering the surface, which frees up active sites on the biochar surface and allows for the adsorption of new H<sub>2</sub>S molecules. At the same time, they indicate that further increasing the water content causes a deterioration of the sorption capacity of the obtained materials.

An attempt to purify biogas was also made by Wuri *et al.*<sup>35</sup> (Table 3). The sugarcane bagasse-derived biochar combined with natural zeolite was used to adsorb carbon dioxide from biogas. The composition of 50 % biochar and 50 % zeolite in the adsorption bed was optimal for CO<sub>2</sub> removal. The carbon dioxide concentration after purification was about 75 % lower than at the beginning of the process. However, at the same time, the concentration of CH<sub>4</sub> was reduced to 20 % of the initial value, which, according to the authors, resulted from the mesoporous characteristic of sugarcane bagasse-derived biochar and can be mitigated by the modification of adsorbent to be microporous-sized via activation process. The low selectivity towards carbon dioxide adsorption and low sorption capacity of pristine biochars are also reported by other authors<sup>40</sup>

The utilization of biochar in biogas upgrading was tested by Lee *et al.*<sup>36</sup> Commercially available biochar obtained from wood biomass by torrefaction at a temperature range of 200–300 °C was used to adsorb carbon dioxide from food waste-derived biogas. A relatively low amount of adsorbed  $CO_2$  (8–10 mg·dm<sup>-1</sup>;

Table 3) is explained by authors as a result of physicochemical properties of biochar such as basicity, aromaticity, and alkali metal content which is connected to the material used as the feedstock for biochar production and the parameters of torrefaction process.

In his comprehensive review<sup>41</sup> Zhao describes *in*situ biogas upgrading technologies, among which the additive of biochar plays an important role in the improvement of biogas quality. The high surface area and porosity of biochars contribute to not only carbon dioxide adsorption but also allow microorganisms to attach to the surface to avoid being washed out which results in increased methane production. Moreover, the alkaline metal content in biochar contributes to a slight increase of pH in digesters, which leads to the conversion of excess carbon dioxide to carbonate/bicarbonate. The presence of carbonate/bicarbonate in the aqueous phase leads to an increase in CH<sub>4</sub> concentration, which is produced via carbon dioxide reduction by hydrogenotrophic methanogens. Furthermore, the trace metals contained in biochars have beneficial effects on the biogas upgrading process. Using too much biochar may have, however a negative impact on biogas production due to the increased content of mono- and divalent cations released from biochar.

### 3. Energy Storage Application

The global energy transition from non-renewable to renewable energy sources like solar or wind is inevitable due to the emission of carbon dioxide during the combustion of fossil fuels. Solar and wind are abundant, but fluctuation of energy production over time (daily, seasonal, and yearly) is an emerging issue. The problem needs to be addressed to provide a steady energy supply regardless of weather conditions or the time of a day<sup>42</sup>. Thus, increasing renewable energy share should be accompanied by the simultaneous development of effective energy storage and conversion technologies<sup>43</sup>.

Energy storage systems are categorized as mechanical (*e. g.*, pumped hydro, compressed air, and flywheel energy storage), electrochemical (*e. g.*, supercapacitors, and Li-ion, Na-ion, lead-acid, flow, and other types of batteries), electromagnetic (*e. g.*, superconducting energy storage), thermal (*e. g.*, latent heat and sensible heat storage), and chemical (*e. g.*, hydrogen)<sup>43,44</sup>.

Biochar was studied for energy storage applications mainly as an electrode material for electrochemical devices, *i. e.*, Li-ion batteries, Na-ion batteries, and supercapacitors, but also for material-based storage of hydrogen and natural gas. Several reviews were published in recent years summarizing those results<sup>2–5</sup>. However, their authors adopted a different definition of biochar than that used in this review.

### 3.1. Hydrogen Storage

Hydrogen is expected to become an important energy vector in the coming decades. It can be utilized as a fuel for fuel cells serving as transportation or stationary power sources, leaving only water as the final product. Directly combusted in internal combustion engines, produces traces of nitrous oxides besides water, but remains the cleanest fuel in terms of exhaust gas pollutants. Moreover, its use for storing excess generated electricity is proposed.

Hydrogen has the highest gravimetric energy density amongst all fuels (LHV: 120 MJ·kg<sup>-1</sup>) which is unfortunately accompanied by an extremely low density under normal conditions: 0.0838 kg·m<sup>-3</sup> (20 °C, 1 atm.). Therefore, it is necessary to increase its density to store hydrogen, either stationary or during transportation. To achieve that, pressure needs to be increased, temperature needs to be decreased, or materials sorbing a high quantity of the gas molecules must be used. It is particularly crucial for storing hydrogen onboard light-duty vehicles (LDVs), where limited space is an important issue. Currently, hydrogen is stored onboard, compressed to 700 bars<sup>45</sup>, which increases density to only 40 kg $\cdot$ m<sup>-3</sup>. Liquification provides a density of 70.8 kg·m<sup>-3</sup> but requires cooling to -253 °C, which poses a problem with a high boil-off ratio during storage. Moreover, the process is energyconsuming and even 40 % of energy content is lost for liquification (10 % during compression)<sup>46</sup>. US Department of Energy (DoE) 2025 technical target for onboard hvdrogen storage for LDVs is 5.5 kg  $H_2$  (kg system)<sup>-1</sup> and  $0.030 \text{ kg H}_2 \text{ (L system)}^{-1}$ , with fill time not longer than 5 min, delivery temperature in the range -40-85°C, and cvcle stability of at least 1500 cvcles $^{47}$ .

Material-based storage is a promising way to achieve that goal, realized either by chemisorption on hydrides (metal, complex, and chemical) or physisorption on sorbents, such as carbon-based materials (carbon nanomaterials, fullerenes, activated carbons), zeolites, MOFs, COFs, and polymers of intrinsic microporosity (PIMs)<sup>48-53</sup>. Hydrides can absorb even 18.5 wt. % of hydrogen, but sorption kinetic is poor, and due to a high binding energy of chemisorption, elevated temperature is required for desorption<sup>48,54</sup>. The enthalpy of physisorption is usually less than 10 kJ $\cdot$ mol<sup>-1</sup>, so it is fully reversible, its kinetic is fast, but hydrogen uptake is the highest at cryogenic temperatures<sup>55</sup>. Gravimetric capacity met the US DoE target by some carbon sorbents in  $77 \text{ K}^{56-58}$ , but it is significantly lower in higher temperatures, reaching values well below 1 % in room temperature<sup>58,59</sup>. The general trend of increasing gravimetric hydrogen uptake with increasing specific surface area (SSA), known as Chahine's rule, has been observed for most porous sorbents, including

carbons<sup>58,60</sup>. Moreover, a predominantly microporous structure is desired because in narrow micropores binding energy is increased<sup>61</sup>. In particular, pores with the size 0.7–1.5 nm are the most efficient hydrogen storage space<sup>62</sup>. However, this effect is more pronounced at lower than room temperatures<sup>63</sup>. Chars' SSA is usually below 500 m<sup>2</sup>·g<sup>-1</sup>, which is substantially lower than superactivated carbons or MOFs with SSA exceeding 7000 m<sup>2</sup>·g<sup>-1</sup> and H<sub>2</sub> capacity reaching 9.95·wt.  $%^{64,65}$ .

Therefore, chars are not promising materials for hydrogen storage unless they are activated, and their pore structure is enhanced.<sup>3</sup> To reach higher binding enthalpy of carbon sorbents, which facilitates adsorption in temperatures closer to 0 °C activated carbons are doping with other elements, such as heteroatoms (*e.g.*, nitrogen, boron)<sup>66</sup> or metals (alkaline, alkaline earth, or transition<sup>67</sup>). Another strategy is preparing carbon-hydride composites that combine the high surface area of microporous carbons with an elevated binding energy of hydrides.

The latter approach was adopted for biochars in an attempt to find low-cost hydrogen storage material. Yeboah *et al.*<sup>68</sup> use the high-temperature pyrolysis palm kernel shell biochar to prepare a composite with magnesium hydride. It turned out that up to 10 % addition of biochar increased hydrogen uptake of MgH<sub>2</sub> at 360 °C from 5.7 % to 6.1 %. Moreover, the hydrogen desorption temperature was reduced by 40 °C, but remained over 350 °C. Similar results were obtained by Zhang *et al.*<sup>69</sup> on a composite of MgH<sub>2</sub> and 10 % biochar made from grapefruit peel. Hydrogen uptake was almost identical but at a lower temperature of 230 °C. Even higher, 100 °C reduction of dehydrogenation temperature of magnesium hydride was achieved. It was proved that the porous biochar serves as a transportation channel during the hydrogen adsorption/desorption process when added to magnesium hydride and improves the hydrogen storage properties of that material.

### 3.2. Supercapacitors

Supercapacitors are electrochemical energy storage devices exploiting a charge accumulation in the electricdouble layer (EDLC) or assisted by reversible Faradaic redox reactions (pseudocapacitors). The former needs highly porous electrodes for efficient electrolyte adsorption, and the latter electrodes with specific functional groups. Thus, porous carbons with higher SSA, such as activated carbons, seem more suitable materials for EDLC electrodes than biochar, the same as for hydrogen storage. However, there is no clear correlation between high SSA and high specific capacitance (see data in the Khiari *et al.*<sup>3</sup>). The reason is that not only micropores are required for effective adsorption of an electrolyte, but also mesopores for efficient diffusion of electrolyte ions into micropores, especially when higher current densities are applied<sup>3</sup>.

Therefore, not-activated biochars were tested as EDLC electrodes but to a very limited extent (Table 4).

| Plant precursor                   | SSA [m <sup>2</sup> ·g <sup>-1</sup> ] | $V_{tot} [cm^3 \cdot g^{-1}]$ | $V_{mic} \left[ cm^3 \cdot g^{-1}  ight]$ | Capacitance [F·g <sup>-1</sup> ] | Ref. |
|-----------------------------------|--|-------------------------------|---|----------------------------------|------|
| Litchi chinensis (Litchi)<br>seed | 364                                    | 0.23                          | 0.12                                      | 351                              | 70   |
| Syzygium cumini<br>(Jamun) seed   | 278                                    | 0.19                          | 0.10                                      | 500                              | 70   |
| Pinus roxburghii (Pine)<br>cones  | 276                                    | 0.15                          | 0.14                                      | 250                              | 70   |
| Chinese firewood                  | 463                                    | 0.22                          | n/a                                       | 165                              | 71   |
| Seaweed (600 °C)                  | 746                                    | n/a                           | n/a                                       | 264                              | 72   |
| Seaweed (900 °C)                  | 1307                                   | n/a                           | n/a                                       | 175                              | 72   |
| Neem leaves                       | 1230                                   | n/a                           | n/a                                       | 400                              | 73   |
| Ashoka leaves                     | 705                                    | n/a                           | n/a                                       | 250                              | 73   |

**Table 4.** Supercapacitor performance of biochar-based electrodes

Plant biomass often contains alkali or alkaline earth metals' compounds: sodium alginate in some species of seaweeds<sup>72</sup> or Ca/Mg compounds in tree leaves<sup>73</sup>. During carbonization, they serve as an internal activating agent. Biochars obtained from such precursors have SSA similar to activated carbons (Table 4).

The carbonization temperature effect on materials performance was examined<sup>70,73</sup>. SSA of the biochars obtained from Neem leaves increases with temperature (600 °C: 49 m<sup>2</sup>·g<sup>-1</sup>, 800 °C: 1230 m<sup>2</sup>·g<sup>-1</sup>). The same relationship was observed for specific capacitance (600 °C: 70 F·g<sup>-1</sup>, 800 °C: 400 F·g<sup>-1</sup>).<sup>73</sup>

Besides SSA also surface chemistry plays an important role in charge storage. Despite lower SSA, seaweed-based biochar obtained at 600 °C exhibits a higher specific capacitance than that prepared at 900 °C. This is due to the rich oxygen functionality of the lower temperature char, which results in a fast redox reaction and enhanced pseudocapacitance<sup>72</sup>. The same observation has been made by Rawat *et al.*<sup>70</sup> for biochars from Jamun seeds, rich with heteroatoms (O, N, S). It has a significantly higher capacitance than pine cone biochar with higher carbon content, despite the same SSA of both materials<sup>70</sup>.

Lu *et al.*<sup>71</sup> studied the capacitance of biochar and activated carbon (AC) obtained by a molten salt activation from the same precursor. AC shows a higher specific capacitance (189 vs. 165  $\text{F}\cdot\text{g}^{-1}$  at 0.2  $\text{A}\cdot\text{g}^{-1}$ ) and a higher high-rate capability (85 % vs. 70 % capacitance retention upon increasing current density from 0.2 to 2.0  $\text{A}\cdot\text{g}^{-1}$ ). However, that increase was not proportional to almost twice the growth of SSA and  $V_{tot}$ .

### 3.3. Batteries

Sodium-ion batteries (SIBs) are a promising replacement for lithium-ion batteries (LIBs) in many applications due to the lower costs and abundance of sodium on Earth compared to lithium. However, graphite used as an anode in LIBs cannot be utilized in SIBs due to a greater size of sodium ion (1.02 Å) when compared to lithium ion (0.76 Å), leading to instability of Na-graphite intercalates<sup>74</sup>. The most extensively studied alternative to graphite in Na-ion batteries anodes is a hard carbon $^{75,76}$ . It is a specific type of char obtained in a high-temperature carbonization (1000–2000 °C) <sup>75,77</sup>. The resultant carbon material has a partially organized graphite-like structure, with the distance between graphene layers higher than in graphite, suitable for Na<sup>+</sup> storage<sup>78</sup>. It resulted in a moderate reversible specific capacity of about  $300 \text{ mAh} \cdot \text{g}^{-1}$  at a low operating potential of < 0.1 V vs. Na/Na<sup>+79</sup>, but low initial Coulombic efficiency (ICE) remains the main obstacle to successful commercialization of SIB, which was pointed out in several recent reviews75,76,80,81

Waste plant biomass, such as various types of wood<sup>82–84</sup>, cork<sup>85</sup>, fruit stones<sup>86</sup> and shells<sup>87</sup>, rice husk<sup>88,89</sup>, sugarcane waste<sup>90</sup>, water caltrop shell<sup>78</sup>, lotus wastes<sup>91,92</sup>, soap-nut seeds<sup>93</sup>, spent coffee beans<sup>94</sup>, and invasive plants biomass<sup>95</sup> is considered a particularly suitable precursor for preparation of SIB anode because it fulfills circular economy goals and has a low cost.

Characteristics of biomass precursor, together with preparation conditions, influence structural features of

biochars, such as the type and quantity of defects, porous texture characteristic (SSA, pore size distribution), and crystallite parameters (size and interlayer spacing:  $d_{002}$ ). Those parameters are crucial for biochar performance as a SIB anode material<sup>77</sup>.

Tang *et al.*<sup>82</sup> studied the effect of the chemical composition of precursor on the structure of obtained chars and their potential for SIB anode material. They found that a high crystalline cellulose content in biomass leads to the formation of biochar rich in closed pores, which are favorable for sodium storage. However, amorphous components, such as lignin and hemicellulose, are also needed in biomass to hinder the graphitization of char, which reduces material capacity. The effect of carbonization temperature was also evaluated and an optimum value of 1500 °C was found. Lower temperature (1100 °C) results in defective graphene layers of insufficient length for closed pore formation, whereas higher temperature (1700 °C) facilitates undesirable pore shrinkage. The optimized sample exhibits a high reversible capacity: 293 mAh $\cdot$ g<sup>-1</sup> for the 2<sup>nd</sup> cycle and good stability (85.4% capacity after 400 cycles). The effect of carbonization temperature in a range of 800-2000 °C on interlayer spacing in a formed char was studied by Gomez-Martin *et al.*<sup>79</sup>. The parameter was the highest in a temperature range of 1200-1500 °C, reaching 3.80 Å. A positive correlation between the interlayer spacing and sodiation capacity in a low voltage region (a plateau part) was observed indicating the Na<sup>+</sup> intercalation storage mechanism. The exact mechanism of sodium interaction with char anode is still unclear<sup>82,96</sup>. However, it was proved that adsorption in open pores has little contribution to the overall capacity. The correlation of capacity with SSA of chars was not observed<sup>79</sup>. The SSA of biochars for the SIB anode is usually below 200  $\text{m}^2$ .  $g^{-1}$ <sup>89</sup>. In contrast to the energy storage systems mentioned above (hydrogen storage and supercapacitors), the low development of porous texture is beneficial for biochar used as the SIB anode material. For the improvement of sodium storage, various defects, and heteroatoms (e. g., P, B, N) have been introduced into char structure<sup>97</sup> However, the excessive content of oxygen groups and defects is undesirable and can result in the deterioration of ICE<sup>98</sup>.

### 4. Chars in Bioprocesses

Biochar produced from the plant biomass is a valuable addition to various bioprocesses (see Fig. 1). These products can have numerous applications like stabilizing production profile in various bioreactors, upgrading produced biofuels, catalyzing or supporting catalysis in biodiesel production as well as improving the biofertilizer production. Thanks to its sorption properties, it may prevent bacterial contamination and remove unwanted components from mixtures.

Biochar can shape significantly and stabilize the production profile. A good example is the application of such materials in biogas production. Biochar from feedstock like wheat straw or discarded fruitwood was reported to increase methane yield and shorten the lag time required for the formation of methane<sup>99</sup>. In this case, the raw material was ground to reduce particle size to under 2.0 mm and pyrolyzed at different temperatures in the range from 350 to 550 °C. Biochar thus prepared was added at a rate of 5 wt. % to chicken manure, which was the feedstock for anaerobic digestion. In general, for both plant biomass, the higher pyrolysis temperature led to a better additive performance. Optimum results were obtained for fruitwood waste treated at 550 °C. Cumulative methane yield was 69% higher than in the control sample.



Fig. 1. Possible routes for application of biochar in bioprocesses. AD – Anaerobic Digestion

The utility of biochar in biogas upgrading has also been demonstrated. Biochar has the ability to adsorb  $CO_2$ from the gas mixture, improving the energetic value of the fuel. The exact temperature and conditions for char production depend strictly on the type of biomass. For relatively mild types like rice straw or husk, temperatures in the range from 122.2 to 550 °C were found to be enough to reach an adsorption capacity of even 138.2 mg·g<sup>-1</sup>. For harder biomass like woodchips or walnut shells, temperatures in the range from 600 to even 900 °C were required, resulting in over twice as high adsorption capacity<sup>100</sup>.

Another significant role of biochar during anaerobic digestion is the removal of hazardous compounds that may harm or even stop biogas production. Numerous studies prove that corn straw biochar can absorb heavy metals directly from digestate<sup>101,102</sup>. This time, the recommended pyrolysis temperature is around 600 °C, with heating times varying from 120 to 180 minutes. Both studies suggest that moderate concentrations of additives gave the best result. By adding around 1 % of biochar, the cumulative methane production was improved by even over 120 % in laboratory tests, proving clearly how important is to protect microorganisms from heavy metals. However, the usefulness of this type of additive does not end only with the removal of metallic impurities. They seem particularly useful if the raw material for fermentation is animal husbandry waste, which may contain antibiotics, including sulfonamide derivatives. Studies show that the addition of pomelo peel-derived biochar allows for efficient methane fermentation even on swine wastewater containing significant amounts of the aforementioned antibiotics<sup>103</sup> Biochar stabilizes the process and can increase the methane content in the produced biogas by even 10 %.

Biochar can also be applied to reshape production profiles, such as increasing hydrogen production instead of methane. In this case, relatively hard plant biomass is preferred. An example of biochar with proven utility in this area is produced from pinewood.<sup>104</sup> In the aforementioned study, a model food waste was supplemented with 1.5 % of pinewood char. This char was prepared by pyrolysis at 650 and 900 °C. Biochar pyrolyzed at higher temperature showed better properties, increasing hydrogen yield by 127.81% compared to 88.91 % of the one prepared at 650 °C. Moreover, in the study, the removal of mineral matter from biochar was done by soaking it with citric acid. The leached biochar showed a weaker impact on the hydrogen yield. However, the difference between them and the control reactor was significant (over 50 % increase). This suggests that in the case of hydrogen production, the mechanism of action of the biochar is complex and does not only involve adsorption but also the release of valuable minerals such as iron (Fe), potassium (K), calcium (Ca), and in smaller quantities also aluminum (Al), zinc (Zn), sodium (Na), magnesium (Mg), manganese (Mn), and nickel (Ni).

An interesting, though not obvious, application of biochar is catalysis. It turns out that it can replace the cumbersome metal catalysts used in transesterification for biodiesel synthesis<sup>105</sup>. Studies show that rice husks subjected to activation by rapid pyrolysis at 510 °C display high transesterification efficiency<sup>106</sup>. Maintaining the stability and sustainability of biochar due to its susceptibility to sulfur poisoning can be somewhat of a challenge. However, the mentioned studies show that the tested catalyst can withstand at least five cycles of operation, which is sufficient at its low price. It is also worth considering the use of typically waste raw materials

like palm kernel shells, a residue from palm oil production. A study by Bazargan *et al.*<sup>107</sup> proves that biochar from the mentioned feedstock indicates a very high selectivity and leads to almost 99 % clarity of Fatty Acid Methyl Ester (FAME) mixture.

In addition to the applications for various biofuels such as biogas, biochar, and biodiesel, it is also possible to use plant-based biochar in much more trivial cases such as composting. Nitrogen loss by ammonia emissions is both an environmental and economic problem. The natural fertilizer produced loses its properties and additionally contributes to environmental nuisance by producing odors. Similarly, unstabilized composting can contribute to greenhouse gas emissions. The studies suggest that the addition of biochar from slow and dry pyrolysis of wheat straw biomass positively affects the mitigation of mentioned emission<sup>108</sup>. The total organic carbon loss (mostly in the form of methane) can be limited by almost a percentage point, while nitrogen loss can be eliminated almost completely (<1 %). However, to get such satisfactory results, it is necessary to support biochar with calcium-bentonite.

Biochar can also exhibit good electrical conductivity, allowing it to be used in Microbial Fuel Cells (MFCs) and related bioelectric processes<sup>109,110</sup>. This material is especially popular for anode production; however, the studies considering this material for cathodes are also present<sup>111</sup>. In the first case, a common feedstock is coconut shells and neem wood so relatively hard plant biomass. In the case of cathodes, banana wastes are proven to be a reliable source of carbon. For both anodes and cathodes, the feedstock was thermally treated in dry conditions up to the temperature of 900 °C. Additional activation or supplementation with metal composites has a positive impact on the properties of the produced electrode. An interesting approach is also providing biochar filling between the anode and cathode to increase an electron transfer<sup>112</sup>. The filling can be prepared by pyrolysis at 600 °C of maize straw. In the referenced study, the pristine biochar was compared with biochar + zeolite and MgO-modified biochar compositions. The metal-oxide-supplemented filling indicated the best conductivity, expected. Biochar+zeolite had as intermediate properties. The clear biochar filling indicated the lowest conductivity however, it was still significantly better than MFC control without biochar.

As can be concluded, the application of plantderived biochar in bioprocesses is very wide and often not even obvious. Research on these additives is being widely developed and cannot be limited to only selected areas. Particularly intensive development of this technology is taking place in the area of biofuels and bioenergy, but one should not forget about the production of fertilizers or even conductive and filling materials for MFCs.

# 5. Biochar-Based Catalyst for Syngas Production

In the past two decades, the usability of biocharsupported catalysts for effective chemical synthesis, production, contamination biofuel removal. and electrocatalytic reactions has been demonstrated. The beneficial features such as the capability of biochar's surface for functionalization, thermal and mechanical stability, chemically hierarchical structure, mesoporosity, the presence of unique active sites including Fe and K, and non-graphitizing character make the potential of using this material as an industrial catalyst and catalyst's carrier countless<sup>113,114</sup>. This material also has important features in catalysis, such as effective tar removal and resistance to carbon deposition. Furthermore, this solid is easily accessible and profitable, especially when it is derived from biomass wastes. Undoubtedly, the most significant drawbacks of using biochar to obtain catalysts are the non-reproducibility of the material properties, which come from diversified raw materials, and the lack of a sufficiently large specific surface, which requires modifications, e. g., activation of materials at the stage of catalyst preparation. Nevertheless, the studies dealing with the obtaining, modifying, and employing of these kinds of materials are frequent, and various reviews on biocharderived catalysts have been available. For instance, the analysis presented by Zou *et al.*<sup>115</sup> gives an overview of biochar manufacturing from agricultural and forestry waste and their employment in biofuels and bioproducts production. The catalytic properties of metal/biochar catalysts and their relevance in catalytic hydrogenation of biomass feedstocks into the fuels have been reviewed by Wang and co-workers<sup>116</sup>. Synthesis of the various types of biochar-based catalysts and their application in oxidation, reduction, and photocatalysis has been reviewed by Lyu and co-workers<sup>117</sup>. Presented here, the short chapter focuses on recent reports on syngas production (including H<sub>2</sub>-rich syngas) by using the waste biomass-originated biochar catalyst and aims to fill the gap in summarizing recent reports in this area.

## 5.1. Syngas Manufacturing from Biomass and Wastes

The thermochemical processes aiming at syngas production from biomass and wastes are divided into two main groups, *i. e.*, direct and indirect. The direct paths of transformation of the mentioned raw materials mainly consist of (*i*) high-temperature and catalytic pyrolysis, (*ii*) steam gasification, (*iii*) wet biomass processing *via* supercritical gasification, and (*iv*) pyrolytic volatiles

conversion through steam reforming. Whereas, the indirect paths go *via* an intermediate stage where bio-oil or waste pyrolysis oil is produced followed by a steam catalytic reforming or gasification. Among the mentioned processes, e. g., steam gasification of biomass and wastes is frequently the subject of surveys because it enables the production of H2-rich synthesis gas. It is also well recognized that improving the quality of the obtained gas can be achieved through the catalytic tar elimination treatment, as the tar consists of miscellaneous hydrocarbons and can also be the source of additional syngas portion. Regardless of the process, it seems that achieving profitability of obtaining good quality syngas depends not only on the process conditions but also on the use of effective and cheap catalysts. Regarding the above, it appears that such groups of catalysts are those based on biochar.

### 5.2. Potential for Using Biochar as a Catalyst for Syngas Manufacturing from Biomass and Wastes

The biochar-based Ni catalysts (Ni/BC) obtained via a one-step pyrolytic approach from waste corncobs have been examined for tar steam reforming in the work by Du *et al.*<sup>118</sup> The investigation of the activity of the Ni/BC catalysts containing 5–30 wt. % of Ni was carried out in two ways, *i. e.*, in the conversion of toluene as a model tar compound and the corncob-derived tar as a real biomass feedstock. It has been discovered that the loading of 5 wt. % Ni and in situ carbothermal reduction at 600 °C led to the Ni/BC catalytic material exhibiting remarkable catalytic properties and simultaneous work stability. The authors claimed, also based on DFT calculations that the small Ni species (4.2 nm) achieved due to the applied synthesis conditions account for the excellent performance of that catalyst. The results clearly showed the suitability of that catalyst for the conversion of heavy biomass tar towards light products, including synthesis gas.

Elsewhere<sup>119</sup>, waste sawdust of poplar, catalpa, pine, and elm was used as a precursor of biochar supports for the synthesis of Ni (5–15 wt. %) catalysts used in reforming of streams after poplar wood pyrolysis (bio-oil, tar, and methane) to H<sub>2</sub>-rich syngas. It has been noticed the beneficial action of biochar supports for the direct reduction of NiO species to active Ni particles and the prevention of Ni sites oxidation which occurs at the same time. The biochar-based Ni catalysts significantly improved the efficiency of steam reforming as compared to their biochar counterparts. After investigating the optimal reforming processing settings (temperature and water flow rate), it has been revealed that the Ni/biochar containing 10 wt. % of Ni at 650 °C afforded the highest yield of syngas in an amount of 34 mmol per 1 g biomass. Moreover, the injection of water  $(0.3 \text{ mL} \cdot \text{min}^{-1})$  into the pyrolysis reactor enhanced the syngas productivity to almost 110 mmol per 1 g biomass due to the intensive reaction of biochar support with water vapor.

The Ni-, Ca- or Fe-nanoparticles (3.9 wt.%) embedded on biochar originating from cotton stalk have also been shown to be efficient in H<sub>2</sub>-rich syngas production in the gasification of biomass (also cotton stalks)<sup>120</sup>. It has been discovered that H<sub>2</sub> yield and tar reforming increased after using the functionalized biochar compared to the case when the catalyst was not employed. The well-spread metallic phase (the particle size smaller than 20 nm) afforded exquisite catalytic properties. Considering the influence of metal type on the behavior of catalysts, it was shown that the one containing Fe has the most desirable effect both in terms of catalytic activity (87 % tar conversion and 43 mmol  $\cdot$  g<sup>-1</sup> H<sub>2</sub> production) and in terms of stability of the biochar microporous structure. The investigation by Liu *et al.*<sup>121</sup> also proved the

enhancement of hydrogen concentration in syngas as an effect of the application of biochar-based catalysts modified with potassium. It was found that the Kfunctionalized biochar produced from rice husk, together with the presence of steam, made it possible to obtain a syngas products yield (19.8 mmol $\cdot$ g<sub>biomass</sub><sup>-1</sup>) and the H<sub>2</sub> yield (11.1 mmol $\cdot$ g<sub>biomass</sub><sup>-1</sup>). According to the authors' discussion, the excellent performance of this integrated process is due to certain mutual effects: (i) the interaction of K and water vapor with the biochar enlarged the specific surface area and improved the textural properties of the biochar catalyst, ensuring the contact surface between pyrolytic intermediates and the active centers, (ii) the inhibiting effect of K and steam on the biochar condensation hindered the decline of the active groups on the aromatic ring of biochar support, (iii) the K and the steam making the biochar catalyst surface oxygen-rich resulting in formation of high reactive groups like -COO and -CO, and (*iv*) the migration of volatile K across the biochar solid together with the inhibiting action of steam on K release from the catalyst surface favored the formation and retaining the active species of -COK and -COOK, which contributed to the catalytic performance of K-promoted biochar catalyst in the hydrocarbon reforming and at the same time supports the operation of the catalyst by enhancing the reaction paths leading to the tar destruction.

The research by Ren *et al.*<sup>122</sup> aimed to develop the basics for an integrated tar reforming process into syngas and then into the methanation process over the Ni catalyst dispersed on the wheat straw-originated biochar carrier. Under experimental conditions, the biochar-based catalyst

showed better catalytic properties in both tar reforming (toluene as a tar model compound) and methane production compared to the commercial Ni/Al<sub>2</sub>O<sub>3</sub>. The use of biochar as a support yielded the Ni (20 wt. %) catalyst of an activity allowing 90.2 % toluene conversion and syngas

yield (261.4 mmol  $\cdot$  g<sub>toluene</sub><sup>-1</sup>). Moreover, it has been evidenced that the highly active biochar-based Ni catalyst provides the H<sub>2</sub>/CO stream with an optimized proportion (3:1) and also high CO conversion to methane, amounting to 80.3 %. The superior catalytic properties of the Ni system deposited on biochar from wheat straw were assigned to the specific porous structure of biochar built of a variety of cylindrical structures and numerous hollows and also to the phenomenon of better dispersion of Ni species (Ni particle size of 2.83 nm) over biochar compared to this obtained over control Ni/Al<sub>2</sub>O<sub>3</sub> catalyst (Ni particle size of 11.0 nm).

A comprehensive examination of biochar (coming from pyrolysis of pine and spruce sawdust) comparing the activity of biochar, N-doped biochar, and Ni-doped ones for syngas manufacturing was presented in the work by Yand et  $al_{123}^{123}$ . The study has shown how the functionalization of biochar, by nitrogen or nickel doping, influences the yield of high-purity syngas in the integrated process of pyrolysis of the applied feedstock followed by a catalytic stage, *i. e.*, reforming. The Ni (30 wt. %) catalyst supported on biochar displayed the highest yield of syngas (78.2 wt. %) together with the highest H<sub>2</sub>+CO concentration (94.6 vol. %), and also minor deterioration of catalytic features after three cycles of activity test. Even though the other two catalysts did not provide such catalytic efficiency, they also had their advantages. In the case of using only biochar, the obtained syngas was characterized by the highest  $H_2/CO$  ratio (1.5), whereas the N-doped biochar afforded the syngas stream with the highest LHV<sub>gas</sub>·  $(18.5 \cdot \text{MJ} \cdot (\text{Nm}^3)^{-1})$ .

A completely different concept of using biochar as a reforming catalyst's component was proposed by Tian et al.<sup>124</sup>. In this work, hydrothermal combined carbonization was applied to get the monolithic biochar-based catalysts characterized by unique porous structures from round pinewood sticks. The monolithic biochar-based materials were decorated with graphitic carbon covered with Co-Ni alloy nanospecies. The activity results showed that the incorporation of the bimetallic Co-Ni phase significantly enhanced the conversion in toluene steam reforming in regard to the monometallic catalysts (Ni or Co). The toluene conversion reached 100 % with the main product being H<sub>2</sub>/CO, together with superior catalyst stability under long reaction time on a stream test. The authors postulated that the most remarkable case explaining the activity is the Co-Ni synergy resulting from the interaction between Co and Ni particles and also the crucial role of abundant and stable active sites, which were a result of anchoring of Co-Ni nanospecies within carbon channels.

An original approach to the utilization of cow guano contaminated with heavy metals for biochar-based catalysts has been projected in the study by Zeng *et al.*<sup>125</sup>. A set of Cu, Pb, and Zn-containing manure-derived biochar catalysts was prepared to apply them in wheat straw conversion *via* fast pyrolysis/gasification to phenols-enriched fraction and to H<sub>2</sub>-rich gas. The Cucontaining catalyst displays the most promising catalytic properties for biomass conversion into the H<sub>2</sub>-rich gas compared to the other tested solids. It provided the maximum gas yield amounting to ca. 52 %, equal to 550 NmL·(gWS)<sup>-1</sup>, with the approximate 35.9 vol. % H<sub>2</sub> concentration equal to 197 NmL·(gWS)<sup>-1</sup>.

Biochar as a supporting material designed for the catalysts for syngas production emerges as a promising and low-cost catalytic material that provides performance comparable to or better than commercially available solids. Investigation into the development of such a catalyst mainly involves the creation of an active Ni biochar-based catalyst or a Ni catalyst modified with other additives. Undoubtedly, the use of biochar in the preparation of an efficient catalyst for syngas production from biomass will enable biomass processing integration as a result of the complete use of biomass and biomass residues. Despite the promising results, much remains to be achieved to make the use of such a catalyst possible, especially in terms of its operational stability due to its complex surface chemistry and heterogeneity, as well as not repeatable physicochemical features. A more precise understanding of biochar structures and the synergy/interaction between the metallic phase and the biochar matrix in order to understand the dominant reaction mechanisms remains a challenge.

223

# 6. Application of Biochar in Agriculture

The soil quality is an incredibly significant factor differentiating the production of plants, flora, and fauna within this ecosystem. In an era of increased demand for food, the soil condition plays a crucial role in ensuring food security and maintaining ecological balance. Various factors such as soil type, climatic conditions, land use practices. and surrounding pollution affect soil characteristics. In recent years, numerous actions have been taken to improve its properties, including using different additives that enhance its qualities, drawing the attention of researchers and experts. Due to its key functions, biochar serves as an incredibly versatile tool (Fig. 2). Its primary application involves capturing and storing carbon in the soil, which can significantly contribute to sustainably mitigating adverse environmental impacts, such as climate change and global warming. This material can serve as a soil additive, improving its physicochemical properties. It possesses adsorptive abilities and can function as a sorbent for various pollutants, including heavy metal ions, excessive nutrients, or organic contaminants.



Fig. 2. Biochar in agricultural applications

### 6.1. Biochar as a Soil Amendment

The addition of biochar to the soil can cause significant changes in its characteristics, including physicochemical alterations in properties and microbiological activity. It enhances soil aggregation<sup>126</sup>. increases its water-holding capacity<sup>127</sup>, promotes better aeration and porosity<sup>128</sup>, and thus positively impacts soil fertility<sup>129</sup>. Retention of nutrients near the root zone is possible through a biochar's cation and anion exchange capacity. These properties enable the modification of transport for important plant cationic  $(K^+, Mg^{2+}, Ca^{2+}, and$ ammonium ions) and anionic (phosphates, and nitrates) nutrients. The characteristics of biochar strongly influence its sorption capacity towards ions; for instance, the presence of oxygen-containing heterocyclic groups promotes a greater affinity for anion sorption<sup>12</sup> . The presence of biochar in the soil can positively impact plant growth. Enhancing the nutrient supply in the root zone can beneficially influence their architecture<sup>128</sup>. The change in the physicochemical properties of the soil results in increased crop yields, as demonstrated in a three-year experiment on rice cultivation<sup>131</sup>

Biochar significantly impacts the biological properties of the soil. The porous structure of biochar can serve as a shelter for numerous beneficial microorganisms for plants. Within these pores, microorganisms are protected from drying out and local predators. Labile carbon compounds act as a food source for microorganisms, biochar may also contain mineral compounds. Biochar's high specific surface area can provide greater reserves of assimilable carbon and nutrients<sup>132</sup>. Intensive agriculture leads to soil acidification, primarily due to the heavy use of nitrogen compounds in fertilization<sup>133</sup>. The addition of biochar affects the soil pH, making it more alkaline<sup>134</sup> due to the presence of alkali cations. Most fungi prefer acidic or slightly acidic pH conditions, while the optimal pH for most soil bacteria ranges from slightly acidic to neutral, around pH 6-7. Altering the environmental pH by introducing biochar influences the composition and diversity of soil microorganisms. Biochar can foster interactions between microorganisms by promoting beneficial relationships or suppressing harmful pathogens and pests, affecting overall microbial community dynamics<sup>135</sup>. Biochar can also be used as a carrier for beneficial bacteria, known as microbial fertilizers<sup>136</sup>. These microorganisms support the efficient absorption of nutrients by plants by converting them into more accessible forms, which helps to reduce the required doses and enhances the utilization of nutrients by plants. The adequate adhesion of cells is facilitated by numerous functional groups present in this material and its significant porous structure. Additionally, hydrogel carriers can support the immobilization of the inoculum and facilitate introduction to the soil<sup>137</sup>.

### 6.2. Biochar as a Nutrient Carrier

Biochar can provide nutrients in two ways: (1) as components released from its surface and (2) as components immobilized in its structure. Biochar is a source of organic carbon and mineral compounds containing phosphorus, nitrogen, and potassium, which are beneficial for plant growth<sup>138</sup>. These components are released from the material in varying degrees, K and P ions as ash fractions are well available for plants, for nitrogen and additional degradation of biochar is necessary due to the organic nature of these compounds.

The sorption properties of biochars can be exploited to prepare nutrient carriers. The traditional approach involves immersing the raw material in micronutrient salt solutions, centrifuging or filtering, and drying the material<sup>139</sup>. For this purpose, digestates, a source of nutrients, can also be used. Such a solution closes the material cycle in sustainable agriculture<sup>140</sup>. An alternative biochar application involves enriching it with micronutrients through a spray method, known for its simplicity and lack of waste. Materials prepared from biochar based on tannery waste, enriched with Cu, Zn, and Mn ions applied in plant studies, exhibited significant biomass growth<sup>141</sup>.

Biochar is also a good candidate for developing slow-release nutrient fertilizers. The slowed release is mainly associated with functional groups, porosity, and the carbon's pH. The use of biochar alongside nitrogen fertilizers has a positive impact on reducing nitrogen emissions and slowing down the release of elements into the environment<sup>142</sup>. It is possible to impregnate biochar with nitrogen compounds (such as urea) using various binders. The sorption of urea can be assisted by the deashing of biochar. Application of this kind of fertilizer significantly reduces the release of various forms of nitrogen (ammonia by 38%, nitric oxide by 52%) compared to urea<sup>143</sup>. Also, the leaching of nitrate nitrogen from the fertilizer produced by coating urea with biochar and polymer binder is strongly reduced compared to the uncoated fertilizer. A noticeable effect of adding biochar on the slowed release rate of nitrogen compounds was also noted<sup>144</sup>.

### 6.3. Biochar for Soil Remediation

Biochar is a versatile component in soil remediation that extracts pollutants such as heavy metals or organic toxins (like pesticides and fuels). Through a range of mechanisms within its structure, biochar diminishes the availability of contaminants. These mechanisms include ion exchange, micro-precipitation, complexation, electrostatic interactions with functional groups, physical adsorption,  $\pi$ - $\pi$  electron donor interaction, and hydrophobic interactions (particularly effective for organic compounds)<sup>145</sup>. The effectiveness of heavy metal binding strongly depends on various factors, such as the type of metal ion (size, valence, ion type, and speciation), the nature of biochar (raw material used, production conditions, porosity, and specific surface area), soil type, and environmental conditions (precipitation, temperature, *etc.*). Understanding the correlation between these parameters allows for predicting the efficiency of metal ion immobilization using machine learning techniques, thereby facilitating effective remediation processes<sup>146</sup>.

The application of biochar together with fertilizer in crop cultivation can yield dual benefits by reducing the concentration of heavy metals in the soil while simultaneously enhancing various soil parameters (pH, carbon content, soil enzymatic activity, fertility, and cation exchange capacity). Two types of biochar derived from eucalyptus wood, pyrolyzed at 400 and 600 °C, showed increased metal binding, especially those treated at higher temperatures. Similar results were obtained for biochars produced from corn cobs at temperatures ranging from 350 to 650 °C, where higher temperatures increased a specific surface area and sorption capacity for copper ions, but also introduced polyaromatic hydrocarbons, potentially exhibiting toxic effects on organisms. It's worth noting that different types of ions may interact with carbon differently; cation ions readily undergo immobilization, while anion ions (e. g., As) may not bind as effectively<sup>147</sup>. Biochar can also be used simultaneously with beneficial microorganisms for plants, promoting the removal of metal ions from the soil while increasing plant biomass, thus facilitating phytoremediation<sup>148</sup>.

### 7. Conclusions

Waste agricultural-based char proved to be effective in several processes of industrial potential. The most frequently analyzed direction, sorption of pollutants from water and air, indicates that even without activation processes, chars obtained by thermal conversion are good sorbents, both in the processes of sorption from water and air pollutants. Especially in the case of removing contaminants from water, the number of analyses in the field of dynamic adsorption should be increased and the conditions of the laboratory testing processes should be adapted to the actual (sewage) conditions (*e. g.*, pH, initial contaminant concentration, and economically justified concentration of the adsorbent in the solution).

Biochars have the potential to be used in energy storage systems. However, their low SSA makes them less suitable for hydrogen storage than other porous carbon materials, such as activated carbons. This feature is not an obstacle to electrochemical energy storage systems, such as supercapacitors and batteries, where biochars are promising materials for electrode manufacturing. Particularly, high-temperature biochars, called hard carbons, are most likely to be commercialized<sup>149</sup>.

Biomass-derived char can stabilize the production profile in various bioprocesses, catalyze or support catalysis in *e. g.*, biodiesel or syngas production, as well as improve biofertilizer production. It may prevent bacterial contamination and, thanks to its sorption properties, remove unwanted components from mixtures.

As a soil additive, biochar significantly alters soil properties, improving fertility, water retention, aeration, and nutrient availability, resulting in better plant growth and yields. As a nutrient carrier, biochar releases essential elements and can be adapted to slow-release fertilizers, reducing environmental impact to support sustainable agriculture. In soil remediation, various binding mechanisms to biochar extract contaminants such as heavy metals and toxins while improving soil parameters. However, its effectiveness in binding pollutants depends on several factors, so it is necessary to know these variables to implement effective reclamation practices.

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### Abbreviations

AC - activated carbon, AD - anaerobic digestion, AY alizarin yellow, BC - biochar, BFR - basic fuchsin red, COF - covalent-organic framework, CV - crystal violet, DFT - density functional theory, EDLC - electric doublelayer capacitors, FAME - fatty acid methyl ester, ICE initial Coulombic efficiency, LDV - light-duty vehicle, LHV – lower heating value, LIB – lithium-ion battery, MB - methylene blue, MEK - methyl ethyl ketone, MFC - microbial fuel cells, MG - malachite green, MO methyl orange, MOF - metal-organic framework, PIMs polymers of intrinsic microporosity, SIB - sodium-ion battery, SSA – specific surface area, TGA thermogravimetric analysis, US DoE - United States Department of Energy, VOCs - volatile organic compounds

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### РОЗКРИТТЯ СТАЛОГО РОЗВИТКУ: ВСЕБІЧНИЙ ОГЛЯД ПЕРЕРОБКИ ВІДХОДІВ БІОМАСИ НА БІОВУГІЛЛЯ ДЛЯ ЕКОЛОГІЧНИХ РІШЕНЬ

Анотація. З точки зору перетворення відходів у цінні продукти та зменшення забруднення навколишнього середовища переробка відходів біомаси в багаті на вуглець матеріали привертає широку увагу. У цьому огляді наведено можливості використання твердого продукту одностадійної карбонізації відходів біомаси рослинного походження. Обговорено ряд застосувань, зокрема виробництво сорбентів, матеріалів для зберігання енергії, носіїв каталізаторів і сільськогосподарське застосуваня.

Ключові слова: карбонізація, вугілля, сорбент, каталізатор, сільське господарство.