The potential of biocarbon as CO₂ adsorbent in VPSA unit

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Abstract
The best solution to the main environmental problem seems to be CO₂ capture to reduce greenhouse gas emissions. The activated carbons derived from biomass have attracted extensive attention as solid adsorbent for carbon dioxide capture process. In this work, we focus on examining the properties of biochar (non-activated porous carbon) produced from biomass. Physicochemical properties of the biochar were investigated by thermogravimetric analysis (TG), Fourier transform infrared spectroscopy, scanning electron microscopy and N₂ adsorption–desorption at 77 K. In order to evaluate the possibility of using biocarbons for CO₂ adsorption in large-scale VPSA units, investigations of these adsorbents in laboratory are necessary. The paper present the potential of biochar for CO₂ capture in VPSA unit. The examination of the CO₂ sorptive capability, stability and regeneration performance of biochar was carried out using a Mettler-Toledo TGA/SDTA 851e thermobalance and TG-Vacuum system. The sorption of CO₂ was carried out isothermally in a flow of a mixture of gasses: CO₂ (100 vol.%) and CO₂ (16 vol.%)/N₂ (84 vol.%). The commercial biochar showed a sorption performance for CO₂ up to 26.4 mg CO₂ g⁻¹ adsorbent at 30 °C and 30 bar. Repeated use of the adsorbent in the sorption/desorption cycle did not affect its performance, which indicates high sorption stability.

Keywords Biocarbon · Carbon dioxide · Adsorption · TG-Vacuum · VPSA

Introduction
Carbon dioxide emissions resulting from the burning of fossil fuels and industrial activities are now the main cause of adverse changes in the atmosphere. As a result of higher energy demand, the level of carbon dioxide emissions in the world has reached a record level in history—37 billion tonnes in 2018 [1]. From the analysis of the carbon balance in the biosphere, it is clear that there is an incredible variation between carbon dioxide emission in the form of carbon dioxide to the atmosphere and its assimilation by sources on Earth [2]. The reduction in greenhouse gas emissions, including CO₂, is now becoming the main goal of the European Union. Among the currently available methods, post-combustion CO₂ capture plays a leading role due to the possibility of modernization of already existing power plants [3]. The method of post-combustion CO₂ capture includes absorption by aqueous solutions, adsorption by solid materials and membrane separation. Among them, the adsorption method is advantageous due to the low energy consumption and easy regeneration of the adsorbent, without producing adverse by-products or contaminated sorbents [4–7]. Activated carbon, zeolites and metal–organic frameworks (MOFs) are carbon dioxide capture adsorbents described in the literature [8–14]. Potential adsorbents for CO₂ capture are also porous carbon obtained from biomass, so-called biochar and biocarbon [15]. Although zeolites and MOFs have a high CO₂ adsorption capacity, it decreases in the presence of water [16]. In contrast, activated carbon is hydrophobic and has a large surface area and excellent thermal and chemical stability. In addition, it is possible to optimize the pore size of activated carbon materials for high CO₂ adsorption. Therefore, they should be considered as potential adsorbents for VPSA CO₂ capture systems. Another advantage of using biocarbon as a CO₂ adsorbent is its low cost. It is know that the overall cost of CO₂ capture could be reduced significantly by using inexpensive carbon precursors and minimizing the number of steps involved in the synthesis procedure [4]. The type of porous carbon precursor used and the preparation method have a significant impact on the structure and
porosity of the obtained porous carbon [17, 18]. European standards condition the production of biocarbon only in the process of pyrolysis of biomass (or identical substrate) in a temperature regime from 350 to 1000 °C, in an anaerobic atmosphere (or in the presence of a small amount of oxygen) in the pyrolysis chamber [19, 20]. According to many researchers [21–23], biochar needs to be activated to generate high surface area and porosity before being employed for CO\textsubscript{2} capture. Scientists are focusing on the modification of biochar, mainly with chemical agents, e.g., KOH, K\textsubscript{2}CO\textsubscript{3}, which affect their structure. Most studies focus on biocarbons after activation (chemically modification) [21–23]. However, the use of chemicals in the adsorbent activation process contributes to increasing environmental pollution. There is hardly any information in the literature related to uses of biochar (non-activated porous carbon) in VPSA CO\textsubscript{2} capture unit. Therefore, in the present article, the CO\textsubscript{2} sorption capacity and biochar stability in multiple cycles was determined using thermogravimetric methods. We focused on the possibility of using biochar in VPSA installations, assessing their performance in the simulation process in the TG-Vacuum installation.

**Method and materials**

**Materials characterization**

The biocarbon from company Fluid S.A. was used in this study. Fluid S.A. technology is the most energy-efficient technology of biocarbon production [24]. The slow carbonization technology, which they use, directly leads to biocarbon production, where the products are mainly biocarbon (65–80%) and process gases (15–35%). It consists in thermal processing of plant biomass and other biomass residues through its autothermal roasting at a temperature higher than 260 °C in anaerobic atmosphere.

**Characteristics of research methods**

A LECO Truspec CHNS analyzer was used to ascertain the amount of carbon, nitrogen, hydrogen and sulfur in the biocarbon. The Zeiss Merlin scanning electron microscope (SEM) was used to record the field emission SEM images. The textural parameters and porosity of the materials were investigated with a N\textsubscript{2} sorption analyzer (Micromeritics Gemini 2360). Samples were degassed overnight at a set temperature of 250 °C prior to analysis, which was carried out at –196 °C. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method from the linear part of BET plot according to IUPAC recommendations using the adsorption isotherm (relative pressure (\(p/p_\text{r}\))=0.05–0.23). The pore size distribution was calculated by the BJH method, and the pore volume was obtained from the maximum amount of adsorption at \(p/p_\text{r}\) of 0.99. The FTIR spectra were recorded on a Nicolet 6700 spectrometer. The tablet preparation consisted of mixing 0.01 g of test material and 0.2 g of KBr powder. The thermal stability of sorbents was tested using a thermobalance TGA/SDTA 851e. Argon was used as the furnace medium, which was supplied into the analyzer furnace at a flow rate of 200 mL min\textsuperscript{−1} within the temperature range. The stand for conducting research on the adsorption/desorption process using a vacuum consists of TGA/SDTA 851e thermobalance (TG) from Mettler-Toledo and a specially selected vacuum set.

**Tests of CO\textsubscript{2} sorption capacity**

The physicochemical properties of the commercial biocarbon and their CO\textsubscript{2} sorption/desorption capacities were examined using thermogravimetric methods. In the programmed adsorption test, the sample was first dried at 120 °C under a stream of nitrogen (100 mL min\textsuperscript{−1}) for 30 min, and then, the sample was cooled to 25 °C to initiate the CO\textsubscript{2} adsorption process. The adsorption process was carried out in a gas atmosphere containing 100 vol.% CO\textsubscript{2} and 16 vol.% CO\textsubscript{2}/84 vol.% N\textsubscript{2}. The sample was kept under test conditions until it reached the adsorption balance, which lasted 60 min. Figure 1 shows road of carbon dioxide adsorption study. Research of adsorption–desorption cycles using thermobalance TGA/SDTA 851e was also carried out. The CO\textsubscript{2} flow rate was set at 100 cm\textsuperscript{3} min\textsuperscript{−1}, while the desorption process was conducted in an anaerobic atmosphere.

Low-pressure CO\textsubscript{2} adsorption experiments were carried out using a TG-Vacuum instrument fitted. TG-Vacuum system was used to obtain information about the usefulness of adsorbent for testing at the VPSA pressure swing adsorption plant. Prior to CO\textsubscript{2} adsorption measurements, the samples were put on overnight degassing under vacuum at 200 °C. Adsorption of CO\textsubscript{2} was carried out at atmospheric pressure, while during desorption it was 30 kPa abs. A single-cycle adsorption/desorption endures 15 min. The test conditions are presented in Table 1.

![Fig. 1 Diagram of the road of carbon dioxide adsorption study](image-url)
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Physicochemical characterization of the biocarbon

As shown in Table 2, the biocarbon used in this study contains a large amount of carbon (91.56% by mass) and a small amount of nitrogen (0.73% by mass) based on CNS elemental analysis. The presence of sulfur in the material was not detected. The carbon content of the biocarbon is a measure of the degree of carbonization. Prior to weighing and analysis, the samples were dried in an oven and stored in a desiccator. Elemental analysis was measured in triplicate. It is known that [4] during carbonization, the C content increased considerably, and the O and N content decreased due to the evaporation of hydrogen, nitrogen and oxygen in the gas phase.

The high elemental carbon content (91.6%) reduces the elasticity of the molecular phase of the material structure, resulting in a simultaneous increase in the degree of cross-linking of the macromolecular phase. Carbon and its derivatives with a high elemental carbon content contain a macromolecular phase with limited stiffness, which means that the porous carbon mass can be expanded when placing molecules in submicropores smaller than the size of sorbate molecules [25]. According to the literature data, efficient CO₂ adsorption on carbon materials is closely related to the high content of carbon as well as nitrogen in their composition. Although the nitrogen content naturally found in this type of material is usually low, it can be incorporated into the structure by inter alia with ammonia [26]. The introduction of nitrogen into the material structure is to allow effective development of the porous surface [27, 28]. Research conducted by Madzaki et al. proves that the high nitrogen content does not reflect the adsorption capacity of CO₂. Carbon materials enriched in nitrogen and equivalents without the admixture of a nitrogen adsorption values were comparable CO₂. Carbon dioxide capture by carbon materials and their counterparts additionally enriched with nitrogen was at the same level [29].

Fourier transform infrared spectroscopy (FTIR) is frequently used to identify functional groups in biocarbon. FTIR analysis requires special sample preparation, because biocarbon is opaque solid. Figure 2 shows FTIR spectra of the used in this study biocarbon. Important and strong extended absorption peak at 3400 cm⁻¹ spectra is the O–H and H–O–H stretch. Poorly visible peaks at 3000–2860 cm⁻¹ are associated with the aliphatic C–H stretch, aromatic C–H bond (3060 cm⁻¹) and carboxylic stretch C=O (1700 cm⁻¹). Other stretching bands can be observed in the FTIR spectra of the around 930 cm⁻¹ (C–CO groups) and with similar trend observed in the range 1410 cm⁻¹ due to C–H bending [30–32].

The SEM technique was used to analyze the surface morphology of the biochar. Figure 3 shows the SEM micrographs of the biocarbon sample.

The SEM images of the sample in Fig. 3 reveal the presence of abundant pores. A large morphological diversity of the material is visible. The biocarbon sample shows irregular (non-uniform) structure pores. The recorded axial image of commercial biocarbon on the right in Fig. 3 clearly indicates that it is hardwood [33]. Two types of pores are shown: tracheids and rays. The rays run perpendicular to the tracheids and are vertical elements of the structure. The image on the left shows the transverse walls, where the porous plates that divide the concentrated vessels are visible. Table 3 summarizes the parameters of the biochar structure.

![Fig. 2 FTIR spectra of the commercial biocarbon](image)

| Material  | C (mass%) | H (mass%) | N (mass%) | O (mass%) |
|-----------|-----------|-----------|-----------|-----------|
| Biocarbon | 91.56     | 1.43      | 0.73      | 6.28      |

Table 2: Content of carbon, hydrogen, nitrogen and oxygen in the biocarbon
The biochar was composed entirely of pores about 4.74 nm (average pore diameter), which presented the surface area only 65 m² g⁻¹. The char has higher carbon content, the surface area of char is rather low due to the blockage of the pores by tars [4]. Similar values of biochar specific surface area can be found in the literature: 26.3 m² g⁻¹ [34], 38–92 m² g⁻¹ [35] and 115 m² g⁻¹ [4]. The small specific surface area of biocarbon 65 m² g⁻¹ does not necessarily mean low adsorption. The adsorption itself depends on many factors such as the presence of functional groups, pore structure or surface chemistry [36].

The low-temperature nitrogen adsorption/desorption isotherm for biocarbon can be classified according to the IUPAC classification [37] as type IV isotherm Adsorption/desorption isotherms overlap perfectly. As follows from the analysis of nitrogen adsorption–desorption isotherms (Fig. 4), the biochar is characterized by poorly developed porosity. Insignificant adsorption is observed in the whole range of low relative pressures. The adsorption capacity of biochar is very low, indicating that not very many pores existed. The results are in accordance with pore size distribution and pore volume. Figures 5 and 6 show the shares of pores of specific sizes in the total specific surface area and total pore volume of biocarbon. Pores with a diameter of 2.04 nm have the largest share in the total specific surface area of biocarbon. The pores with a diameter of 22.9 nm have the largest share in the biocarbon pore volume.

Figure 7 shows the TG and DTG curves of the biocarbon in the temperature range of 25 °C–800 °C. The first loss of mass, caused by dehydration of moisture, existed between 30 °C–180 °C. The loss was caused by removing moisture from the sample. A net mass loss is 11%. The second mass loss

![Fig. 3 SEM photographs of biocarbon](image-url)

![Fig. 4 Nitrogen adsorption–desorption isotherms of biocarbon](image-url)

![Fig. 5 Specific pore surface distribution as a function of the pore diameter for biocarbon](image-url)
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is due to devolutilization. The minimum of this peak for the biocarbon sample took place at 500 °C. During this process, most elements other than carbon, hydrogen, nitrogen and oxygen are removed in gaseous form, leaving a solid residue enriched in carbon [4].

Results

**CO$_2$ sorption capacity**

To determine the CO$_2$ sorption capacity of the biocarbon, the first step was the temperature programmed adsorption test. This test was carried out according to the procedure shown in Fig. 1. Figure 8 shows the results of the programmed adsorption test for biocarbon.

Carbon dioxide adsorption capacity in the atmosphere of 100 vol.% CO$_2$ was higher and amounted to 26.4 mg CO$_2$ g$^{-1}$ adsorbent (0.98 mmol g$^{-1}$). In an atmosphere of 16 vol.% CO$_2$ with N$_2$ doping, it was 17.8 mg CO$_2$ g$^{-1}$ adsorbent (0.66 mmol g$^{-1}$). The carbon dioxide capture efficiency of a biocarbon sample can be considered satisfactory given that it is a biocarbon sample without activation. Creamer et al. [38] studied CO$_2$ adsorption on non-activated porous carbons prepared from sugarcane bagasse and hickory wood. According to [38] data, the CO$_2$ sorption capacity of biochar was 73.55 mg g$^{-1}$ and 35 mg g$^{-1}$ CO$_2$ (depending on the conditions for obtaining biochar). Research conducted by Cramer et al. [38] proves that physisorption driven by weak van der Waals forces is the main operating mechanism for adsorption and the quadrupole nature of the CO$_2$ molecule was put forward to be a useful attribute in creating a surface interaction with biochar via the process of dispersion and induction. According to the literature data [38], surface area was the main factor controlling the process of physisorption of CO$_2$ onto biochar. The authors emphasized the role of the presence of nitrogen groups on the surface. According to Singh et al. [35], activated porous carbons are superior to biochars as they have higher specific surface areas and a more developed porosity, although biochars have their own advantage when it comes to the presence of abundant functional groups on the surface. The authors also stated that the nature and the quantity of the functional groups on the surface of carbon materials depend on the methods of preparation and the nature of the biomass precursors used [35].
In the article, we present the results of research carried out on commercial biochar obtained from the cutting of deciduous trees. Considering that the material has not been modified in any way, the test results are satisfactory. This gives hope for the possibility of using non-activated porous carbon obtained from biomass for carbon dioxide adsorption. The conducted analyzes showed that biocarbon can be used at temperatures around 25 °C (yield 0.98 mmol g⁻¹ in 100 vol.% CO₂), which is beneficial from the point of view of the future use of this adsorbent in adsorption systems. The conducted studies of biocarbon regeneration under reduced pressure conditions confirmed the possibility of using this type of adsorbent in VPSA adsorption installations. The sorption capacity was 26.4 mg CO₂ g⁻¹, additionally without losing its efficiency in repeated sorption/desorption processes. The porous structure of biochar and unique surface properties make it an effective CO₂ adsorbent.

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