Adsorption of CO₂ on In Situ Functionalized Straw Burning Ashes—An Innovative, Circular Economy-Based Concept for Limitation of Industrial-Scale Greenhouse Gas Emission

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Abstract: A new, innovative approach in the search for an effective and cheap carbon dioxide sorbent, in line with the circular economy and sustainable development principles, directs the attention of researchers to various types of waste ashes generated as a result of biomass combustion. In addition to the use of environmentally safe materials that have been experimentally identified, and that, in some way, have adjustable sorption capacity, it is also possible to rationally develop a widely applicable, simple, and inexpensive technology based on large amounts of this type of post-industrial waste, which is also an equally important issue for the natural environment (reducing the need for ash storage and accumulation). Even the lower sorption capacity can be successfully compensated for by their common availability and very low cost. Thus, the CO₂ adsorption capability of the ashes from the combustion of straw biomass was experimentally investigated with the use of a high-pressure adsorption stand. The presented original technological concept has been positively verified on a laboratory scale, thus a functionalization-based approach to the combustion of substrate mixtures with nano-structural additives (raw, dried, calcined halloysite, kaolinite), introduced to improve the performance of straw biomass combustion and bottom ash formation in power boilers, clearly increased the CO₂ adsorption capacity of the modified ashes. This allows for an advantageous synergy effect in the extra side-production of useful adsorbents in the closed-loop “cascade” scheme of the CE process. The addition of 4 wt.% kaolinite to straw biomass caused an over 2.5-fold increase in the CO₂ adsorption capacity in relation to ash from the combustion of pure straw biomass (with a CO₂ adsorption capacity of 0.132 mmol/g). In the case of addition of 4 wt.% nano-structured species to the straw combustion process, the best effects (ash adsorption capacity) were obtained in the following order: kaolinite (0.321 mmol/g), raw halloysite (0.310 mmol/g), calcined halloysite (0.298 mmol/g), and dried halloysite (0.288 mmol/g). Increasing the dose (in relation to all four tested substances) of the straw biomass additive from 2 to 4 wt.% not only increase the adsorption capacity of the obtained ash, thus enriched with nano-structural additives, but also showed a significant reduction in the differences between the maximum adsorption capacity of each ash is observed. The experimental results were analyzed using five models of adsorption isotherms: Freundlich, Langmuir, Jovanović, Temkin, and Hill. Moreover, selected samples of each ash were subjected to porosimetry tests and identification of the surface morphology (SEM). The obtained results can be used in the design of PSA processes or as permanent CO₂ adsorbents, based on the environmentally beneficial option of using ashes from biomass combustion with appropriately selected additives.
1. Introduction

One of the most common harmful products of fossil-fuel combustion is carbon dioxide, which is directly responsible for the ever-worsening greenhouse effect [1]. Due to the scale of the global energy processes related to CO\textsubscript{2} emissions [2], possible new, more effective, but at the same time, simple and cheap methods of its separation from waste gases are being sought. The introduction of economic factors as the main criteria and constraints in the development of green technologies is becoming more and more common [3].

Various methods are currently being used in industry to capture CO\textsubscript{2} from gas streams. Examples include absorption methods (aqueous solutions of various inorganic or organic compounds in particular amines, dimethyl glycol ether, and others are used as absorbents), membrane processes, or low-temperature condensation processes. On the basis of the specific properties of the considered gas mixtures, adsorption methods can provide potentially large processing possibilities [4]. Due to the energy demands of the aforementioned processes for CO\textsubscript{2} separation from gas mixtures, new and cheaper process solutions are being sought.

A desired adsorbent should demonstrate simultaneous selectivity and process efficiency. This should be due to the development of the relatively large specific surface area of the adsorbent, which should also have a selective chemical affinity for the CO\textsubscript{2} component to be removed. Some details regarding the performance of the adsorbent bed structure during the process are also important [5]. A particular emphasis is also placed on the key element of the adsorbent, its structure, which is especially important for industrial processes characterized by large scale CO\textsubscript{2} emissions (e.g., zeolites, metal–organic frameworks, polymers with a microporous structure, carbon molecular sieves, amine-modified structured sorbents [6]). When analyzing potential adsorbents, attention is paid to its availability, the degree of crystallinity of the structure, the available adsorption surface, the possibility of an indirect influence on the regulation of the size and volume of its pores (and the properties of their available internal surfaces), mechanical and thermal stability, as well as the adsorption capacity and selectivity towards CO\textsubscript{2} [7]. The processing method and regeneration of the adsorbents have also gained importance [8]. As a consequence of the difficulties in finding suitable natural sorbents showing both these technologically desirable properties, attention should focus on the rational and appropriate selection of pairs of components, which are independently responsible for the developed contact surface and a possibly high adsorption selectivity, which allows to obtain technologically desirable synergy effects, controlled as early as in the design stage.

The process of adsorptive separation of CO\textsubscript{2} from flue gases is relatively expensive, and has resulted in the search for an effective and cheap adsorbent that can be easily disposed of after its lifetime. A cheap substance with a large specific surface area, which is available in large quantities, on the other hand, and is necessary for any disposal are ashes [9–15], especially if they are subjected to a special preparation process [16], e.g., synthetic zeolites obtained by the reaction of fly ash with NaOH, using various processing conditions [17]. In addition, solid amine sorbents can be obtained using chemical synthesis with fly ash as the main substrate. In this way, the obtained structures turn out to be good CO\textsubscript{2} adsorbents [18]. The possibility of CO\textsubscript{2} adsorption through the use of fly ash zeolites has already been already experimentally verified; in particular the possibility of using this technology in postcombustion carbon-capture processes was examined [19]. Fly ash zeolites synthesized under various conditions and using various methods showed a CO\textsubscript{2} adsorption capacity in the range of 0.24–4.16 mmol/g. Clear similarities were identified between zeolites available on the market and the obtained fly ash zeolites, as well as fully reversible (in some conditions) physisorption mechanisms [20].
Ashes from biomass, due to their chemical composition (lignin, hemicelulose, proteins, lipids, water, various sugars also simple ones, starch, hydrocarbons) [21] show a large structural diversity, as well a chemical affinity to various types of impurities (which can be additionally modified using various preprocessing methods resulting in an increase in active adsorption sites on the surface towards increase in the adsorption potential or selectivity), in terms of naturally occurring surface functional groups [22–24]. Research covered, among other things, the adsorption capacity of barley straw ash [25], bagasse fly ash [26,27], rice husk ash [27], wheat and rice straw ashes [28], waste wood, and straw [29].

Rice husk (preprocessed by calcination at 600 °C in nitrogen and steam environments) demonstrated a maximal CO$_2$ adsorption capacity of 0.86 mmol/g [30]. Experimental investigations of the CO$_2$ adsorption abilities of biochar have focused both on the important influence of its intrinsic structural properties (such as its microporosity, the specific area developed in porous structures) and the chemical properties (especially with chemically activated rice husk char) of the surface (such as hydrophobicity, the presence of basic functional groups, and aromaticity) [31,32]. Wheat bran (agricultural biomass) combustion experiments provided fly ash and bottom ash fractions (which were also further arranged into pellets), which were investigated at different temperatures with respect to CO$_2$ adsorption abilities (without any thermochemical activation). The bottom ash demonstrated a higher maximum adsorption capacity when pelletized, 0.07 mmol CO$_2$/g, and non-pelletized, 0.06 mmol CO$_2$/g (25 °C). Moreover, the physical CO$_2$ adsorption mechanism was identified for bottom ash, but the in case of fly ash, the physical and chemical adsorptions of CO$_2$ were reported [23].

Some of the potentially advantageous and rationally selected combinations of component materials may be ash from biomass combustion combined with layered aluminosilicate, such as halloysite or kaolinite. It should be emphasized that such a composition of ingredients is environmentally inert and complies with CE rules. Due to its fragmentation, ash can provide an appropriately developed specific surface, enabling an appropriate exposure of halloysite particles, the unique nanostructure of which allows the achieving of a desired selectivity in the defined process system.

One should also pay attention to important ecological aspects related to the possible current use of ash produced in relatively large amounts. In addition, halloysite or kaolinite, as nano-structural additives, can be added to biomass during combustion, where, under high temperature conditions, it has a positive effect on the process itself, preventing slag formation and significantly affecting the characteristic temperatures of thermal ash conversion. Under such synthesis conditions, original and highly porous ash spatial structures with embedded halloysite or kaolinite particles, with unique adsorption properties, can be directly used as adsorbents. This allows for a synergistic effect in the production of adsorbents in the closed-loop, “cascade” scheme of the CE process.

Halloysite itself also has CO$_2$ adsorption properties, which was confirmed by the work of other authors. Among the various aluminosilicates, geopolymers represent amorphous compounds, formed at 30–90 °C using alkaline treatment of selected natural minerals, as well as of industrial wastes [33]. It has been experimentally proven that geopolymers synthetized based on K-silicate and metakaolin [34] show significant CO$_2$ adsorption (0.27–0.29 mmol/g), together with a relatively high selectivity (>100), considering CO$_2$/CH$_4$ or CO$_2$/$N_2$ reference systems. However, thermally (calcinated) or chemically (acid treatment) modified halloysite, with relatively low initial adsorption properties, can be improved using some surface modification methods; the adsorption rate is high, and over 85–89% of the CO$_2$ adsorption capacity is reached within 7–16 s [35]. In addition, EDTA surface-modified halloysite shows some limited effects towards increasing the CO$_2$ adsorption capacity, especially at low pressures (up to 3 MPa) [36]. In other work, the gravimetric method was used for CO$_2$-sorption isotherm determination (0–1.5 MPa, 313 K), resulting in adsorption capacities of 0.54–0.63 mmol/g [37].

Other authors have reported similar observations. In particular, halloysite nanotubes (HNTs) were investigated with respect to CO$_2$ adsorption parameters. Two amine-
functionalized HNTs, (3-aminopropyl)triethoxysilane (APTES)-grafted HNTs and polyethyleneimine (PEI)-impregnated HNTs, were considered, resulting in 0.15 (APTES-HNTs) and 0.21 (PEI-HNTs) millimoles of CO$_2$ adsorbed per millimole of amine group. Stable working conditions were reported for the adsorbent after ten CO$_2$ adsorption/desorption cycles, confirming the advantageous inherent structural features of HNTs as an essential part of CO$_2$ capture system [38]. Another study on (PEI)-impregnated HNTs also provided advantageous results (the highest CO$_2$ adsorption capacity was 156.6 mg/g-PEI and the optimal adsorption capacity was 54.8 mg/g-adsorbent), with a high stability at 80 $^\circ$C, good reversibility, and stability during the cyclic adsorption–regeneration mode of operation [39].

The examples presented above show that it is reasonable to combine the unique structures of halloysite and ashes from the combustion of straw biomass in a novel way. Such a combination can already be obtained before the biomass combustion process, when alumino-silicate addition allows, apart from the beneficial effect on the overall combustion process, the formation of advantageous and complex adsorbent structures at high temperatures for selected target applications. Nevertheless, such systems should be subjected to experimental verification before practical application so that the possibility of a purposeful, direct or indirect, influence (type of additive, proportion, set of parameters of the combustion process of straw with additives) on the resulting complex synergy effects in the adsorptive removal of CO$_2$ is identified based on the characteristic surface produced in the defined process conditions.

The changes taking place in current EU economic policy, mainly conditioned by considerations of environmental protection, created the necessity to introduce technological changes in the energy sector. The implementation of the clear objectives of a circular economy (CE) strategy requires, above all else, an innovative and comprehensive structural approach to both the conditions of combustion processes and, at the same time, it needs to be fully ecological and economic, providing secondary measurable benefit management of combustion by-products. This approach is generally characterized by the organization of a so-called closed loop or “cascade sequence” of subsequent technological processes, in which waste from previous processes is directly used as a desired raw material in subsequent stages. This type of thoughtful, multi-stage reuse of post-production waste from each technological stage enables a global reduction in the post-production waste stream that is otherwise introduced into the environment. Another beneficial effect of the CE stretch is the minimization of the consumption of virgin raw materials (which are necessary only for supplementation of the stream of recycled raw materials) and the energy required for only technological adjustments of the properties of the substrates (mainly purification) as opposed to the full production cycle, based on the virgin natural resources.

The authors, taking into account the EU framework strategy, focused their research on complex combustion processes of biomass, a fuel that has become more popular in the energy sector all over the world (energy “mix”). In particular, they identified the beneficial effects of certain additives, not only on the overall complex combustion process, but also on the increase in the adsorption properties of the solid residues (ash) formed under the combustion conditions, which directly enabled their further useful application. These ashes not only cease to be a waste, which is harmful to the natural environment, but they also have a positive effect on the state of the atmosphere, contributing to a global reduction in the dynamics of processes affecting global warming. The multi-directional optimization of biomass-combustion processes through targeted introduction of nanostructured additives (layered aluminosilicates), not only allows for an improved combustion course, but also creates an environment of favorable chemical thermoconversion for these additives along with non-flammable fractions of the biomass that is burned for the synthesis of new adsorptive materials. Formally categorized as waste products, these can potentially be widely used due to there being virtually no cost of production. According to the authors’ idea, this type of adsorbents can be widely used, especially in regions of the world where economic factors inhibit the implementation of effective, but expensive, carbon dioxide sequestration technologies, and where the energy sector is based on local inexpensive
biomass resources. The presented method makes it possible to simultaneously solve both the problems of the reduction of CO\textsubscript{2} emissions and the potential threat related to the accumulation of permanently increasing amounts of biomass ashes. The presented technological approach, demonstrated for straw biomass, can also be successfully adapted for other types of biomass, through individual identification of the most favorable conditions for the thermal synthesis of sorbents, ensuring, at the same time, optimal conditions for the exothermic reaction of biomass combustion. In addition to proposing specific areas of application for such an environmentally safe material, in the future, this technology may also enable the effective management of large amounts of this type of post-industrial waste, which, for example, are originally designed substitutes for mineral materials.

A new CE approach in the energy economy focuses on multi-criteria optimization of combustion technology. This forces the inclusion of LCA aspects in a broader, multi-faceted assessment of integrated processes, in particular due to their environmental balance. Often, when quantifying the requirements of the individual properties of recovered products, different, sometimes non-obvious “weights” are assigned to evaluation criteria. However, these reflect a broader, deeper view, taking into account the multidimensional nature of the complex problem. In the discussed case, even a smaller unit of adsorption capacity for such a product can be successfully overcompensated by considering its widespread availability and very low (practically zero) cost, taking into account, e.g., the benefits of avoiding waste management costs.

This paper presents an original investigation of the possibility of using such a defined (not presented earlier in accessible literature) system of biomass-derived ash (common straw was chosen since it represents agricultural waste) halloysite (or kaolin) as a potential “combined” proecological adsorbent for CO\textsubscript{2} separation and storage under high-pressure conditions (process intensification aspect). Agricultural straw, after combustion, gives rise to ashes with specific properties and adjustable chemical compositions, which can become a fully functional and are relatively inexpensive, proecological CO\textsubscript{2} adsorbents, which are environmentally inert and allow, in accordance with CE principles, to subject the by-products of combustion to a targeted functionalization (during the combustion process) in order to reuse them in the CE “cascade” processes.

It should be also emphasized that the “self-functionalization” of the production of process-beneficial adsorption structures with the incorporated nano-structural additives that are responsible for advantageous changes in chemical affinity of the surface, already takes place during the combustion process of straw with these additives (thermochemical surface reactions system), when functionalized under the conditions of a high-temperature process, in accordance with general circular economy guidelines. The authors emphasize that the paper presents only promising preliminary research results, which, however, illustrate the general idea of the presented two-stage (“combustion-adsorption”) technical solution sufficiently well. To increase the unit CO\textsubscript{2}-adsorption capacity, more extensive research should be carried out at various process scales to better identify the synergy effects of combustion and the synthesis of ash-additive structures, characterized by a possibly higher unit CO\textsubscript{2}-adsorption capacity.

2. Materials

2.1. Straw Biomass

Straw biomass was chosen due to its universal availability, wide application as biofuel in the energy generation sector, and the need to develop a process in accordance with the principles of the EU’s “green deal”. Straw is not a desirable material for anaerobic fermentation in biogas plants (its natural lignin–cellulosic structure provides technological problems in terms of preprocessing, based mainly on the steam explosion process requiring special design solutions, ensuring a high level of operational safety); thus, its spontaneous decay under natural conditions generates uncontrolled emissions of greenhouse gases. For this reason, its use in the alternative combustion process is justified, both ecologically and economically, and finding alternative mass applications for its ashes is, thus, of key
importance for this CE strategy. Taking these aspects into account, our research was focused on identifying the CO$_2$ adsorption abilities of straw biomass ashes.

The basis for the combustion process of common straw, and the ash adsorption tests with and without fuel additives, was agricultural biomass in its original form as ground straw pellets. In order to identify the properties of the fuel, technical and elemental analyses were done (central laboratory in ENERGOPOMIAR, Gliwice, Poland), the heating value was determined and ash oxide analysis was performed using the ICP-OES method. The results are presented in Table 1.

Table 1. Elemental composition of straw biomass used as a fuel.

| Element | wt.%           |
|---------|----------------|
| Silica  | 73.60 (as SiO$_2$) |
| Calcium | 8.54 (as CaO)   |
| Potassium | 8.53 (as K$_2$O) |
| Phosphorus | 1.46 (as P$_2$O$_5$) |
| Aluminum | 1.30 (as Al$_2$O$_3$) |
| Sulfur  | 1.17 (as SO$_3$) |
| Magnesium | 0.99 (as MgO)  |
| Iron    | 0.73 (as Fe$_2$O$_3$) |
| Sodium  | 0.21 (as Na$_2$O) |
| Titanium | 0.10 (as TiO$_2$) |
| Manganese | 0.05 (as Mn$_2$O$_4$) |
| Strontium | 0.04 (as SrO)  |
| Barium  | 0.03 (as BaO)   |

The other properties of the common straw fuel are as follows. The roasting loss (LOI, based on weight method) was 3.10%. Concentration of chlorides was 0.22 wt.% (as Cl), carbonates—1.61 wt.% (as CO$_2$) identified with combustion method with IR detection. Total organic carbon content (TOC) was—1.42% (based on calculation method). Total moisture (for working state) was 7.4 wt.%, whereas for ash (dry state) it was 8.26 wt.%. Heats of combustion were as follows: dry fuel—18,060 J/g, raw fuel—16,720 J/g. Their calorific values were: dry fuel—16,790 J/g, raw fuel—15,370 J/g. Also contents of the following elements were identified (wt.%): carbon (C) 45.60, hydrogen (H)—5.81, nitrogen (N)—0.43, total sulfur (S)—0.07, chlorine (Cl)—0.086, inorganic carbon < 0.01. Characteristic ash melting temperatures were: SST—830 °C, DT—1010 °C, HT—1260 °C, and FT—1330 °C.

2.2. Additives—Halloysite and Kaolinite

To obtain environmentally inert sorbents, and, at the same time, integrate the process of biomass combustion with the simultaneous thermosynthesis of sorption materials (unique composition of the obtained ash mixtures), layered alumino-silicates were selected.

The fuel additives used, the main task of which was to influence the combustion process and the properties of the process by-product (fuel), were alumino-silicates: kaolin and 3 types of halloysite—as a raw mineral directly and after two different pretreatment methods (drying or calcination). Kaolin is available on the market in a pure form (99.99% purity), whereas halloysite differs in composition and processing technology. An approach was applied that was in line with the CE philosophy recommending the organization of a kind of closed-loop “cascade” of subsequent processes. In these defined loops, it is necessary to properly design and manage technological processes so as to use the resulting by-products as useful raw materials, as much as possible, in subsequent stages of production processes. This makes it possible to achieve a substantial reduction in the
global stream of post-production waste, while advantageous minimizing the need for virgin fossil and natural resources.

During technological application of both aluminosilicates as biomass (straw) fuel additives, a number of positive properties were identified, both in relation to boiler operation conditions and the post-process residue quality. One of the identified advantages is their ability to capture alkali metals (sodium and potassium) and heavy metals in the thermochemical process environment [40].

The mentioned additives are also responsible for the increase in AFT temperatures (characteristic ash phase transition temperatures) [41], which is regarded as being very advantageous with respect to the combustion process, effectively limiting the tendency of ash to contaminate the heating surfaces of an industrial boiler [42].

In its raw form, halloysite has additional layers of water molecules \( (\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \times 2\text{H}_2\text{O}) \), distinguishing it from kaolinite \((\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4)\); moreover, there are also differences in their structures. Nanotubes are observed in the structure of halloysite, whereas a nanoplate structure is more specific to kaolinite. Nevertheless, both alumino-silicates demonstrate an extensive specific surface area and can be considered very good sorbents. It should be noted, however, that while kaolinite, in its commercial form, appears to be a product of high purity (the manufacturer declares 99.99% purity), halloysite, especially that described in this study as raw halloysite (RAW), shows numerous admixtures of other chemical compounds, in particular iron oxides, which are responsible for its color properties and physicochemical characteristics [43,44].

An analysis of the particle size distribution of straw particles before combustion was carried out based on the image volume analysis method, using a Sympatec GmbH QUICPIC instrumental analysis apparatus.

The three respective statistical parameters of the volumetric size distribution \( (d_{10}, d_{50}, \text{ and } d_{90}) \) for the straw provided by the above-mentioned method are, respectively:

\[
\begin{align*}
    d_{10} &= 209.5 \, \mu \text{m}, \\
    d_{50} &= 531.2 \, \mu \text{m}, \\
    d_{90} &= 1101.6 \, \mu \text{m}.
\end{align*}
\]

With regard to the straw (mineral) additives introduced into the combustion process, the particle sizes of each additive sample were within the 0–100 \( \mu \text{m} \) range fraction. Due to the particle sizes, it was possible to effectively premix the fuel sample with the mineral additive before the combustion process.

3. Methods

3.1. Biomass Samples Preprocessing

Experiments included nine ashes, derived from the incineration of:

- Pure straw biomass (denoted as S-UPS);
- Straw biomass with addition of 2 and 4 wt.% raw halloysite (HalRaw2 and HalRaw4);
- Straw biomass with addition of 2 and 4 wt.% dried halloysite (HalDry2 and HalDry4);
- Straw biomass with addition of 2 and 4 wt.% calcined halloysite (HalCalc2 and HalCalc4);
- Straw biomass with addition of 2 and 4 wt.% kaolinite (Kao2 and Kao4).

First, the biomass samples were properly prepared for the incineration process. These were blended in an appropriate proportion with fuel additives, and were kaolinite, raw halloysite (mineral), dried halloysite, and calcined halloysite. Weighted amounts of additives were added to previously weighed samples of fragmented agricultural biomass.

The weighing process was carried out using a RADWAG AS 220.R2 balance with a measurement precision of 0.0001 g. Then, the mixtures prepared in this way were introduced into string bags, where the blending process took place over 10 min so that each sample attained full homogeneity. The samples obtained this way were then inserted into ceramic vessels that were suitable for the incineration process. The ashing process was performed in an FCF 22HM muffle furnace at a temperature of 550 °C, according to current norms [45–53].

The process consisted of two stages:
- Heating the furnace with the samples from 25 °C up to a final temperature of 550 °C for 90 min with a constant supply of air (drying and degassing stage);
- Incineration at 550 °C with a constant air supply and periodic mixing of the sample for approx. 3 h (residue combustion stage).

All nine samples were prepared using identical methods. The incinerated samples were cooled down in a drying cabinet to a temperature of about 100 °C, packed into string bags, and then stored in a desiccator until they were used in the laboratory adsorption tests. Before packing, samples were weighed using a RADWAG AS 220.R2 balance. Optimization of the complex processes of straw biomass combustion, in particular the purposeful and rational integration of the improvements in the energy process with the simultaneous synthesis of porous solid waste products with adsorption properties based on straw biofuel and its additives (halloysite, kaolinite), is a new area of research in the developing the inexpensive sorbents that can be directly used on a mass scale in industry, where economic factors significantly inhibit the introduction of more effective, but also much more expensive, adsorption technologies.

3.2. High-Pressure Adsorption Stand

The stand for the adsorption tests consisted of two independent measuring lines, in which it was possible to perform sorption measurements of two different powder materials, using the same type of gas at the same time, e.g., as in this carbon dioxide adsorption analysis. In order to maintain isothermal conditions, the setup was placed in a water bath. After each sample/pressure change, etc., the system was stabilized to achieve a temperature of 30 °C, thus possibly eliminating pressure–temperature effects. Each of the measuring lines consists of three volumes, which are separated from each other by valves.

The first volume is the volume common to both measuring lines, and is the volume to which the gas or vacuum source is connected; it is the only volume that can exchange mass with the external environment and there is a shut-off valve and a gas connection.

The second volume is the reference volume (the so-called reference cell), which is characterized by a known volume and enables the calculation of the amount of gas supplied to the system, along with its known parameters (pressure, temperature).

The third volume is the sample cell (), which includes a piece of conduit and a tank containing powdered material subjected to the physical adsorption tests. In the reference volume and in the sample volume there are KELLER-DRUCK X33 pressure transducers (0.05% full scale accuracy) with digital temperature compensation, connected to a data acquisition system that records pressure readings every 5 s using CCM software that allows it to be determined with an accuracy of 0.001 bar.

The entire system is located in a water bath with a heater to keep a constant temperature during the measurements and to isolate the measuring volume from the external environment. A water bath also eliminates leaks, as air bubbles indicate where leaks occur. Due to the constant temperature of the water bath, it may be assumed that the entire process is isothermal. In the reference volume and in the volume in which the measuring sample was placed, temperature was also measured in order to control the achievement of steady-state conditions, and thus ensure the isothermal nature of the entire process. Due to its properties, helium (an inert gas) was used to identify the so-called void volume, i.e., the volume between the valve and the measuring cell into which the analyzed powdered material was placed. The calculation of this volume allowed for the complete dimensioning of the system, which is the basis for measuring gas component adsorption by the solid phase. The stand was also equipped with a vacuum pump with which the gas was removed from the measuring volume after termination of the measuring series, and a vacuum was then established before the start of the measuring series in order to remove air from the system, which could adversely affect the sorption process itself since it contains chemically reactive elements, i.e., oxygen, and would also change the gas density depending on the temperature (in the case of a known gas, helium, this can be determined using the ideal gas state equation).
Both pressure transmitters and temperature transmitters were connected to a meter displaying the values in real time, which transmitted the data streams to a data acquisition system.

The professional laboratory-accurate KELLER-DRUCK pressure transducers with digital temperature compensation allowed accurate measurements, which, in combination with the adequate and accurate equations of state (such as Span–Wagner for CO$_2$) and class 1/10B Pt100 temperature sensors ($\pm 0.03$ °C accuracy) provided the highest possible technical accuracy.

Therefore, with this range of pressure, the accuracy of the measured values should not exceed a $\pm 0.5\%$ error for the maximum sorption effect. Moreover, the authors would like to note that the error increased in higher-pressure ranges, mainly due to the transformation of CO$_2$ into a supercritical state.

3.3. Adsorption Experimental Procedure

Ashed and weighed samples that were protected against atmospheric moisture were placed in measuring volumes, and the whole system, after assembly and sealing, was placed in a water bath with a constant temperature of 30.15 °C. The system was pre-tested under overpressure in order to identify and eventually eliminate some possible leaks. The next step was to remove the nearly total amount of gas from the system and bring it into a defined partial-vacuum state (called “technical vacuum”). At this stage, it was possible to re-check whether the system was tight, and the conditions were maintained at a constant underpressure for 2 min.

Helium was injected into the volume with the measuring volume was cut off using the valve, which, after stabilizing the parameters and using the known volume of the reference cell, allowed calculating the mass. Then, the valve between the measuring cell and the reference cell was opened, helium then accumulated in the reference volume and filled the entire system, and it was then possible to determine the volume of the measuring cell on the basis of the observed pressure drop. To accurately determine the volume of the measuring cell, the above process was repeated three times. The measuring volume was shut off using a valve, an additional amount of helium was pumped into the reference volume, increasing the pressure in the entire system, and then the valve between the two volumes was opened. For each measurement step, the volume of the measuring cell was determined using the ideal gas equation (due to the relatively low pressure), and the measuring volume was then determined as the arithmetic mean based on all steps results.

After dimensioning the system according to the procedure described above, a technical (partial) vacuum (0.003 mbar) was once again established to remove the helium from the measuring system and empty the pore volume in the ash structure. Carbon dioxide formed in this way was injected into the system, using the measuring cell cut off by the valve, and then, after the parameters stabilized (pressure, temperature), the valve between the two volumes was opened. Opening the valve caused a pressure drop in the entire system and started the process of physical sorption of carbon dioxide by the powdered material under analysis. The pressure drop in the system progressed over time, which enabled the determination of the adsorption rate. Due to its physical nature, the greatest rate of the adsorption process occurred in the first seconds or minutes after the valve was opened, followed by stabilization and a further slow adsorption run. Based on the observations and the adsorption rate data, it was decided that the measurement time from the moment of opening the valve would be 1 h, due to the stabilization of the adsorption process, as well as the possible occurrence of micro-leaks (that were imperceptible to the human eye) of gas over a longer period of time.

The measurement procedure described above was repeated for each sample (nine times) to obtain several measurement values in the range of absolute pressure up to 11 bar (overpressure of 10 bar). As a result, it was possible to determine the equilibrium amount of adsorbed carbon dioxide per 1 g of sample (adsorbent) as a function of CO$_2$ pressure equilibrium at a constant temperature.
For both measuring lines, the values of the reference space volumes (reference cell, RC) were determined, and were 151.382 cm$^3$ (RC1) and 154.039 cm$^3$ (RC2), respectively; these were determined as a constructional constant – intrinsic parameter of the laboratory test stand. After stabilizing the parameters based on pressure, temperature, and $z$ parameter (compressibility factor), the number of moles of He in the measuring volume was (1) \[54\]:

$$n_{He} = \frac{pV_{ref}}{T(MR)z}$$ \hspace{1cm} (1)

where $V_{ref}$ is the reference volume (m$^3$), $p$ is the absolute pressure (Pa), $T$ is the temperature (K), $MR$ is the universal gas constant with a value of 8.314472 (kJ/kmol/K), and $z$ is the thermodynamic compressibility coefficient.

When the pressure and temperature stabilized after opening the valve dividing the measuring volume and the reference volume, the amount (number of moles) of gas in the measuring volume was calculated as the difference between the total amount of gas injected into the system, decreased by the amount that filled the reference volume at the new pressure and temperature (2):

$$n_{HeSC} = n_{He} - \frac{pV_{ref}}{T(MR)z}$$ \hspace{1cm} (2)

Knowing the amount of gas in the measuring volume, after stabilization of the pressure and temperature, it is possible to calculate the volume occupied by the gas, and thus determine the volume of the measuring cell (3):

$$V_{SC} = \frac{n_{HeSC}(MR)Tz}{p}$$ \hspace{1cm} (3)

In the case of the second and third measuring cycles, the amount of gas remaining in the measuring volume after closing the valve between the two volumes was taken into account in order to increase the pressure again and force another portion of gas into the reference volume. Hence for the 2nd and 3rd measurements, the initial gas amount was (4):

$$n_{He} = n_{HeSC} + \frac{pV_{ref}}{T(MR)z}$$ \hspace{1cm} (4)

Further calculations remained unchanged. The volume of the measuring cell was determined as the arithmetic mean of three measurements.

Since each sample had a slightly different weight and volume, the measurements of the void volume had to be repeated each time when the sample was placed—prior to the start of the experiment with carbon dioxide.

Carbon dioxide density, and thus its quantity, was determined on the basis of the gas equation of state \[55\].

Due to the determination of the amount of gas in the system and the known volume of the measuring cell, it was possible to determine the amount of gas adsorbed by the mineral substance, based on the pressure drop. The amount of adsorbed gas was determined as the difference between the total amount (mass) of gas in the system and the amount (mass) of gaseous carbon dioxide calculated on the basis of the pressure and temperature, 1 h after opening the valve (5):

$$v_{mol} = \frac{\rho CO_2}{M CO_2}$$ \hspace{1cm} (5)

where $v_{mol}$ represents the molar density (mmol/cm$^3$) and $M CO_2$ is equal to 44.0098 (kg/kmol). The total amount (number of millimoles) of carbon dioxide, $n_{tot}$, is (6):

$$n_{tot} = v_{mol}' V_{ref}$$ \hspace{1cm} (6)
The number of millimoles of free carbon dioxide, \( n_{\text{free}} \), after 1 h of the adsorption process is (7):

\[
n_{\text{free}} = \frac{V_{\text{ref}}}{V_{\text{mol}}} \left( V_{\text{ref}} + V_{\text{SC}} \right)
\]  

(7)

The number of millimoles of adsorbed carbon dioxide, \( n_{\text{adsorbed}} \) (8):

\[
n_{\text{adsorbed}} = n_{\text{tot}} - n_{\text{free}}
\]  

(8)

The number of millimoles of adsorbed carbon dioxide in relation to 1 g of adsorbent, \( n_{1g \text{adsorbed}} \) (9):

\[
n_{1g \text{adsorbed}} = \frac{n_{\text{adsorbed}}}{m_{\text{sample}}}
\]  

(9)

The individual steps in measuring the adsorption equilibriums and the schematic diagram of the laboratory pressure stand are presented in Figures 1 and 2, respectively.

**Figure 1.** The individual steps in measuring the adsorption equilibriums of porous materials through the use of a laboratory pressure stand.

**Figure 2.** Schematic diagram of the laboratory pressure stand for measuring the adsorption equilibriums of porous materials.

### 3.4. CO₂ Adsorption Isotherms

The obtained equilibrium data were analyzed theoretically using five adsorption isotherms: Freundlich, Langmuir, Jovanović, Temkin, and Hill (where \( q_e \)—specific equilibrium adsorption (mmol/g), \( P_{\text{CO}_2} \)—CO₂ pressure (bar), and the explanation of all parameters and constants in Equations (10)–(14) is presented in Table 2).
Table 2. The values of adsorption isotherm parameters according to the Freundlich, Langmuir, Jovanović, Temkin, and Hill models.

| No | Freundlich | Langmuir | Jovanović | Temkin | Hill |
|----|------------|----------|------------|--------|------|
|    | K_F | n | R^2 | q_L | K_L | R^2 | q_J | K_J | R^2 | B_T | K_T | R^2 | q_H | K_H | n_H | R^2 |
|----|-----|---|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1  | 0.01 | 1.04 | 0.981 | 1.79 | 0.008 | 0.982 | 0.92 | 0.016 | 0.982 | 34.70 | 0.57 | 0.975 | 0.34 | 30.81 | 1.29 | 0.983 |
| 2  | 0.02 | 1.01 | 0.994 | 5.04 | 0.005 | 0.995 | 2.54 | 0.010 | 0.995 | 22.30 | 0.66 | 0.958 | 0.54 | 31.04 | 1.36 | 0.998 |
| 3  | 0.03 | 0.99 | 0.995 | 13.62 | 0.002 | 0.995 | 7.99 | 0.004 | 0.995 | 16.40 | 0.66 | 0.957 | 0.71 | 32.04 | 1.40 | 0.999 |
| 4  | 0.02 | 1.04 | 0.982 | 1.75 | 0.012 | 0.984 | 0.89 | 0.023 | 0.984 | 29.30 | 0.89 | 0.997 | 0.20 | 18.99 | 1.29 | 0.998 |
| 5  | 0.04 | 1.19 | 0.998 | 1.15 | 0.034 | 0.999 | 0.65 | 0.060 | 0.999 | 19.20 | 0.83 | 0.970 | 0.77 | 21.44 | 1.11 | 0.999 |
| 6  | 0.02 | 1.15 | 0.993 | 0.77 | 0.028 | 0.995 | 0.43 | 0.050 | 0.996 | 29.10 | 0.64 | 0.991 | 0.33 | 20.08 | 1.31 | 0.998 |
| 7  | 0.04 | 1.22 | 0.996 | 1.04 | 0.039 | 0.998 | 0.65 | 0.060 | 0.999 | 17.50 | 0.69 | 0.989 | 0.69 | 19.16 | 1.14 | 0.999 |
| 8  | 0.03 | 1.04 | 0.988 | 2.83 | 0.011 | 0.990 | 1.45 | 0.021 | 0.990 | 18.40 | 0.67 | 0.972 | 0.46 | 26.72 | 1.59 | 0.998 |
| 9  | 0.03 | 1.02 | 0.993 | 47.43 | 0.001 | 0.995 | 2.89 | 0.012 | 0.994 | 16.00 | 0.67 | 0.966 | 0.64 | 28.58 | 1.45 | 0.999 |

- Freundlich (10) [56–63]:
  \[ q_e = K_F P_{CO_2}^{1/n} \] (10)
- Langmuir (11) [56–63]:
  \[ q_e = \frac{q_L K_L P_{CO_2}}{1 + K_L P_{CO_2}} \] (11)
- Jovanović (12) [58,61–65]:
  \[ q_e = q_J \left( 1 - \exp \left( -K_J P_{CO_2} \right) \right) \] (12)
- Temkin (13) [57,58,63,66,67]:
  \[ q_e = \frac{RT}{B_T} \ln \left( K_T P_{CO_2} \right) \] (13)
- Hill (14) [58,68]:
  \[ q_e = \frac{q_H P_{CO_2}^{1/h}}{K_H + P_{CO_2}^{1/h}} \] (14)

3.5. Ash Structural Analysis

Particulate solid samples of the resulting ashes were characterized off-line via electronic environmental scanning microscopy (ESEM Quanta 200 FEI, THERMO FISHER SCIENTIFIC Inc., OR, USA). Images were taken of uncoated samples, at a working distance of 22.7 mm and using a 5.0 kV voltage, at the Institute of Science and Technology for Ceramics, CNR-ISTEC, Faenza, RA, Italy.

A mercury intrusion porosimeter (MIP), with a surface tension of 0.48 N/m and a contact angle of 140° (Thermo Finnigan Pascal 140 and Thermo Finnigan Pascal 240) was used to analyze the pore size distribution of the bulk materials, in the range of 5.8–100,000 nm.

Specific surface area measurements (SSA) were performed on powder samples using a Thermo ScientificTM Surfer instrument and they were calculated using the Brunauer–Emmet–Teller (BET) method by means of nitrogen adsorption at 77 K.
4. Results and Discussion

The experimental equilibrium data in a pressure (bar) adsorption equilibrium capacity (mmol/g), for all nine ashes investigated, are presented in Figure 3.

Figure 3. The experimental CO₂ adsorption equilibrium data in a $P_{CO2}$ (bar)—adsorption equilibrium capacity $q_e$ (mmol/g).

The parameter values obtained for each isotherm model ((10)–(14)) and for each ash type are presented in Table 2. The calculations were done using a professional adsorption-oriented scientific calculator, CAVS—Adsorption Evaluation software [69].

4.1. Results of Microstructure, Porosimetry and Specific Surface Area Investigations

For the selected samples, namely the reference ash S-UPS, HalRaw4, and Kao4, instrumental characterization was done to explain the observed differences in CO₂ adsorption capacity.

Scanning electron microscope (SEM) images, obtained at two different magnifications, are presented and compared in Figure 4. The fibrous shape of the straw ash clearly appears in all three images at a magnification of 250× as a consequence of the chemical conversion of straw; of course there was an anisotropic and elongated cell configuration. However, a deeper inspection of the images of the samples with additives (HalRaw4 and Kao4) in Figure 4b,c highlights the presence of other particles, also adhering to the biomass fibers, likely due to the additives present in the fuel. This is well evident for Kao4 (Figure 4c).

The volume distributions of the pores in the adsorbent samples based on straw biomass ash with nano-structural additives are shown in Figure 5. The size distributions for pores over 0.1 µm were similar for the three samples, while HalRaw4 (Figure 5b) and Kao4 (Figure 5c) exhibited a greater number of pores between 0.01 and 0.1 µm. The higher amount of mesoporosity is attributable to the presence of nano-structured additives with a beneficial effect on mass transfer and adsorption phenomena. In turn, for straw ash (Figure 5a), the cumulative pore volume is slightly higher, i.e., 1850 mm³/g, compared to 1650 and 1520 mm³/g for HalRaw4 and Kao4, respectively.
Figure 4. SEM images of the obtained adsorbent samples based on straw ash with the nano-structural additives (magnification 250× and 500×): (a) S-UPS; (b) HalRaw4; and (c) Kao4.

The true density (\(\rho\)) and the specific surface area (SSA) of the adsorbent samples, based on straw biomass ash, are reported in Table 3. As can be seen, although the true density is very similar for all samples (2.42–2.54 g/cm\(^3\)), the comparison turns out to be largely...
favorable for those containing halloysite (HalRaw4) and kaolinite (Kao4), with an SSA value around 5-fold higher than that of raw straw ash (S-UPS). This result is congruent with the already reported findings about mesoporosity; the greater the number of smaller pores, the larger the SSA.

Table 3. True density and specific surface area (SSA) of the obtained adsorbent samples based on straw biomass ash with nano-structural additives: S-UPS; HalRaw4; and Kao4.

|          | True Density, g/cm$^3$ | SSA, m$^2$/g |
|----------|------------------------|-------------|
| S-UPS    | 2.42                   | 12.31       |
| HalRaw4  | 2.54                   | 63.55       |
| Kao4     | 2.49                   | 65.84       |

Figure 5. Cont.
A new, CE-compliant approach for designing possibly waste-free technologies, with the “cascade” use of waste products from each subsequent stage, changes the current priorities of economic analysis, which will increasingly be based on decisions that take into account the complex influence of many factors, which, only when considered together, show a full understanding of the problem (for example, for the cheap CO₂ sorbent in question the question might be a lower unit sorption capacity, but, at the same time, positive aspects such as adsorbent availability, adsorbent price, integration of adsorbent production technology with the local energy plant structure, significant environmental benefits, postprocessed waste storage costs, etc., exist). Only a comprehensive analysis of the problem will possibly enable a rational and optimal choice of technological solutions.

This should enable the management of large streams of this type of mass waste from the energy industry in the future. This type of waste can become a real substitute for, inter alia, mineral materials of fossil origin, which is an equally important problem for environmental protection. When analyzing the direct measurement data of the CO₂ adsorption equilibrium conditions established in the tested systems, and presented in Figure 3, it can be noticed that the introduction of nano-structural additives, in the form of both halloysite (raw, dried, calcined) and kaolinite, into the combustion system of the biomass (straw) increase the capacity of CO₂ adsorption of the combustion by-products. Therefore, these additives, not only have a positive effect on the straw combustion process itself, but also later, by producing certain structures of combustion by-products (ashes), under high-temperature process conditions, enabling a more effective sorption of CO₂.

The most visible effects of the influence of additives of the combusted biomass on the produced adsorbent structures corresponded to the maximum values of carbon dioxide pressure during the tests (ca. 10 bar). In relation to the adsorption capacity of ashes derived from the combustion of only pure straw (without additives reference system), for which the equilibrium concentration of the adsorbate on the sorbent was 0.131 mmol/g; in some cases, a favorable increase in this value, even up to 0.321 mmol/g, was observed, i.e., by as much as 145% (corresponding to 4 wt.% addition of kaolinite to straw). On the other hand, 2 wt.% addition of kaolinite increased the adsorption capacity of the ash modified in this way up to 0.276 mmol/g (an increase of 111%).

In addition, the alternative introduction of halloysite into the straw biomass combustion process increases the adsorption capacity of the thus-obtained ash with nano-structured additives in relation to CO₂. In the case of raw halloysite, its 2 wt.% addition to the burned
straw made it possible to improve the sorption capacity of CO$_2$ by up to 0.229 mmol/g (increase by about 75%); doubling the dose of raw halloysite (4 wt.%) resulted in a higher effect of 0.310 mmol/g (increase by about 137%).

Dried halloysite in an amount of 2 wt.% additive allowed obtaining the lowest effect of improving the adsorption capacity of straw ash (0.165 mmol/g, an increase of only about 26%). However, increasing its addition to 4 wt.% led to a relatively high value of 0.288 mmol/g (an increase of about 120% in relation to pure straw ash).

Subjecting halloysite to the calcination process increases the adsorption capacity of the obtained mixture by up to 0.200 mmol/g (2 wt.% additive showed an increase of about 53%) and 0.298 mmol/g (4 wt.% showed an increase of over 127%).

When analyzing the quality trends in the dataset, it can be noticed that, for both analyzed amounts of the introduced additive 2 and 4 wt.%, the best results for the adsorption capacity of the enriched ash, with respect to CO$_2$, were obtained in the case of raw halloysite. Calcination of halloysite prior to its addition to the straw combustion system in the energy generation sector significantly reduces the CO$_2$ adsorption capacity of the thus-obtained ash. After the halloysite drying process, such an additive introduced into the technical combustion system resulted in the formation of ash with worse adsorption properties. However, it should be emphasized, that both results were still higher than the reference value for ash without additives (0.131 mmol/g).

It was also clear, that improved CO$_2$ adsorbents could be obtained using ash from the combustion of straw biomass, together with appropriate nano-structured species, and can be obtained using 4 wt.% additives: kaolinite (0.321 mmol/g), raw, calcined and dried halloysite (0.288–0.310 mmol/g) and a 2 wt.% addition of kaolinite (0.276 mmol/g). Raw and preprocessed halloysite thus represent an “intermediate” CO$_2$ adsorption capacity, limited by the adsorption parameters of straw ash produced with the addition of 2 and 4 wt.% kaolinite, respectively.

In the case of lower values of CO$_2$ equilibrium pressure, the observed quality trends mostly coincided with the observations regarding the highest pressure value. Small deviations may have been due to the limited accuracy of the measurement data for lower pressures.

Theoretical interpretation of the experimental data was performed on the basis of the parameters of the adsorption isotherms.

The $R^2$ values for the four analyzed isotherm models: Freundlich, Langmuir, Jovanović, and Hill, were practically the same, in the range of 0.991–0.997. A clearly lower value for $R^2$ was observed in only the case of the Temkin isotherm model (0.975).

The values of the Freundlich isotherm parameters (used to model non-ideal adsorption on surfaces with a heterogeneous structure) relate to both the adsorption capacity ($K_F$) and the intensity of the process. Higher values of the $K_F$ parameter indicate a higher affinity of the adsorbent to the adsorbate. When analyzing the $K_F$ values, it can be seen, that all ashes with additives were characterized by significantly higher $K_F$ values (0.021–0.045) than the $K_F$ value corresponding to the reference system (ash from burning pure straw, 0.015). Thus, the positive effect of the addition of halloysite or kaolinite on the adsorption surface structure of the produced ash, which increased its affinity to CO$_2$, is clearly visible. In the case of dried and calcined halloysite, increasing the amount of nano-structured additive (from 2 to 4 wt.%) caused an almost two-fold increase in the $K_F$ parameter value (and, thus, the represented affinity to CO$_2$). However, in the case of raw halloysite, this effect did not exceed 50%.

The data in Table 2 show that, in the case of a 2 wt.% halloysite dose, the level of affinity of the adsorbent structure to CO$_2$ was practically constant (0.021–0.024). Only increasing its dose up to 4 wt.% clearly increased the affinity of the dried (0.045) and calcined (0.043) halloysite in comparison to the raw halloysite (0.032).

In the case of kaolinite, its addition in the amount of 2 wt.% caused more than a two-fold increase in affinity to CO$_2$ compared to ash from the combustion of pure straw
Nevertheless, a further increase in the amount of additive (twice up to a value of 4 wt.%) caused a minimal increase in the value of the $K_F$ parameter (up to 0.034).

The analysis of the second parameter of the Freundlich isotherm, representing the intensity of the process, the exponent $1/n$ (the range $0.1 < 1/n < 1$ indicates favorable conditions for adsorption) is also important. An increase in the value of $n$ (i.e., a decrease in the value of $1/n$) is favorable in terms of CO$_2$ adsorption. In the case of raw halloysite, irrespective of dose (2 and 4 wt.%), the value of $n$ fluctuates around 1, indicating a boundary, but they were still favorable conditions for the process. The same applied to 2 and 4 wt.% of kaolinite dose relative to the burned straw biomass. The effect of improving the conditions of the adsorption process along with the increasing dose of additive was only clearly visible in the case of using nano-structured additives, the calcined and dried halloysite.

For $n = 1$, a concentration-independent partition between both contacting phases was observed. Normal adsorption is indicated by $1/n < 1$, whereas $1/n > 1$ suggests a cooperative adsorption.

Since $1/n$ may be also interpreted as a heterogeneity parameter, a smaller $1/n$ thus represents greater expected heterogeneity (with the linear adsorption isotherm for $1/n = 1$). For $1 < n < 10$, a favorable adsorption intensity is indicated.

It should be noted, for all nine tested adsorbents (in the form of thermally co-modified ashes with the additives) that this parameter showed a relatively low variability ($n = 0.995–1.225$). Nevertheless, some clear differences indicated a noticeable increase in the degree of heterogeneity of the adsorbent structures’ ashes, resulting from the combustion of straw and additives: 2 wt.% dried halloysite ($n = 1.155$), 4 wt.% calcined halloysite ($n = 1.192$), and 4 wt.% dried halloysite ($n = 1.225$), in relation to the reference level determined by ash from the combustion of pure straw (where $n = 1.040$).

The Langmuir isotherm model, based on the assumption that there is no interaction between the adsorbed molecules, states that one layer is formed and that the adsorbent can precisely show a defined number of active sites for the adsorbate, enables the determination of, among others, maximum adsorption capacity of the tested structure. When analyzing the available maximum adsorption capacities according to the assumed monolayer model, it is clear that the highest value of this parameter corresponds to the addition of raw halloysite (5.037 mmol/g for 2 wt.% additive and as much as 13.621 mmol/g for 4 wt.%), calcined (1.754 mmol/g and 1.153 mmol/g, for 2 and 4 wt.% addition to straw, respectively), and the dried one (0.775 mmol/g and 1.041 mmol/g, for 2 and 4 wt.% addition). It should be also noted, that this corresponds to the trends observed directly in the experimental data (Figure 3).

By analyzing the results of calculations using the so-called separation factor, $R_L$, which is an additional characteristic parameter of the Langmuir isotherm model, is defined as (15):

$$R_L = \frac{1}{1 + K_L P_{CO_2 \text{initial}}}(15)$$

and taking into account individually determined initial CO$_2$ pressure for each case ($P_{CO_2 \text{initial}}$) from each measurement series, the values of separation factor $R_L$ were determined for each of the nine obtained ash adsorbents. Based on the Langmuir theory, it follows that $R_L > 1$ indicates an unfavorable process condition of adsorption in the adsorbent–adsorbate system, which is linear when $R_L = 1$, and favorable conditions exist when $0 < R_L < 1$ is met. The adsorption process is irreversible when $R_L = 0$.

Based on the calculations, the following results were obtained. For the reference system (pure straw ash), from the measurement data for the initial CO$_2$ pressure in the range of 2.579–10.143 bar, the values of the $R_L$ parameters were obtained in the range of (with indication of the direction of change) $0.980 \rightarrow 0.925$ (six measuring points). The use of raw halloysite (2 wt.%) in the straw combustion process causes the formation of ash, which when used as a CO$_2$ adsorbent with an increase in its pressure in the range of 1.842–10.310 bar, is characterized by a corresponding change in $R_L 0.991 \rightarrow 0.951$ (seven test points). Its doubled increase (up to 4 wt.%) causes, that in the initial CO$_2$ pressure
range of 1.838–10.442 bar, the corresponding values of the \( R_L \) parameter to be 0.996 → 0.980 (seven test points). In the case of ash with the addition of calcined halloysite (2 wt.%), an increase in the initial pressure of the CO\(_2\), from 2.586 to 10.221 bar, caused the \( R_L \) parameter to decrease from 0.970 to 0.891 (six measuring points). However, the 4 wt.% dose in the range of the initial CO\(_2\) pressure of 1.672 → 10.745 bar caused a much greater reduction in \( R_L \), corresponding to the range of 0.946 → 0.732. The data corresponding to the addition of dried halloysite (2 wt.%) indicate that, by increasing the initial pressure of CO\(_2\) from 2.547 to 10.158 bar, the resulting change in the \( R_L \) parameter was reported in the range of 0.933 – 0.779 (six points). Increasing the dose of the dried halloysite up to 4 wt.% causes the obtained ash to be in the range of the initial CO\(_2\) pressure, from 2.649 to 10.500 bar, which is characterized by the \( R_L \) parameter changing in value in the range of 0.906 → 0.709 (six points). The use of 2 wt.% kaolinite as an additive to straw in the energy generation sector causes that the range of the tested initial CO\(_2\) pressure change from 1.800 → 10.613 bar, and the values of the \( R_L \) parameter showed a change of 0.981 → 0.895 (seven points). A two-fold increase in the concentration of this additive (4 wt.%) corresponds to the range of the initial pressure of the adsorbate (CO\(_2\)) 1.783 → 10.698 bar, and induces the following change in the \( R_L \) parameter value: 0.998 → 0.989 (seven points).

In all tested cases, a decrease in the \( R_L \) value can be noticed with an increase in the initial pressure of CO\(_2\), which suggests an increase in the favorable conditions of the adsorption process for increasingly higher adsorbate concentrations. However, the most pronounced effects of initial CO\(_2\) pressure increase on the improvement of CO\(_2\) adsorption conditions could be observed when using calcined and dried halloysite as straw burning additive (both as 4 wt.% doses); in these cases, the beneficial reductions in the \( R_L \) parameter values were 22.59% and 21.72%, respectively (although for the value predicted by the Langmuir model, the maximum sorption capacities of the monolayer are not the representatives of the highest values among the considered cases). A large, beneficial effect of initial CO\(_2\) pressure was also observed in the case of 2 wt.% addition of dried halloysite and the resulting effect in \( R_L \) reduction was 16.59%. Moderate effects were observed in the case of the following additives: 2 wt.% kaolinite with an 8.68% reduction in \( R_L \), 2 wt.% calcined halloysite with 8.16% and 2 wt.% raw halloysite with a 4.03% reduction (in the case of the reference system the selected ash from the raw straw combustion was comparable in terms of increase in the initial pressure of the adsorbate (CO\(_2\)) and caused a 5.60% decrease in the \( R_L \) parameter). For raw halloysite (4 wt.% dose to burning straw), only a 1.69% decrease in \( R_L \) was observed, whereas for the 4 wt.% dose of kaolinite, only a 0.88% favorable decrease in \( R_L \) value was identified.

When analyzing the data from Freundlich and Langmuir isotherm models together, it can be seen, for example, that by increasing the dose of the nano-structured additive (from 2 to 4 wt.%) in the form of calcined halloysite, an unfavorable decrease in the capacity of the adsorption monolayer determined according to the Langmuir isotherm model was observed from 1.754 to 1.153 mmol/g, while, according to the Freundlich isotherm model, it was related with a favorable, more than two-fold increase in the affinity of the adsorbent to CO\(_2\) (represented by \( K_F \)) and the intensity of the process (represented by parameter \( 1/n \)), which was clearly visible in the direct measurement data concerning the established adsorption equilibriums. Due to the practically identical \( R^2 \) values for both models, it was not possible to clearly indicate which adsorption mechanism took place in the analyzed experimental system. This also suggests a more complex, indirect mechanism of the process, taking into account the theoretical assumptions of both models and thus justifying a common theoretical interpretation of the parameters obtained from the analyses of both isotherm model parameters. One should also pay attention to the slightly different quality (\( R^2 \)) of the isotherm models for the reference system (represented by the ash derived from the pure straw combustion), which may affect the interpretation of the results of the adsorption equilibrium measurements.

The values of the maximum theoretical adsorption capacity were also determined independently from the Jovanović isotherm model (also based on some basic assumptions
of the Langmuir adsorption model, where it was also possible to take into account some mechanical interactions between the adsorbate particles involved in the adsorption and desorption processes and the adsorbate’s surface binding vibration), and then compare them with the values determined according to the Langmuir isotherm model. The qualitative correlations between the predictions of monolayer capacity provided by the Langmuir and Jovanović isotherm models are clearly outlined.

In turn, in the Temkin adsorption isotherm model, the \( B_T \) parameter is a model constant related to the heat of sorption (representing in the model adsorption energy, the positive value of which indicates favorable conditions for the adsorption process). The Temkin model is based on the assumption that the adsorption heat of all molecules in the layer decreases linearly with coverage and there is a uniform distribution of binding energies up to maximum binding energy level. Thus, the enthalpy of adsorption shows linear changes with adsorbate (CO\(_2\)) concentration.

In the Hill adsorption isotherm model, \( q_m \) represents some theoretical maximum adsorption capacity, whereas another parameter, \( n_H \), shows the Hill’s cooperativity coefficient of the binding interaction. According to the theory, adsorption is a cooperative process for \( n_H > 1 \). For all investigated cases obtained in the combustion process of straw-based adsorbents with additives (or without the reference system, Table 2), values of \( n_H > 1 \) were reported. \( n_H \) values higher than 1.286 ash from pure straw burning were observed for raw halloysite (2–4 wt.%) and the values are: 1.358 and 1.401, for the addition of 2 wt.% calcined halloysite (1.864) and the addition of kaolinite (2–4 wt.%). These are represented by the following values: 1.595 and 1.454, respectively.

In addition to estimation of the overall fitting quality (\( R^2 \)) of a given model (cumulative effect of all regression parameter values), the potential error contributions (in a statistical form of standard deviation) of the individual coefficients (parameters) of the given equation representing a specific theoretical model of the adsorption isotherm are also provided Table 4. In Table 5, the values of mean deviation (MD), mean square deviation variance (MSD), and root-mean square deviation (RMSD) for the measurement data modeled with all five adsorption isotherm models are presented.

The following definitions (16)–(18) were used:

\[
MD = \frac{\sum_{i=1}^{n} (x_{\text{exp}} - x_{\text{mod}})}{n} \tag{16}
\]

\[
MSD = \frac{\sum_{i=1}^{n} (x_{\text{exp}} - x_{\text{mod}})^2}{n - 1} \tag{17}
\]

\[
RMSD = \sqrt{MSD} = \sqrt{\frac{\sum_{i=1}^{n} (x_{\text{exp}} - x_{\text{mod}})^2}{n - 1}} \tag{18}
\]

where \( n \) number of experimental data points, \( x_{\text{exp}} \) is the experimental value, \( x_{\text{mod}} \) is the model prediction.

Porosimetry analysis of the S-UPS sample shows the presence of two distinct maxima in the pore volume distribution, corresponding to diameters of approx. \( 2 \times 10^{-2} \) \( \mu \)m and 30 \( \mu \)m (Figure 5). The predominant relative pore volume fraction is concentrated in the range of adsorbent pore diameters of 0.3–70 \( \mu \)m.

In the case of the HalRaw4 ash sample, there is a similar bimodal distribution of the first maximum that corresponds to a pore diameter value of approx. 0.02 \( \mu \)m, while the second is 20 \( \mu \)m (Figure 5). The predominant relative pore volume fraction covers a slightly broader range of adsorbent pore diameters (0.2–100 \( \mu \)m) compared to the previous case.
Table 4. The values of standard deviation in respect to each adsorption isotherm (model) parameter according to the Freundlich, Langmuir, Jovanović, Temkin and Hill adsorption isotherm models (statistical data derived from CAVS software [69]).

| No | Freundlich  | Langmuir  | Jovanović  | Temkin  | Hill  |
|----|-------------|-----------|-------------|---------|------|
|    | $K_f$ | $q_L$ | $K_L$ | $q_j$ | $K_J$ | $B_T$ | $q_T$ | $K_T$ | $q_H$ | $n_H$ |
|    | mmol/bar$^n$/g | mmol/g | 1/bar | mmol/g | 1/bar | (kJ g)/(kg mmol) | 1/bar | mmol/g | bar$^n$ |
| 1  | S-UPS   | 0.003   | 0.09   | 3.00   | 0.014  | 1.48 | 0.027  | 2751 | 0.085 | 0.37  | 20.917 | 0.49 |
| 2  | HalRaw2 | 0.002   | 0.05   | 7.20   | 0.007  | 3.48 | 0.014  | 2095 | 0.087 | 0.15  | 5.045  | 0.15 |
| 3  | HalCalc4 | 0.003  | 0.04   | 48.84  | 0.009  | 26.22 | 0.014  | 1568 | 0.087 | 0.13  | 3.292  | 0.11 |
| 4  | HalDry4 | 0.003   | 0.12   | 3.35   | 0.024  | 1.61 | 0.045  | 1075 | 0.029 | 0.06  | 5.262  | 0.50 |
| 5  | HalCalc2 | 0.003  | 0.04   | 0.19   | 0.008  | 0.19 | 0.003  | 1391 | 0.104 | 0.14  | 2.890  | 0.07 |
| 6  | HalCalc4 | 0.004  | 0.07   | 2.61   | 0.011  | 1.24 | 0.020  | 1366 | 0.071 | 0.06  | 2.581  | 0.18 |
| 7  | HalDry2 | 0.002   | 0.06   | 0.19   | 0.008  | 0.43 | 0.013  | 1366 | 0.042 | 0.08  | 2.581  | 0.18 |
| 8  | Kao2    | 0.004   | 0.05   | 0.11   | 0.005  | 0.05 | 0.008  | 900  | 0.052 | 0.19  | 3.472  | 0.12 |
| 9  | Kao4    | 0.004   | 0.05   | 671.37 | 0.010  | 3.58 | 0.015  | 1352 | 0.079 | 0.10  | 2.318  | 0.11 |

Table 5. The values of mean deviation (MD), mean square deviation variance (MSD) and root-mean square deviation (RMSD) for measurement data modeled with the Freundlich, Langmuir, Jovanović, Temkin and Hill models.

| No | Freundlich | Langmuir | Jovanović | Temkin | Hill |
|----|------------|----------|------------|--------|------|
|    | MD | MSD | RMSD | MD | MSD | RMSD | MD | MSD | RMSD | MD | MSD | RMSD | MD | MSD | RMSD |
| 1  | S-UPS | 19.38  | 2.73  | 52.22  | 27.45  | 2.64  | 51.35  | 27.65  | 2.64  | 51.34  | 2.98  | 3.51  | 59.24  | -9.11  | 2.37  | 48.66  |
| 2  | HalRaw2 | 42.78  | 2.70  | 51.92  | 67.35  | 2.50  | 49.98  | 68.05  | 2.49  | 49.94  | 1.43  | 20.30  | 142.47  | 1.97  | 0.99  | 31.42  |
| 3  | HalCalc4 | 65.05  | 4.46  | 66.75  | 104.22  | 4.38  | 66.17  | 106.70  | 4.39  | 66.24  | 5.41  | 38.38  | 195.91  | 2.00  | 0.91  | 30.14  |
| 4  | HalCalc2 | 3.33  | 3.19  | 56.47  | 39.59  | 2.61  | 51.07  | 40.54  | 2.60  | 51.00  | -0.36  | 15.00  | 123.20  | -3.32  | 3.19  | 56.47  |
| 5  | HalCalc4 | 45.13  | 2.59  | 50.94  | 34.22  | 0.82  | 28.71  | -31.76  | 0.75  | 27.45  | -7.10  | 24.18  | 155.51  | -3.00  | 0.48  | 21.84  |
| 6  | HalDry2 | 21.38  | 1.50  | 38.71  | 27.41  | 0.96  | 30.97  | 27.98  | 0.93  | 30.45  | -1.04  | 1.83  | 42.74  | -4.31  | 0.47  | 21.72  |
| 7  | HalDry4 | 24.07  | 2.31  | 48.08  | 20.83  | 0.99  | 31.51  | -19.03  | 0.94  | 30.64  | -4.04  | 6.21  | 78.83  | -4.09  | 0.71  | 26.58  |
| 8  | Kao2    | 93.67  | 9.10  | 95.40  | 143.41  | 7.86  | 88.65  | 146.45  | 7.81  | 88.37  | 0.87  | 21.27  | 145.85  | 0.76  | 1.35  | 36.79  |
| 9  | Kao4    | 88.44  | 6.97  | 83.50  | 175.94  | 6.79  | 82.42  | 20.83  | 0.99  | 31.51  | -19.03  | 0.94  | 30.64  | -4.04  | 6.21  | 78.83  | -4.09  | 0.71  | 26.58  |

The analysis of the Kao4 ash sample showed that the size range of the dominant relative pore volume fraction corresponded to practically the same range of pore sizes as before. However, this distribution was more flattened. This indicated a more statistically uniform distribution of pore sizes within the ash-based adsorbent structure. Due to its systematic gradation, this enabled both the self-forming of a structural network of pores enabling access to the internal adsorption surface, as well as more favorable internal diffusion conditions (greater proportion of pores with an intermediate diameter). This specific structure effectively reduces the diffusional resistances in these porous systems, explaining the best performance of Kao4 ash (Figure 3).

In the case of HalRaw4 and Kao4 ash samples, there is a clear increase in surface heterogeneity and porosity in relation to the reference sample, corresponding to the S-UPS ash (Figure 4). Porosity is related, in particular, to the increase in the available adsorption surface (additionally, independently chemically modified in thermochemical processes in the straw biomass combustion environment due to the presence of nano-structural additives, establishing an appropriate structure, composition, and proportions of functional groups under the conditions of biomass combustion, which are then directly or indirectly related to complex CO$_2$ adsorption processes).
Presence of nanostructured additives is directly responsible for higher mesoporosity of the resulting ashes, providing better internal diffusion conditions, which together with a five-times higher specific surface area (SSA) contributed to higher CO$_2$ adsorption capacity of such thermally modified straw ashes (Table 3), in spite of their slightly lower cumulative pore volumes.

4.2. Comparison of Results with Literature Data Technical and Economic Aspects of CO$_2$ Adsorption on the Straw Ashes

The aim of this research was, first of all, to identify the CO$_2$ adsorption potential of ash from straw biomass combustion, as well as to increase it, if necessary, through appropriate additives and appropriate preprocessing, e.g., [70] (process intensification aspect). The overriding goal was, however, an important scientific aspect (despite the need to take into account some economic conditions before applying it in post-industrial gas stream purification technologies).

The results of carbon dioxide adsorption in the range of about 0.03–0.35 mmol CO$_2$/g identified in this work, using a pressure range of about 2–10 bar CO$_2$, can be confronted with the results presented in the available literature, collected in two review articles [37,71].

Analyzing the results of CO$_2$ adsorption corresponding to the process pressure range comparable to the discussed research (ca. 0.10–1.0 MPa), a significant differentiation of the adsorption abilities of the tested materials could be noticed [37]. However, these adsorbent structures are mainly represented by isolated fly ash derivatives.

One of these, SWCNT (single-walled carbon nanotubes) functionalized with zwitterions (308 K) reached only 0.10 mmol CO$_2$/g, whereas that functionalized with COOH ions—reached as much as 3.20 mmol CO$_2$/g. This proves the key significant influence, not only of the process temperature and the applied pressure, but also of the adsorbent preparation methodology and the optimal combination of the components, porosity, degree of fragmentation, the order of application of individual components (structural support, active element(s)), etc.

For example, the use of MOFs-1C'-Li, 2C'-Li (metal–organic framework composites) (298 K, 0.10 MPa) in the adsorption process makes it possible to achieve 4.60–5.30 mmol CO$_2$/g.

However, the use of reduced graphene oxide produced by the modified Hummer’s method, depending on the process temperature (278–348 K) and pressure window (0.10–1.0 MPa) allows to achieve a sorption in the range of 0.22–0.90 mmol CO$_2$/g (278–283 K), 0.18–0.80 mmol CO$_2$/g (308–313 K), and 0.10–0.50 mmol CO$_2$/g (348 K). It can be clearly seen, that, for the highest values of the processing pressure used in this study, a comparable adsorption results can be considered. Increasing the maximum process pressure up to 1.5 MPa results in some, though practically insignificant, improvement to the maximum adsorption capacity, to 1.0, 0.90, and 0.60 mmol CO$_2$/g, respectively.

Other adsorbent represented by MWCNT (multi-walled carbon nano tubes) nanotubes in the temperature range of 278–353 K and for pressure 0.10–1.0 MPa gave the following results: 0.11–0.60 mmol CO$_2$/g (278–283 K), 0.09–0.40 mmol CO$_2$/g (308–313 K), and 0.05–0.20 mmol CO$_2$/g (348–353 K), respectively.

Similar results can be obtained using coal from Polish hard coal mines in the adsorption temperature range of 278–353 K and for a process pressure of 0.10–1.0 MPa. These are as follows: 0.40–1.70 mmol CO$_2$/g (278–283 K), 0.12–1.20 mmol CO$_2$/g (308–313 K), and 0.20–0.80 mmol CO$_2$/g (348–353 K).

Technologically advanced adsorbent, such as the highly porous activated graphene-derived carbon (GDC) from KOH activated TEGO (Thermally Exfoliated Graphite Oxide), provides a significant increase in the adsorption capacity, where at 298 K and in the pressure range of 0–3.5 MPa, a value of 21.1 mmol CO$_2$/g was reported.

Similarly, the results of CO$_2$ sorption on various adsorbents presented in [71] indicate a significant differentiation of the adsorption capacity of the analyzed materials from very high values for MEA (monoethanolamine) (9.09 mmol CO$_2$/g), FAA$_{13}$ (amine-fly ash composite) (6.89 mmol CO$_2$/g), FAA$_{23}$ (amine-fly ash composite) (5.99 mmol CO$_2$/g), CoF-
6 (covalent organic framework) (3.61 mmol CO$_2$/g), and HAC (hydroxyapatite-biochar composite) (3.49 mmol CO$_2$/g) to some lower values comparable with the results obtained in this work, e.g., for MCM 41 (amino-silane-silica composite) (0.14 mmol CO$_2$/g), SBA-15 (amino-silane-silica composite) (0.15 mmol CO$_2$/g), and MCF-HAS (amine-functionalized mesocellular foam) (0.47 mmol CO$_2$/g).

However, some other aspects must be simultaneously taken into consideration in design. Biomass straw ash, despite its lower maximal unit adsorption capacity (ca. 0.30-0.35 mmol CO$_2$/g), represents a direct waste product that does not require further technological treatment (there is no costs related to the purchase of sorbent and the separation of its specific fractions, as it is generally provided in some literature examples describing similar technological approaches based on cost-effective adsorbent structures [23,31,72–75]) and taking into account the volume of its annual global production, it can be concluded, that it compensates even at an excess of its lower unit sorption capacity. In addition, the ecologically important problem of the disposal of these large amounts of the ash may be additionally, partially solved.

The obtained adsorption results, therefore, fall within the lower range of the comprehensive research described in the review literature [37,71], which is based rather on - what should be emphasized - the technologically most promising ash fractions, not directly on the ash as a whole. One should also pay attention to the basic economic aspect as there is no need to prepare the sorbent or preprocess it before use. It is obtained “by way” of the basic function of a commonly available biofuel in the energy generation sector, and the deliberately added nano-structural additives also play an important role in the combustion process itself.

Research on CO$_2$ sorption capacity of raw fly ash from biomass has not been presented thus far in the literature available to the authors. There was no need to use a complicated and sometimes expensive adsorbent preparation technology by extracting only certain ash fractions with the desired sorption properties through the use of physicochemical methods which is an unambiguously advantageous aspect of using this type of ash with additives in terms of CO$_2$ adsorption processes as a low-cost (practically no-cost) material, of one of the considered technological options.

It should be noted, that most of the studies available in the literature refer to substances derived from fly ash. Certain chemical compounds are extracted from the ash and subjected to a process of appropriate treatment: heating, calcining, washing, mixing (addition), etc. Only these compounds, after modification, constitute a sorbent that is used to capture CO$_2$. Some examples include zeolites, activated carbon, or various types of amines.

A new, CE-compliant design and organizational approach, considering the future energy economy based on biomass and biofuels, will be based on the aforementioned “cascade” use of waste products from each successive stage of integrated processes. Thus, the waste-free technology based on the idea of “cascade” (re)use of post-production waste will be the deciding criterion for = economic evaluation of any new or improved technology.

In the discussed case, the authors decided to directly test raw ashes in order to check the potential of a sorbent with very low costs (and even negative costs, taking into account the simultaneous solution to the problem of inducing storage and the possible adverse interactions with the biosphere), which, moreover, does not require further specialized treatment. This potential is also analyzed more broadly in the terms of possible underground carbon dioxide sequestration, in which fly ash can form a kind of deposit with two purposes: to increase the sorption capacity of a warehouse, and also affect its strength by filling this space, thus preventing, for example, so-called “mining damage”. One should also remember the pressure and temperature of the process, which strongly affect the adsorption capacity of materials, allowing the process to be intensified to some extent. First of all, from the new point of view, in line with the new approach to circular economy (CE), it is possible to assign different, sometimes non-obvious “weights” to individual criteria of economic and technological evaluation of a given process concept. In such a case, even a lower unit sorption capacity of waste materials can be successfully overcompensated with
their widespread availability and very low cost (in most cases this cost is virtually zero; additional profit exists in the elimination of the waste utilization costs). The obtained status of a “waste-free technology” a direct effect of the “cascade” (re)use of post-production waste and is the basic technological idea behind the integrated technological solution “biomass → combustion → ash → sorbent” presented by the authors.

5. Conclusions

The presented approach of the authors is in line with CE assumptions; in this case, based on an attempt to integrate the conditions for improved biomass combustion processes (with functional additives) while simultaneously having the same conditions of chemical thermosynthesis for more and more effective adsorbents. Nevertheless, in order to obtain mixtures characterized by higher and higher adsorption parameters simultaneously constantly improving combustion conditions the research signaled here must be continued and extended.

Therefore, multi-criteria optimization should be carried out in relation to the combustion, but taking into account two different aspects of this process energy conversion course via the exothermic process, as well as the simultaneously running complex thermochemical synthesis of adsorbive materials.

Due to the particle size distribution, which determines the development of a large specific surface area of contact with the treated medium, and the natural surface properties of the biomass (functional groups), the ashes generated as by-products of the energy use of biomass can be used as a convenient material for CO$_2$ adsorption. Modern straw combustion technologies, using certain fuel additives, introduce modifications not only in the course of the process itself, but also significantly affecting the final chemical composition and morphological structures of the obtained ash.

The presented measurement data confirm that process additives in the form of nanostructured halloysite and kaolinite, in addition to having a beneficial effect on the process parameters in energy systems, enable the obtaining of ashes with a more complex chemical and structural composition, showing much more favorable adsorption capacity in relation to CO$_2$.

The most advantageous additives to the straw combustion process (in the experimentally tested range), from the point of view of the effective use of the post-combustion residues (ash) as a CO$_2$ sorbent, turned out to be kaolinite and raw halloysite (2–4 wt.%), for which an almost 2.5-fold increase in adsorption capacity was reported. A significantly lower effect (though still beneficial) was observed for dried and calcined halloysite additives. This shows, that the modification of the surface properties of halloysite through drying and calcination achieved different interactions with the straw biomass during the combustion process and clearly reduced the CO$_2$ adsorption capacity of the ash formed under the defined process conditions (ash spatial structure, its surface functional groups, etc.).

The presented research shows, that through the appropriate selection of the type and dose of additive (e.g., nanostructured halloysite, kaolinite), it is possible to optimize in accordance with circular economy assumptions and standards, and the overall cycle using additive improvements to the combustion process itself along with the simultaneous production of an appropriate ash structure with increased CO$_2$ adsorption capacity.

The results can be adopted in the technological design of the pressure swing adsorption (PSA) process based on the obtained information relatively inexpensive adsorbents from the energy generation sector, using large amounts of biomass straw. Furthermore, due to their huge availability, biomass ashes can be also used for improving and stabilizing CO$_2$ storage in geological sites as permanent adsorbents [70]. Such a systemic technological approach, in addition to the experimental identification of the promising application areas for an environmentally safe material, in the future, will also enable effective management of the constantly growing global streams of these types of post-industrial waste, which are newly developed substitutes for mineral materials, which is an additional, equally important situation for natural environment protection and sustainable development.
standards. A similar approach was also reported by one of the co-authors of this work, using CE-based technological conversion of waste phosphates (V) into valuable mineral fertilizer (struvite) [76].

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Abbreviations:

- S-UPS is ash resulting from burning straw without additives;
- HalRaw2 is ash resulting from burning straw with the addition of 2 wt.% raw halloysite;
- HalRaw4 is ash resulting from burning straw with the addition of 4 wt.% raw halloysite;
- HalCalc2 is ash resulting from burning straw with the addition of 2 wt.% calcined halloysite;
- HalCalc4 is ash resulting from burning straw with the addition of 4 wt.% calcined halloysite;
- HalDry2 is ash resulting from burning straw with the addition of 2 wt.% dried halloysite;
- HalDry4 is ash resulting from burning straw with the addition of 4 wt.% dried halloysite;
- Kao2 is ash resulting from burning straw with the addition of 2 wt.% kaolinite;
- Kao4 is ash resulting from burning straw with the addition of 4 wt.% kaolinite.
- $K_F$ is the Freundlich isotherm constant (mmol·bar$^n$/g);
- $N$ is the parameter of the Freundlich isotherm model (adsorption intensity) [-];
- $q_L$ is the theoretical maximum monolayer capacity (mmol/g);
- $K_L$ is the Langmuir isotherm constant (adsorption equilibrium constant) [1/bar];
- $Q_J$ is the theoretical maximum monolayer capacity (mmol/g);
- $K_J$ is the Jovanović isotherm constant (1/bar);
- $B_T$ is the energy of adsorption (kJ g/(kg kmol));
- $K_T$ is the Temkin isotherm constant (1/bar);
- $q_H$ is the theoretical maximum monolayer capacity (mmol/g);
- $K_H$ is the Hill isotherm constant (bar$^n$);
- $n_H$ is the parameter of the Hill isotherm model (Hill cooperativity coefficient of the binding interaction) (-);
- $R^2$ is the coefficient of determination (-);
- Mean $R^2$ is the arithmetic mean of $R^2$ values for a given adsorption isotherm model (considering all cases no. 1–9), Table 2.

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