High-Energy Solid Fuel Obtained from Carbonized Rice Starch

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Abstract: The paper describes the investigations of the physicochemical properties of biocoal, a solid fuel obtained following the carbonization of rice starch. The production of biocoal (carbonization) was completed at the temperature of 600 °C in the nitrogen atmosphere. As a result of the carbonization, amorphous carbon with high monodispersity was obtained, devoided of oxygen elements and was a very well developed BET specific surface—360 m² g⁻¹. The investigations of the technical parameters have confirmed a very high concentration of energy. The calorific value of 53.21 MJ kg⁻¹ and the combustion heat of 54.92 MJ kg⁻¹ are significantly higher than those of starch before carbonization (18.72 MJ kg⁻¹ and 19.43 MJ kg⁻¹, respectively) and these values for typical biomass fuels. These values are also greater than those of hard coal. Other advantageous features of the obtained fuel are low ash (0.84%) and moisture content. These features predispose this fuel for the application as an alternative to conventional fuels.

Keywords: solid fuel; biocoal; starch; carbonization

1. Introduction

Biomass has been used as an energy source since the beginning of mankind. Collecting wood, brushwood or straw for fuel for the production of thermal energy had been used centuries ago. Biomass is understood as the biodegradable part of products, residues of biological origin from agriculture (plant substances), forestry and related industries or processed biomass, in particular in the form of briquette, pellet and biocarbon. Modern use of biomass for energy purposes focuses mainly on obtaining material from specially created plantations of species with the best energy parameters and the use of all waste from the wood or agricultural industry.

Biomass is the least capital intensive source of green energy. It arises all the time on Earth and it is a virtually self-contained process. Forests, meadows and oceans are places where biomass production is an ongoing process. To use it for energy purposes, certain activities must be carried out to intensify production: fertilization, irrigation or protection against pests. The production of biomass in many countries, including Poland, is becoming an important branch of agriculture—it allows waste management and opens up the possibility of growing crops intended solely for energy purposes.

Raw biomass is characterized by poor energy-related properties (low energy density, high moisture and heterogeneity). These properties have a bad influence on the wide application of biomass as
fuels. Therefore, methods are sought to improve their properties in order to boost their energy related attractiveness. One of the simpler methods that do not require additional processing other than shredding and briquetting is co-combustion with other fuels [1–4]. The conversion of biomass to solid, liquid and gaseous fuels is completed as a result of biochemical processes such as digestion and fermentation and thermochemical processes such as pyrolysis, gasification, hydrothermal liquefaction or the process of carbonization in the oxygen atmosphere [5].

The emission of carbon dioxide, the obvious combustion product of both coal and biomass, is a separate issue. It is assumed that in the biomass combustion process, the CO₂ emission balance is zero, because it emits only as much carbon dioxide into the atmosphere as the plants absorb in photosynthesis. In the case of multi-annual energy crops, the amount of CO₂ absorbed may even exceed the amount emitted [6].

This demonstrates the beneficial impact of energy processes using biomass to reduce the greenhouse effect. Another value in favor of using biomass is the smaller amount of ash remaining after the combustion process—the ash content for biomass is 1% and for coal 22%. The ecological effect of changing coal for biomass on an individual farm indicates that, assuming 8 tonnes of coal per year, you can reduce emissions by the following values: CO—92%; SO₂—97%; NO₂—80%; TOC—77% (total organic carbon) and CO₂—100%.

Unfortunately, the combustion of biomass can lead to insignificant emissions of harmful substances: HCl (Hydrogen Chloride), furans and dioxins. It is caused by high heterogeneity and different chemical composition of biomass and the presence of, among others, chlorine and nitrogen oxides. This is often caused by biomass contamination with pesticides, plastic waste or chlorinated compounds [7]. Compared to conventional fuel combustion, however, the problem of introducing less harmful substances into the environment is not really that obvious. Research comparing biomass and hard coal shows that hard coal is not always inferior in terms of emissions. In many cases, it appears to be even more beneficial. The use of combustion temperatures above 900 °C causes the coal to produce much less CO than biomass. Additionally, when it comes to emissions of nitric oxide, hard coal does not generate the highest amounts of this component. Emission indicators place it among materials that cause low emission of this component (comparable to wood and sawdust), while the highest NO emission is characteristic of energy plants such as rapeseed oil cake [8,9]. At temperatures above 800 °C, carbon, similarly to biomass, releases smaller amounts of total organic carbon. Only at 700 °C is the TOC emission from hard coal higher.

Among the liquid fuels, second generation biofuels are preferred [10]. The most popular and available plant materials are rapeseed, soy, corn and crops. An example of plant-derived fuels is biocoal manufactured in the process of HTC (hydrothermal carbonization). The HTC process enables converting biomass into solid fuels characterized by higher calorific value compared to the input material. Usually, this parameter is close to that of coal (22–30 MJ kg⁻¹) for different types of biomass such as seaweed [11], palm kernel shell [12], rice husk [13], macroalgae [11], Miscanthus [14], Jatropha [15] or eucalyptus [4]. The provided examples show the universal nature of the HTC technology. It is noteworthy that the properties of biofuel obtained with this method chiefly depend on the parameters of the method, particularly the temperature and time of carbonization. Usually, longer time and higher temperature have a positive effect on the final properties of biocoal [16]. Aside from the calorific value in the HTC process, also other parameters of biofuels are improved such as the reduction of moisture or heterogeneity. Another thermochemical method of production of biofuel is the method of pyrolysis. Similar to HTC, pyrolysis is a technology of production of high-energy fuel from different types of biomass such as lignocellulosic [17], thuja wood [18] or banana waste [19].

A frequently used plant-derived compound in the production of fuels is starch. One of the possibilities of the application of starch is its use as a bonding material in the production of briquette made as a mix of biomass and coal [20,21]. Such an application of starch not only improves the physicochemical properties of the briquette material and its durability, but also its calorific value. Another way to use starch is the production of fuel ethanol from corn [22,23] and potato [24] starch.
Starch, otherwise known as homopolysaccharide, is perceived as a plant-derived product of high energy potential [25–27]. Starch can be found in, among others, corn, potatoes, rice, wheat, pea and many other plants. The majority of these plants are characterized by a relatively low price of production and a wide presence in the environment. This polymer aside from the chains of amylose and amylopectin contains small amounts of ashes, proteins, fats and sulfur oxides (IV) [28].

Moreover, in order to obtain carbon material, it is possible to use rice starch resources that are unsuitable for consumption (waste). In this way, we do not exploit other resources. In addition, to obtaining coal, it is possible to use starches of other origins (potatoes, corn, etc.).

The real threat of depletion of global fossil fuel resources is forcing global research laboratories to search for new reserves of energy in order to satisfy the energy demand of the human population. Everything indicates that the only rational solution to the current situation is to use renewable energy sources. Terms such as ‘energy crops’ and ‘energy plantations’ are used increasingly. Starch is a renewable energy source, which is why its processing appears far more appropriate.

In relation to the research conducted in Research & Development (R & D) centers and universities, the authors of this paper present the investigations of selected physicochemical properties of thermally modified starch as a solid fuel (biocoal).

2. Materials and Methods

Several tests were carried out in order to characterize the physicochemical properties of the carbon material obtained from rice starch. In order to explore the morphology, the authors proposed the SEM (Scanning Electron Microscopy) analysis. The FTIR (Fourier Transform Infrared Spectroscopy) spectra were additionally added to get the information on the functional groups. XRD (X-ray Diffraction) was performed to obtain information on the sample crystallinity. The TG (Thermogravimetric) analysis was applied to determine the temperature adopted for the carbonization process. The BET (Brunauer-Emmett-Teller) analysis showed an adsorption–desorption trend and revealed information about the pores (surface area and pore diameter). Additionally, distribution of the particle size was attached and characterized.

In order to characterize the carbon material as biofuel, the fuel moisture, combustion heat and calorific value were determined.

2.1. Starch

The authors used rice starch for the investigations (Sigma-Aldrich, MO, USA), ID number S7260-500G. In order to obtain the appropriate type of amorphous carbon, starch was subjected to thermal processing in the nitrogen atmosphere. A quartz pipe furnace was used in the process (Nabertherm GmbH, Lilientha, Germany, 2015). The process took place at the temperature of 600 °C, the temperature was increased by 300 °C h−1 in the nitrogen atmosphere. The volumetric flow of nitrogen was 50 dm³ h−1 [29].

2.2. Size of Particles and Assessment of Polydispersity

In order to perform the particle size analysis, the authors used Zetasizer Nano ZS by Malvern Instruments (UK, 2000) [30]. The equipment dynamically disperses light and analyzes the Brown movements converted into size and distribution utilizing the Stokes-Einstein relationship. The NIBS (non-invasive back-scattering) technology operates at the highest range in the widest range of concentrations.

The polydispersity index (PDI) provides much information whether the structures (dispersed in an isopropanol solvent) are monodisperse or polydisperse, which further leads to a conclusion as to the number of particles of homogeneous or heterogeneous particle size. The values below 0.3 nm are interpreted as exhibiting monodispersity, while those above 0.3 nm as polydispersity [31]. Monodispersity denotes an identical size of the particles of the dispersed substance and polydispersity denotes a varying particle size. The index of polydispersity (PDI) is commonly referred to as the
square of standard deviation or the average particle diameter. According to other data, the particles are deemed monodisperse if the PDI is lower than 0.1. Above 0.1 or if the cumulant error is greater than 0.001 or if low quality is the result, the obtained measurement results should be scrutinized in more detail. Polydispersity provides information on the spread of the particle masses [30,32].

2.3. Determining the Specific Surface Area, Diameter of the Pores and their Volume

In order to calculate the density of the surface load, it is necessary to perform the BET (Brunauer–Emmett–Teller) specific surface area analysis. An important aspect is the determination of the size of the pores, their volume and the structure of the adsorption isotherms. The test was performed using the ASAP 2020 by Micromeritics Instrument Co. (Norcross, GA, USA, 2015). Low temperature nitrogen adsorption was applied and the samples were subjected to a 4 h gas elimination at the temperature of 120 °C prior to the analysis.

2.4. FTIR Measurement Methodology

The analysis of the spectrum functional groups was performed using the EQUINOX (Bruker, MA, USA, 2015) spectrometer and the substances subjected to the test were analyzed in the form of a KBr pellet. In the vibration grinder, 0.1 g of nonaqueous potassium bromide with the 1 mg of the analyzed material was grounded. KBr was applied for its transparency. The obtained mixture was pressed in a steel ring under the pressure of 100 MPa. The result was a transparent pellet that was subsequently placed in the measurement cuvette. The last stage was placing the cuvette in the holder in the focus of the radiation beam. The measurement was performed in the wavenumber range of 400–4000 cm$^{-1}$.

2.5. Thermogravimetric Analysis (TG/DTG-DTA)

The aim of the examination was the determination of the changes in the structure of starch during its heating. For the completion of the analysis, the authors used a TG 209 F3 Tarsus® (Netzsch, Selb, Germany, 2018) thermogravimetric analyzer. TG allows an accurate evaluation of the thermal stability of materials in the temperature range from 29.6–1062.1 °C, in an inert gas atmosphere (nitrogen, gas flow rate 20 mL min$^{-1}$). For the thermogravimetric analysis (TGA), 5 mg of the sample of each starch was used and then changes in the material mass subjected to the thermal analysis were recorded (the samples were heated to a given temperature). The result of the analysis was a thermogram showing the chemical and physical changes related to heating. The differential thermal analysis (DTA) curve described the physical and chemical transformations such as crystallization, melting or sublimation, i.e., phase conversions. The method can be used to determine the stability and crystallinity of starch as well as for research on distribution and cryoprotection [33].

2.6. X-ray Diffraction

For the determination of the crystalline structure, the method of X-ray diffraction was applied (XRD). The XRD analysis was carried out using a D8 Advance (Bruker, Berlin, Germany, 2015) diffractometer using Cu Kα ($\alpha = 1.5418$ Å) radiation with the Ni filter. The diffractograms were obtained through step scanning ($\theta 2\theta = 0.05^\circ$) in the angle range of 5–60°.

2.7. XPS-Analysis

The X-ray photoelectron spectrometry (XPS, X-ray photoelectron spectroscopy) is a variety of electron spectroscopy involving the analysis of the kinetic energy distribution of photoelectrons emitted as a result of excitation of the sample with characteristic radiation from the soft X-ray range.

The X-ray photoelectron spectra were obtained using Mg Kα ($hv = 1253.7$ eV) radiation with a Prevac system (Prevac, Poland, 2018) equipped with Scienta SES 2002 electron energy analyzer operating at constant transmission energy ($E_p = 50$ eV). The base pressure was kept under $1 \times 10^{-9}$ mbar.
The samples were attached to the molybdenum sample holder by means of a double-sided adhesive tape. The binding energy scale of the XPS figures was corrected due to charging.

2.8. Determining the Fuel Moisture

Free moisture \( W_{\text{ex}} \) of biocoal was determined. This measurement consisted of drying the fuel sample in ambient air for approximately 24 h. The mass of the sample was prepared with the accuracy of 0.5 g. The measurement of the mass reduction was performed approximately every 1–2 h. The end of the measurement took place when the reduction of mass was lower than 0.1% of the initial sample mass.

\[
W_{\text{ex}} = \frac{m_1 - m_2}{m_1 - m_p} \times 100\%
\]

where:

- \( m_1 \) — initial mass of the sample (g),
- \( m_2 \) — final mass of the sample (g),
- \( m_p \) — mass of the container (g).

The measurement of the hygroscopic moisture \( W_h \) of biocoal was also performed. This measurement consisted of preparing a fuel sample of the mass of approximately 10 g with the accuracy of 0.0002 g, in a state of equilibrium with the ambient humidity of the laboratory. The sample was dried for 1.5 h in a dryer at the temperature 105–110 °C. The sample was dried in a glass vessel with a slightly open lid to allow the moisture to be evacuated. The total fuel moisture \( W_t \) was determined as the sum of free moisture and hygroscopic moisture of the fuel. The content of ash \( A^a \) was determined. The measurement consisted in preparing a fuel sample of the mass of 1.2 g with the accuracy of 0.0002 g. The sample was calcined in a ceramic bowl at the temperature of approximately 815–820 °C. The rapid method was applied; the preliminary calcination of the sample took 10 min in the front part of the muffle furnace and then further calcination continued for 25 min. The content of ash was determined from the following relation:

\[
A^a = \frac{m_1 - m_2}{m_1 - m_p} \times 100\%
\]

2.9. Combustion Heat and Calorific Value

The measurement of the combustion heat \( Q_s \) and the calorific value \( H_i \) was performed using a water calorimeter. A dry fuel sample was prepared in the form of a pellet of the mass of approximately 1.2 g with the accuracy of 0.0002 g. The pellet was prepared by pressing the biocoal without the use of a bonding material. The principle of this measurement consists in a full and complete combustion of the sample in a calorimetric bomb in the oxygen atmosphere under elevated pressure and a measurement of the increase in temperature as a thermal effect of the combustion.

3. Results and Discussion

Morphology is important in any characteristics of obtained materials (chemical treatment). This property very often plays an important role in the possibility of being used in various branches.

Figure 1a,b presents the images of the obtained fuel made using the scanning electron microscopy (SEM). The obtained biocoal was characterized by a structure similar to graphene (flake structure) [34].

The narrow range of the particle sizes for the analyzed starch may be related to the limited gelification resulting from the swelling of the grains caused by the intensification of the steam pressure within the particles. The reason may also be the lack of retrogradation connected to the ordering of the amylose structures that form micellar aggregates stabilized by the hydrogen bonds among the hydroxyl groups. The change, thus, pertains to the linearization of the polysaccharide chain. This phenomenon
is identified with the conformational conversion of a biopolymer (second order) from the helical to the linear form, i.e., with the reduction of the susceptibility of starch to crystallization (Figure 2).

![SEM images of rice starch](image1.png)

**Figure 1.** SEM images of rice starch (a) 100 μm, (b) 10 μm.

![Distribution of the particle sizes for rice starch](image2.png)

**Figure 2.** Distribution of the particle sizes for rice starch.

Starch exhibits a monodisperse nature, which is confirmed by a single peak in the size range from 240 nm to 845 nm at a low polydispersity index of 0.338 (PDI; Figure 2). In order to increase the specific surface area and obtain a pure carbon structure, the process of carbonization of starch as a potential biofuel was carried out.

Easy availability of activated carbons is associated with an uncomplicated production process using natural and synthetic materials containing carbon atoms in their polymeric construction. The most popular natural materials, from which active carbons are currently obtained are, among others, peat, lignin, fruit stones and nut shells, while synthetic materials used for this purpose include polymers such as polyvinylidene chloride or polyfurfuryl alcohol. The process of producing activated carbons consists of two stages: carbonization and activation aimed at developing the porous structure of coal. Initially, the raw materials are subjected to a heat treatment carried out at a high temperature in the absence of air to form a carbonizate. Due to the poorly developed porous structure, the carbonizate is subjected to further processing—referred to as the activation, resulting in a micropore system as well as surface functional groups that give the product the desirable sorption properties. During the synthesis of activated carbon, the stage of activation carried out by physical or chemical methods is very important. During the physical activation, the development of the porous structure takes place following the use of oxidizing gases such as steam or carbon dioxide at a high reaction temperature (800–1000 °C).
The use of physical activation allows an easy modification of the structure of activated carbon, e.g., by changing the temperature or time of pyrolysis. Chemical activation carried out at a lower temperature (600 °C) using chemical reagents (e.g., zinc chloride, potassium or sodium hydroxide) is a more efficient process, but requires the removal of the chemicals used for activation by washing [35].

It should be taken under consideration that bioenergy could occur in forms of biomass or biofuels. Figure 3 presents possible routes for conversion of different kinds of biomass to biofuel and an overview of biofuel-based bioenergy. Additionally, direct combustion and combustibles other than biomass play a truly important role in the presented technologies.

![Figure 3. Overview of possible paths for conversion of biomass into biofuel and biofuel-based bioenergy. Adapted from [36].](image)

The specific surface area for rice starch (prior to the processing) was only 0.901 m² g⁻¹ (Figure 4a). Due to the very poorly developed surface, relatively large sizes of the pores occurred, which is quite common. We could also observe relatively large sizes of the pores (20.6 nm). Figure 4b shows a clear reduction in the pore diameter (to 4.3 nm) after carbonization. One may assume that, for starch, the granules occur in the form of single cylindrical pores of a given volume and cylinder wall surfaces. For example, for the rice starch type of polysaccharide, one may observe single cylindrical pores of the volume of 0.0025 cm³ g⁻¹.

For the phenomenon of adsorption, the most desirable are micropores. In the micropores, however, the phenomenon of capillary condensation takes place in the gaseous phase related to the sudden increase of the adsorbed mass along the increasing pressure following the filling of the particles with gas. This phenomenon is a combination of adsorption and condensation without applying the extreme conditions, which characterizes the formation of supercritical fluids. The possibility of capillary condensation that could be observed in pores is taken into account in the BET constant value. This phenomenon also takes place in the case of mesopores.
Biochar obtained at temperatures below 400 °C has a very small specific surface area and a poorly developed pore structure. Therefore, it does not show the desired adsorption properties. This refers to biochar, which is a residue from the processes of obtaining gas and liquid products from plant materials. One of the methods of modifying the porous structure of the carbon material is activation in an oxidizing atmosphere (H₂O, CO₂, H₂O₂ and O₂ + N₂). During this process, partial gasification of coal occurs with the use of oxidizing agents. Therefore, the authors’ application of a higher temperature resulted in a much larger specific surface area in relation to the original material [37–41].

From the DTA analysis one may infer the endothermic nature of the reactions occurring for starch, which is confirmed by the course of the curves towards negative values when the temperature increases (Figure 5). One may assume that the observed peaks are relatively clear, which may confirm the occurring changes in the crystallinity or fusion of the particles related to the modifications of the physical properties. The peak maxima in the DTG (Derivative Thermogravimetry, Figure 5) curve represent the maximum rate of the mass loss.

The process of the loss of mass had four stages (Figure 5). For rice starch, the first reduction of mass occurred in the temperature range of 32–90 °C, i.e., when all water was removed (the first loss). The main mechanism of decomposition is based on the reaction of the reactive hydroxyl groups elimination (the second loss). One should assume that the smaller the number of hydroxyl groups remaining in starch, the greater its stability. It is noteworthy that the number of reactive hydroxyl groups on the surface of starch is very high, which contributes to such a great mass reduction. According to the Staudinger theory, the more the reactive groups on the surface of a polymer, the shorter the polymer chain and lower the viscosity. The total loss of mass amounts to approximately 85% of the initial mass, 54% of which is related to the loss of the hydroxyl groups and 10% to the elimination of water. A really high loss of mass was observed under the influence of an increased temperature after the first mass release. When the dehydration process is located in its own neighborhood, the hydroxyl groups OH in the glycosidic ring form a C=C bond or cause a degradation of the ring. When the monosaccharide ring is damaged, the CHO and C=O groups are formed at the same time. When the temperature rises, the -CH₂- or -CH₂-O-CH₂- groups are formed as the main binders between the aromatic rings in the substituted benzene or furan. For the temperatures in the range of 550–600 °C (the fourth loss) an amorphous region is built. The slight mass loss during the third loss could be the result of the formation of really strong covalent C-C bonds. Due to high stability of the aromatic rings, the C=C bonds are still present as the ones of the predominantly occurring groups. Thus, it should be noted that before the carbonization process, rice starch contains water in its structure and after processing at 600 °C all water is removed. The fastest loss of mass was observed for the temperatures of 300–350 °C and upon exceeding the temperature of 600 °C the mass loss is almost constant (the fourth stage). On this basis, the authors selected the parameters for the process of carbonization. Utilizing the
TGA-FTIR technique, in line with the literature data, in this process, one may observe a formation of H$_2$O, C=O, CH$_4$, C$_2$H$_2$ and C$_2$H$_4$O$_2$ during the thermal decomposition [42].

The heating rate and type of process gas can simulate various reactions and processes such as combustion, pyrolysis, carbonization, crystallization, etc. The thermogravimetric analysis provides a wide range of information if the curves are properly presented. TG analyses have been widely used to study the kinetics of combustion processes. The main advantages of this analysis are its rapid assessment of the values and temperatures, at which the combustion begins and ends [43–45]. Due to the thermogravimetric curves, three stages of the combustion process can be easily distinguished [46]. First of all, the dehydration and the drying process take place followed by degassing of organic matter where the main loss of mass occurs. Finally, the inorganic material in the sample decomposes by oxidizing the carbon that remains after removing volatiles from the samples. In addition, TG is an excellent method for accurate determination of the flash point of solid fuels [47]. Some researchers have developed a method for obtaining “auto-ignition potential” by testing different heating rates [48].

Rice starch exhibits high intensity of the stretching O-H bond (Figure 6), similar values of wavenumbers and intensities are observed [49]. The wavenumbers in the C-O bond range (1597–1652 cm$^{-1}$) may correspond to H$_2$O molecules strongly bonded with starch. The displacements of the wavenumbers in the range 1034–1043 cm$^{-1}$ are characteristic of the crystalline area of starch. The displacements in the range 993–1026 cm$^{-1}$ refer to the amorphous region (C-O from the C-O-C bond) and describe the state of organization of the double helices within the crystallites. The bond in the range 995 cm$^{-1}$ is characterized with the sensitivity to water [50]. The greater value of absorbance for individual areas may confirm a greater organization or disintegration of areas, which may be related to the occurrence of retrogradation (characteristic of starch molecules). The most dominant in the obtained structure are the C-H bonds stretching because of the aromatic ring, whose presence is...
also confirmed by the TG/DTG-DTA data where the C-H bonds are built past the third stage (Figure 5). Additionally, the strong covalent C-C and C=C bonds from the aromatic structures are seen.

![FTIR spectrum of the fuel before and after thermal processing.](image1)

**Figure 6.** FTIR spectrum of the fuel before and after thermal processing.

After the process of carbonization, a pure carbon structure was obtained. A smooth double band was observed at the wavenumber of approximately 2900 cm\(^{-1}\) responsible for the non-intensely occurring C-H group. The obtained spectrum is characteristic of a carbon structure. No bands deriving from the O-H groups were observed, which confirms total dehydroxylation, as confirmed during the TG examination (loss of mass approximately 54% is responsible for the decrease of O-H). The entire degradation of the ‘finger print’ area also excludes the presence of oxide structures, hence one may assume that the obtained carbon structure is devoid of other groups. This is also confirmed by the XRD examination that allows determining of the sample crystallinity. It is noteworthy that after the thermal processing, as expected, majority of biocoal obtained from starch is amorphous [51]. Starch before carbonization exhibited crystalline peaks for \(\theta\) 15.5, 17, 18 and 23 angles [52–54] (Figure 7).

![XRD analysis before and after carbonization.](image2)

**Figure 7.** XRD analysis before and after carbonization.

Following Szymonska and Wodnicka [55], degradation is usually accompanied by a separation of double helices in the amylopectin that influence the organization of the crystallines causing a disorganization of the structure. It is believed that mostly amylopectin is responsible for the crystallinity of starch [56]. One may conclude that carbonization entirely degrades the crystalline structure of starch. We may observe two smooth wide peaks of starch at \(\theta\) values of 30 and 41. Their presence indicates an existence of an amorphous carbon phase, which is confirmed in [57] (Figure 7).

It should be remembered that carbonization is one of the methods of obtaining carbon from biomass (starch), however, other biomass processing technologies are also distinguished in the industry:
• Pyrolysis—the most common way of obtaining energy from biomass (90% of the world production of energy from biomass comes from the use of this technology), used for the production of both heat and electricity. Combustion installations in boilers are suitable for processing various types of biomass, primarily wood, wood chips, sawdust and straw. In addition, this process can be carried out at a temperature of over 600 °C and without access to air, the production of which is liquid biofuel. The best raw material for pyrolysis is wood, but since this technology is only at the initial stage of development, it can be assumed that any type of biomass is suitable for transformation in this process,

• Gasification—a thermochemical conversion process, different from combustion in that the product of the process is not heat but gas, which, after combustion, provides the desired thermal energy. Gas can also be used in special turbines to produce electricity. The advantage of gasification is the high efficiency of the process (reaching 50%),

• Cogeneration—a process of simultaneous production of heat and electricity. Cogeneration systems achieve lower emissions,

• Biochemical processes—some forms of biomass containing a large amount of water are used in the fermentation process, where the product of biomass degradation is alcohol used for the production of biofuels. Methane fermentation processes, the product of which is biogas (a mixture of methane and carbon dioxide) are also included in these technologies. For energy purposes, animal feces, food processing waste, municipal waste at landfills and sewage sludge are used in the fermentation process.

The X-ray photoelectron spectroscopy (XPS) analysis of the carbon produced from rice starch showed hybridization. While performing the XPS measurements, the sample was irradiated with 200 unmonochromated Al Ka X-rays. The C 1s region of the carbon obtained from rice starch (284.8 eV) confirmed that our compound consists of the sp² hybridized carbon (Figure 8a).

![Figure 8. XPS analysis of carbon obtained from rice starch: (a) C 1s spectrum peak position: 284.8 eV; (b) high binding energy featured at approximately 290 eV; (c) O 1s spectrum peak position: 532.8 eV and (d) D-parameter for the rice starch carbon compared to another carbon.](image-url)
Additionally, since the shake-up feature occurred at nearly 292 eV, we could infer that the compound was devoid of the sp\(^3\) bonding. The D parameter in the XPS spectra provides the energy difference between the highest and the lowest peaks of the derivative [58]. These parameters provide the information regarding the quantity of carbon in the hybridization of sp\(^2\) and sp\(^3\) [58]. The D parameter was found to be 21.1 eV, which is in line with the properties displayed by pure sp\(^2\) carbon. The XPS analysis shows that our compound consisted of approximately 98% carbon and the rest was oxygen. The peak height of O 1s spectrum was relatively low (Figure 8c) implying that the sample probably contained 2% oxygen and 98% carbon. This implies that it is mostly made up of pure carbon (Figure 8b). This data confirmed the C Auger region. The D parameter was found to be 21.1 eV, which confirms the presence of pure sp\(^2\) carbon (Figure 8b). The data resembled those of graphene materials.

Additionally, the literature describes that there is a method for assessing the sp\(^2\)/sp\(^3\) content from the spectra. This method consists of determining the distance D between the most positive and the most negative minimum of the first derivative of the spectrum [59]. Since the fine structure of the C transition was greatly influenced by the sp\(^2\)/sp\(^3\) configuration, parameter D can be considered as a fingerprint of the carbon atom system with respect to part C in the sp\(^2\) and sp\(^3\) hybridization. Lascovichet et al. [60] proposed an approximation starting from D = 14.2 eV for diamond and going to D = 22.1 eV for graphite, which allows the extrapolation of the D values for other compounds. We obtained D = 13.1 eV for another carbon and D = 21.1 eV for carbonized starch (Figure 8d). The results were quite similar considering the experimental errors [61]. The obtained results revealed that the samples of charred wood powder and carbon black pellets were characterized by a low content of the sp\(^2\) carbon (approximately 5–10%), while the DLC (diamond-like carbon coating) sample contained approximately 15% sp\(^2\). A very high sp\(^2\) carbon content (approximately 50%) was found in the SWCNTs (single-walled carbon nanotubes). Finally, it is noteworthy that the spectrum of the valence band can also be examined to determine the hybridization of C (sp\(^2\) and sp\(^3\)) [62], although in this analysis, it is difficult to quantify the sp\(^2\)/sp\(^3\) ratio.

The assessment of environmental impact of biomass as an energy source can be divided into two main aspects. The first is the emission of gases resulting from the combustion of various forms of biomass. The second is the assessment of the impact of energy crops on the natural environment. We believe that the obtained material has a positive impact in relation to both of the above.

The process of biomass combustion involves the emission of harmful substances to the environment. Comparing it with the emission of pollutants from the combustion of coal, the following conclusions can be drawn:

- Biomass contains less sulfur—the average sulfur content in biomass is 0.01%, for coal this value is 0.9%. Therefore, replacing it also reduces sulfur oxides, thereby solving the problem of flue gas desulfurization.
- Biomass combustion is associated with a reduced emission of nitrogen oxides
- When burning biomass, however, much more dust is generated, because it contains more volatile components. In the case of straw combustion, the content of volatile components reaches 70%, which necessitates the use of appropriate combustion technologies including boiler gas after treatment.

Renewable energy from biomass is an actual alternative to the use of fossil fuels and it represents an opportunity, particularly for small rural communities, of boosting their economy.

The analysis of the obtained biocoal in terms of its technical properties (Table 1) predisposes it for the application as a fuel. It is particularly noteworthy that it has a high calorific value and combustion heat, 53.92 MJ kg\(^{-1}\) (18.72 before carbonization) and 54.21 MJ kg\(^{-1}\) (19.43 before carbonization), respectively. The calorific value of the obtained fuel exceeds the majority of commonly applied solid fuels such as coal (25–30 MJ kg\(^{-1}\)) or biomass (10–15 MJ kg\(^{-1}\)) and is even slightly higher than liquid fuels such as heating oil, diesel fuel or ethanol (40–45 MJ kg\(^{-1}\)). The technical properties of the obtained biocoal exceed those of biocoal obtained with other technologies. Usually, these values are close to
hard coal: 25 MJ kg\(^{-1}\) \[18\], 25–28 MJ kg\(^{-1}\) \[14\], 18 MJ kg\(^{-1}\) \[15\] and 28–30 MJ kg\(^{-1}\) \[63,64\]. A similar technology of biocoal production (also in the nitrogen atmosphere) to the one described in this paper was applied by Asadullah et al. \[65\], yet the carbonization process took place at the temperature of approximately 300 °C, i.e., a much lower temperature, which, at the same time, confirms a lower energy consumption during the production process. Besides, in a comparable case, the input material was different (kernel shell palm biomass). The content of ash is small but acceptable for this type of fuels \[12,66\]. It is lower than the content of ash in conventional fuels (Table 1). The low values of moisture in the fuel are also noteworthy, which was already noticeable during the preparation of the pellet for the tests in the water calorimeter. The preparation of biocoal in the form of briquette will require a bonding material or increasing the moisture in the fuel. Given the lower content of ash, one may suppose that the combustion of biocoal will result in a lower amount of slag, which will make this fuel more efficient.

### Table 1. Technical properties of biocoal and other fuels.

| Type of Measurement       | Carbonized Rice Starch | Hard Coal | Brown Coal | Biomass (Straw) |
|---------------------------|------------------------|-----------|------------|----------------|
| Free moisture %           | 0.489 ± 0.01           | 7.8–8.4   | 16–20      | 15–20          |
| Air-dry fuel moisture %   | 3.04 ± 0.03            | 1.8–2.4   | 6–20       | 7–10           |
| Total moisture %          | 3.52 ± 0.03            | 9.6–10.4  | 22–30      | 22–30          |
| Ash content %             | 0.84 ± 0.01            | 6.0–9.0   | 12–20      | 4–7            |
| Combustion heat MJ kg\(^{-1}\) | 54.21 ± 0.81       | 28–33     | 15.22      | 16–20          |
| Calorific value MJ kg\(^{-1}\) | 53.92 ± 0.80     | 27–31     | 8–19       | 12–17          |

The calorific value of biomass is twice lower than coal. It is assumed that 1 mg of hard coal is equal to the energy of 2 mg of dry biomass. The calorific value of straw or wood oscillates around 10–14 MJ kg\(^{-1}\). For hard coal it is 25 MJ kg\(^{-1}\). Direct biomass combustion in steam boilers reaches the efficiency of approximately 70%. Further conversion to electricity in the steam cycle has an efficiency of 20%.

In short and mid-term perspective, measures need to be implemented to reduce the anthropogenic emissions. One of the possibilities is decarbonization of the heating sector. An important role in the reduction of emissions and decarbonization may have plant-derived fuels. Yet, despite the fact that their share is increasing, there exist certain properties that make their wide application difficult. One of the possibilities of improvement of plant-derived fuels is their thermal processing (green chemistry) that significantly improves the properties of these fuels and leads to their increased competitiveness compared to conventional ones.

The presented results confirm the great potential of biocoal. The possibility of reducing the exploitation of fossil fuels behooves the scientists to define it as biofuel. It is, however, forecasted that the research will be continued and aimed at determining the parameters of combustion of biocoal (emissions). It is also forecasted that the works will continue aiming at a development of technologies of mass production at the same time allowing for the economic aspects.

Regarding solid biomass, two critical aspects should be considered: its low energy density, which causes transport and usability problems and limited production (e.g., crops or residues) from the exploitation of the agricultural and forestry areas. While gas synthesis/pyrolysis processes are being investigated as part of the research activities, advanced direct combustion technologies are already available for the conversion of biomass into thermal or mechanical energy. It is therefore important to achieve a higher efficiency in energy conversion and heat exchange processes as well as reduce pollutant emissions.

### 4. Conclusions

In the paper, the authors described the results of investigations of plant-derived biocoal. The obtained results of investigations and technical analyses of biocoal confirm its applicability in the energy industry. Its application is mainly perceived as an alternative to conventional fuels, hard
coal in particular. The possible area of application is the heating industry—combustion or co-combustion with other fuels in small-scale boilers that are still quite commonly used in energy-generating systems of many countries worldwide. This is particularly the case for areas, where the use of conventional fossil fuels has the greatest share. It is noteworthy that the presented investigations pertain to rice starch, but in the authors’ opinion, fuels of similar parameters can be obtained from starch produced from other widely grown plants worldwide. This is confirmed by the authors’ preliminary research. The most advantageous feature of this fuel appears to be its high energy density. The calorific value and combustion heat of the obtained fuel are 53.92 MJ kg\(^{-1}\) and 4.21 MJ kg\(^{-1}\) respectively, which places this fuel in the high-energy fuel group. The produced biocoal is characterized by a high BET (360 m\(^2\) g\(^{-1}\)), which results in increased sorption properties of carbon. Amorphous carbon was obtained, devoid of oxygen elements and of high monodispersity.

Our scientific novelty, not yet with extensive coverage in scientific literature, is the use of biodegradable material whose carbonization process is not highly energetic, therefore, not generating gas products (among others, reduction of the emission of carbon dioxide formed during the combustion in the aerobic conditions) or products directly or indirectly harmful to the natural environment or the atmosphere. In addition, the energy properties obtained for this material are many times better than those of the materials commonly used as solid fuels. The main disadvantages of the combustion of solid fuels are as follows: fuel sintering, slag formation, CO emission, uneven fuel distribution and volatile matter release (gases, solid and coke residue). It is noteworthy that the material obtained in this research has none of the above-mentioned disadvantages, which makes our carbon better than other conventional biofuel carbon materials. Due to the fact that these defects have been eliminated, the energy values of the obtained biofuel are significantly better than those of the above-listed solid and many liquid fuels (petroleum). Another great advantage is the reduction of the excess air coefficient denoting lower energy loss and providing better energy-related properties. In these studies, a graphene-like structure, obtained without any modifications, except for thermal treatment (not very high), allowed us to obtain an economical green source when heating the furnace.

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