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## THE USE OF SPECTRAL METHODS TO IDENTIFY THE MICROSTRUCTURE AND CHEMICAL STRUCTURE OF BIOCARBONS USED IN THE PROCESSES OF THE EXPLOITATION OF TECHNOLOGICAL LIQUIDS

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**Key words:** biocarbons, biocarbon structure, X-ray energy dispersion spectroscopy (EDS), infrared spectrophotometry (FTIR), the Raman spectroscopy.

**Abstract:** In the dynamic development work in the use of plant waste to produce biocarbons, the assumed sorption capacity resulting from the chemical structure of the surface determines the need to adapt the advanced spectral methods to test the quality of newly-manufactured materials. In this paper, the usefulness of X-ray energy dispersion spectroscopy (EDS), infrared spectrophotometry (FTIR), and Raman spectroscopy techniques to determine the chemical composition and identification of functional groups and the ordering of the biocarbon crystal structure were determined. In particular, examples of the interpretation of obtained spectra are presented. The EDS technique allows the determination of changes in the chemical composition occurring during pyrolysis under certain thermal conditions. Thanks to infrared spectrophotometry (FTIR), information was obtained about functional groups present on the surface of biocarbon, as well as directions of structural changes occurring in cellulose waste due to pyrolysis, which are dependent on temperature conditions. The Raman spectroscopy allowed the assessment of the degree of ordering of biocarbon structures based on the identification of the intensity of spectral signals corresponding to the D band, characteristic for the amorphousness of carbon structures and the G band, indicating the ordering of carbon structures. These techniques are a package of complementary analytical methods that allow for a comprehensive study of the chemical structure of biochar, which is a product of the pyrolysis of waste of plant origin, which is used, among others, in processes of the exploitation of technological fluids, particularly for purifying industrial waters.

### Zastosowanie metod spektralnych do identyfikacji mikrostruktury i budowy chemicznej biowęgla wykorzystywanych w procesach eksploatacji cieczy technologicznych

**Słowa kluczowe:** biowęgle, budowa biowęgla, rentgenowska spektroskopia dyspersji energii (EDS), spektrofotometria w podczerwieni (FTIR), spektroskopia Ramana.

**Streszczenie:** Dynamiczny rozwój prac w zakresie wykorzystania odpadów roślinnych do produkcji biowęgla o założonych zdolnościach sorpcyjnych, wynikających m.in. ze struktury chemicznej powierzchni, determinuje konieczność adaptacji zaawansowanych metod spektralnych do badania jakości nowo wytwarzanych materiałów. W niniejszej pracy określono przydatność techniki spektroskopii rentgenowskiej z dyspersją energii (EDS), spektrofotometrii w podczerwieni (FTIR) i spektroskopii Ramana do określenia składu chemicznego oraz identyfikacji grup funkcyjnych oraz uporządkowania struktury krystalicznej biowęgla. W szczególności przedstawiono przykładowe sposoby interpretacji uzyskiwanych widm. Technika EDS pozwala na określenie zmian w składzie chemicznym zachodzących podczas pirolizy w określonych warunkach termicznych. Dzięki spektrofotometrii w podczerwieni (FTIR) uzyskano informacje o grupach funkcyjnych obecnych na powierzchni biowęgla, a także o kierunkach przemian strukturalnych zachodzących w odpadach celulozowych na skutek pirolizy, które są zależne od warunków temperaturowych. Natomiast spektroskopia Ramana pozwoliła na ocenę stopnia uporządkowania struktur biowęglowych na podstawie identyfikacji intensywności sygnałów spektralnych odpowiadających pasmu D, charakterystycznemu dla amorficzności struktur węglowych i pasmu G, świadczącym o uporządkowaniu struktur węglowych. Wymienione techniki stanowią pakiet uzupełniających się metod analitycznych, pozwalających na kompleksowe zbadanie struktury chemicznej biowęgla, stanowiących produkt pirolizy odpadów pochodzenia roślinnego, znajdujący zastosowanie m.in. w procesach eksploatacji cieczy technologicznych, w szczególności do oczyszczania wód przemysłowych.

## Introduction

Currently, a significant increase in interest in biocarbons is observed, including their specific surface, properties, and the possibility of their application in environmental protection [1]. The biocarbon is similar in structure to charcoal. The developed specific surface, microporosity, or the presence of functional groups make biocarbon an increasingly popular sorbent, and thus encourage researchers to carry out more and more extensive work on their properties and practical application [1]. The chemical structure of the surface of coals significantly affects its adsorption, acid-base, oxidation-reduction, as well as catalytic and electrochemical properties. These properties depend to a large extent on the occurrence of function groups (mainly oxygen and nitrogen) on the surface, arising directly at the pyrolysis stage or introduced during the physical or chemical activation of carbon precursors [2–6]. A characteristic feature of biocarbon is their very well-developed porous structure [7]. However, the structure and physicochemical properties of biocarbon differ depending on the biomass from which they were obtained, as well as the thermal parameters of pyrolysis [8].

The knowledge of the structure and, above all, the chemical composition of biocarbon and the presence of functional groups formed on their surfaces determines the areas of the application of this type of products as effective sorbents intended for removing pollution from sewage and industrial oils, removing toxins and odours from the air, improving the quality of produced pharmaceutical, petrochemical and food products, as well as drinking water treatment [9–14].

The correct selection of biocarbon for specific applications requires knowledge of their structural features, including their chemical structure. Therefore, checking the impact of their production technology on the chemical structure is essential in forming the physicochemical properties of the biocarbon at the stage of their production. Thus, it is necessary to use advanced analytical techniques enabling comprehensive analysis of biocarbon quality. The spectral techniques are very useful in this area. To determine the physicochemical properties of biocarbon, i.e. the structure, chemical composition or the presence of functional groups on their surface, it is necessary to use advanced spectral analysis techniques, in particular, infrared spectrophotometry (FTIR), X-ray energy dispersion spectroscopy (EDS), and Raman spectroscopy [15–18]. The analysis of biocarbons using these techniques allows obtaining information on their microstructure, the presence of functional groups on their surface, and their chemical composition.

The aim of the work was to present a comprehensive approach to the determination of the microstructure and chemical structure of biocarbon, obtained pyrolytically from plant biomass, using spectral analysis methods.

The paper presents sample results illustrating the scope of information obtained from spectral analyses carried out using the FTIR method, Raman spectroscopy, and the EDS technique.

## Materials and method

### The characteristics of research objects

The vegetable waste, i.e. cherry stones and biocarbon obtained during the pyrolysis of cherry stones at temperatures up to 500°C and up to 700°C were used as demonstrative materials used in spectral tests. The waste plant that was used during laboratory work was dried and characterized by a moisture content not exceeding 10%. The procedure for preparing and carrying out cherry stones pyrolysis was described in an earlier work [19]. Infrared spectrophotometry (FTIR), X-ray energy dispersion spectroscopy (EDS), and Raman spectroscopy were used to study the microstructure of biochar obtained from cherry seeds and to identify their elemental composition.

### FTIR infrared spectrophotometry

The FTIR technique is used to identify the structure of biochar functional groups. By using the FTIR technique, it is possible to identify the types of bonds, and the effects of the vibration of ions and molecules in crystal lattices in the tested material. The most important groups that can be analysed by the FTIR technique include carbonyl groups, -OH groups, C-H bonds, double and triple bonds (C=C, C≡C). The shape of the spectrum depends on the rotation and oscillation of chemical bonds [20]. In the FTIR spectrum, several ranges of key wave numbers can be distinguished for identifying the chemical structure of the material being tested. For example, the range 4000–2500 cm<sup>-1</sup> corresponds to the valence vibrations of O-H, N-H, C-H, S-H, CH<sub>2</sub> and CH<sub>3</sub> bonds. The range of 2500–2000 cm<sup>-1</sup> is the valence vibrations of the C=C=C system and the triple bonds C≡N and C≡C. The 2000–1500 cm<sup>-1</sup> range includes valence vibrations of C=C, C=O, C=N, N=N double bonds, deformation vibrations of N-H and O-H bonds from water. The range of 1500–650 cm<sup>-1</sup> is a dactyloscopic area, which is difficult to interpret, and contains mainly valence vibrations of C-C, C-N, C-O bonds and C-H deformation vibrations [21]. Due to the above, spectrum analysis allows the identification of emerging functional groups during radical reactions occurring during pyrolysis, and also allows the destruction of bonds, e.g., glycosidic, which is present in waste cellulosic products.

The FTIR spectra of biocarbons were obtained using a FTIR 6200 spectrometer (from Jasco) in reflection mode. For recording spectra of biocarbon, a Pike type diamond

crystal attachment was used. The following parameters were used during spectral measurements: spectral range: 4000–600  $\text{cm}^{-1}$ , spectral resolution: 4  $\text{cm}^{-1}$ , TGS detector, and averaging the spectrum from 30 scans.

### The Raman spectroscopy

The Raman spectroscopy is used to determine the biocarbon structure. This technique involves measuring inelastic radiation of photon scattering. Very strong radiation sources are used for excitation, currently only lasers. The Nd: YAG (yttrium-aluminium), XeF or KrF lasers are most commonly used. The Raman spectroscopy gives spectra containing oscillatory bands corresponding to the normal vibrations of the molecules. The intensity of Raman bands is determined by the change in polarizability during normal vibration, not the change in the electric dipole moment, as for infrared bands. Using this technique, it is possible to determine the crystal form, chemical composition, intermolecular interactions, the degree of ordering, and the spatial distribution of stresses in the tested material [22–26].

The Raman spectra were taken at room temperature using an NRS-5100 spectrometer from Jasco (Japan), using green laser excitation with a wavelength of 532 nm and an exposure time of 100 seconds. The spectra were recorded in the Raman range from 260  $\text{cm}^{-1}$  to 3900  $\text{cm}^{-1}$  with a resolution of 3.2  $\text{cm}^{-1}$ .

### The X-ray energy dispersion spectroscopy (EDS)

The X-ray energy dispersion spectroscopy (EDS) is used to determine the chemical composition of biocarbon. This technique is usually connected

with scanning electron microscopy (SEM) enabling the selection of x-ray examination sites in the microstructure. The EDS is a technique that uses the measurement of X-rays emitted by the material under study as a result of its excitation with an electron beam. In the EDS technique, the energy of individual x-ray photons produces a current charge in a semiconductor detector, where it is converted into a voltage pulse. The content of elements is determined by the proportional dependence of the number of characteristic X-ray pulses emitted on the concentration of elements in the tested sample [27]. The EDS technique allows for elemental qualitative and quantitative analysis of the tested material, which consequently allows the verification of the presence of molecular structures identified by other spectral techniques.

A Hitachi SU-70 scanning electron microscope equipped with EDS x-ray microanalyser was used to identify the biocarbon elemental composition. The analyses were carried out under the following conditions: magnification x500, x1000, and x2000, accelerating voltage 15 kV, receiving angle 30°, and vacuum  $10^{-8}$  Pa.

## Results and discussion

### Evaluation of surface chemistry of biocarbon

The approach to the interpretation of FTIR spectra enabling the determination of functional groups was presented on the basis of a comparative analysis of spectra obtained for biocarbons obtained from cherry stones (Fig. 1).

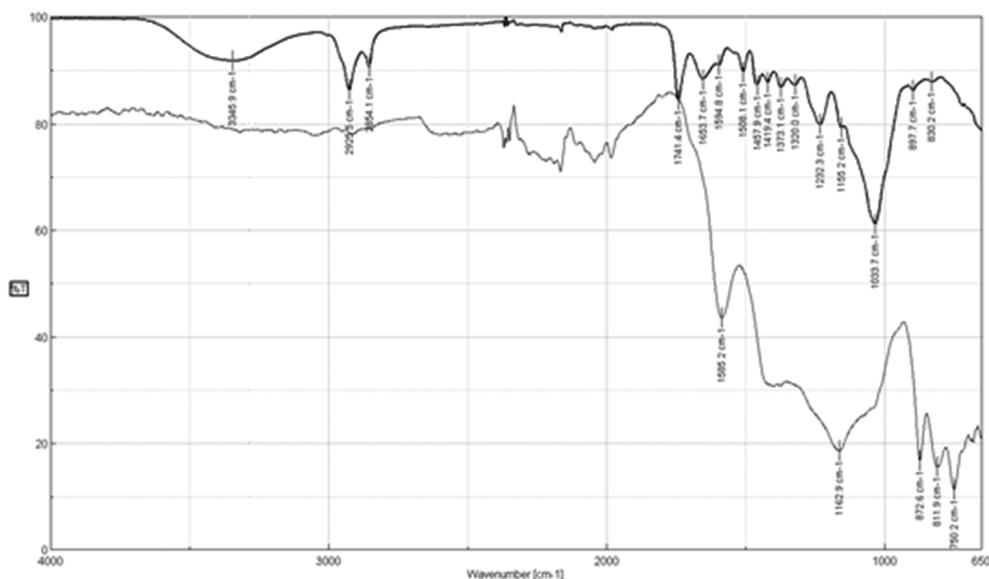
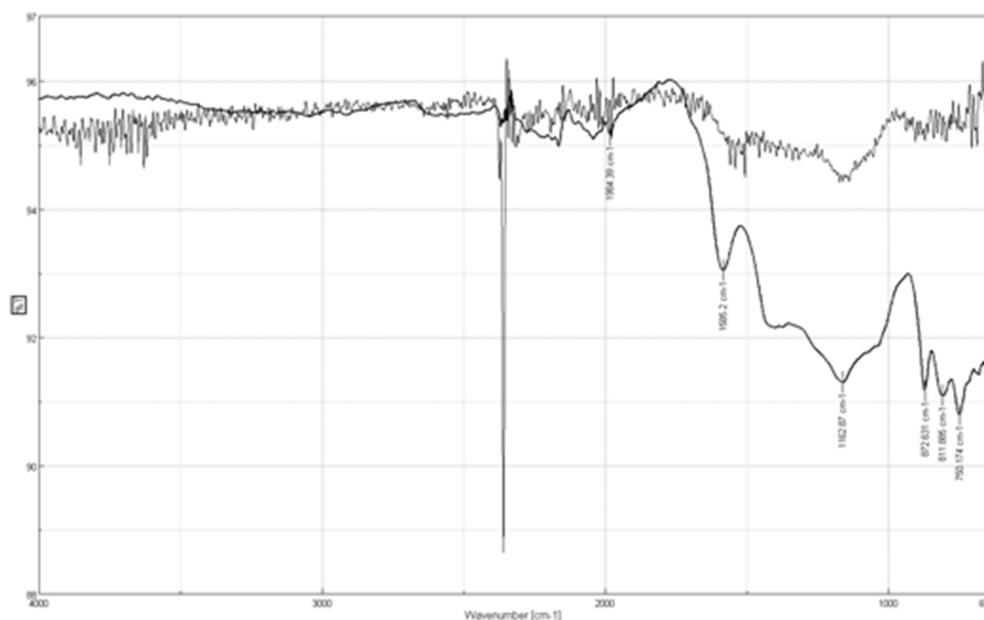


Fig. 1. The comparison of FTIR spectra of cherry stones (a) before and (b) after pyrolysis at 500°C

The analysis of recorded infrared spectra indicates the lack of vibration signals stretching the oxygen-hydrogen bond in hydroxyl groups, which were recorded in the spectra of plant waste before pyrolysis. In the spectrum obtained for cherry stones, the extreme spectral band was located at approx.  $3346\text{ cm}^{-1}$ . This means that the hydroxyl group present in cellulose is destroyed by pyrolysis. Therefore, hydroxyl, optionally hydrogen and oxygen radicals can be generated. It should also be noted that hydrocarbon functional groups also undergo structural conversion during pyrolysis, which is manifested by the disappearance of spectral bands in the  $3000\text{--}2800\text{ cm}^{-1}$  wave number range (valence vibrations of C-H structures in methyl, methylene and methine groups) in FTIR biocarbon spectra compared to the waste spectra before pyrolysis. The binding of glycoside in cellulose is also destroyed, as evidenced by

the lack of bands in the biocarbon spectra corresponding to the -C-O-C- group, i.e. located at a wavelength of about  $1034\text{ cm}^{-1}$ . A detailed analysis of the biocarbon spectra obtained during pyrolysis allows us to conclude that structural products containing oxygen and nitrogen are present in the obtained products. In particular, in the spectra of biocarbon from cherry stones obtained, a clear signal is observed located at a wave number of  $1585\text{ cm}^{-1}$ . These bands are located in the vibration region of coupled C=C and C=O bond systems, and thus aromatic ring structures with a ketone group may be formed.

The presented comparative analysis clearly shows that the FTIR technique allows the description of chemical changes occurring during pyrolysis. In addition, this technique allows the assessment of the impact of technological parameters on the chemical structure of pyrolysates. Exemplary results are shown in Fig. 2.



**Fig. 2. The comparison of FTIR spectra of biocarbon obtained from cherry stones under the following thermal conditions: a) up to  $500^{\circ}\text{C}$ , b) up to  $700^{\circ}\text{C}$**

The analysis of recorded infrared spectra indicates that the temperature conditions of pyrolysis determine the chemical structure of the products obtained. Under thermal conditions up to a temperature of  $500^{\circ}\text{C}$ , carbon products are formed, containing organo-oxygen structural groups in their structure coupled with carbon-carbon double bonds in aromatic rings. This is evidenced by spectral bands located in the biocarbons spectra obtained from cherry stones at a wave number of  $1585\text{ cm}^{-1}$  [15]. Increasing the pyrolysis temperature to  $700^{\circ}\text{C}$  leads to the disappearance of the abovementioned bands in the FTIR spectra of the biocarbon. High-temperature pyrolysis reduces the possibility of the formation of active organo-oxygen structures on the biocarbons

surface. Biocarbons obtained from cherry stones when heated to  $700^{\circ}\text{C}$  do not contain functional groups such as carbonyl or quinone group independently occurring on the carbon surfaces of oxygen, identifiable by means of infrared spectrophotometry. The C=O bond vibration band in quinones occurs at a wave number of  $1657\text{ cm}^{-1}$ . However, the band at the wave number  $1617\text{ cm}^{-1}$  corresponds to the vibrations of the aromatic ring. The confirmation of the occurrence of the mentioned molecular structures is the band discussed earlier at the wave number  $1576\text{ cm}^{-1}$ , associated with the vibrations of the C=C moiety in the aromatic ring, connected with the C=O carbonyl group. However, the incorporation of oxygen into carbon cyclic structures in the form of ether bridges is likely, which

can be indicated by spectral bands present in the spectra of products obtained at higher temperatures, whose maxima are in the range of  $1020\text{--}1075\text{ cm}^{-1}$  (aromatic ethers) or  $1060\text{--}1150\text{ cm}^{-1}$  (aliphatic ethers). However, the lack of clear signals from the aromatic rings in the spectra obtained indicates that, in carbon structures, C=C bonds are only a small remainder

### The identification of elemental biocarbons structure (EDS)

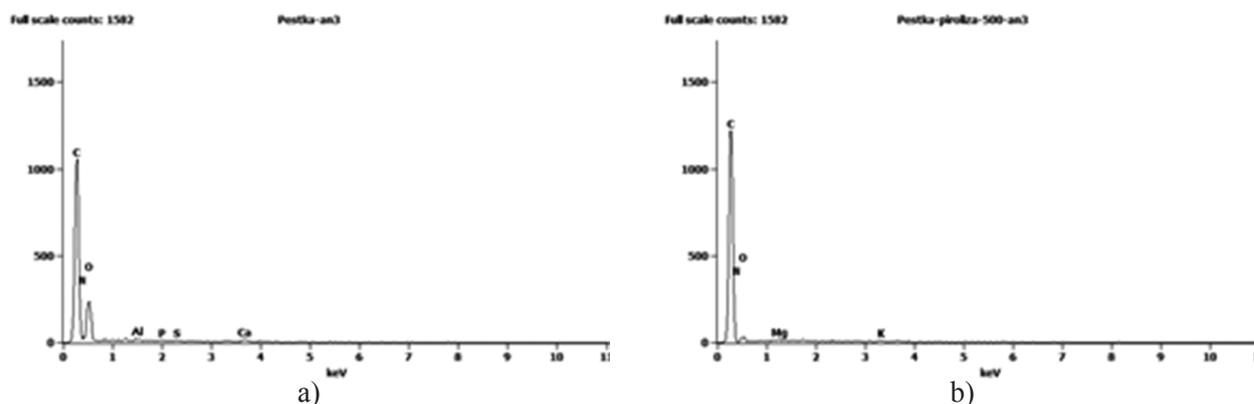


Fig. 3. The EDS spectra recorded during cherry stones testing: a) before pyrolysis, b) after pyrolysis at  $500\text{ }^{\circ}\text{C}$

In the tested material before and after pyrolysis, the presence of carbon, oxygen and nitrogen, i.e. elements that are part of the building material, is observed, and additionally signals from magnesium, phosphorus, calcium and potassium, i.e. elements that could be absorbed by plants from artificial fertilizers [14]. However, the current sulphur in cherry stones before pyrolysis comes from chemical compounds that create resin-oil substances. After the heat

of the originally occurring structures rebuilt during thermal treatment [28–31].

Considering the above observations, it can be concluded that the FTIR analyses carried out allow the identification of functional groups on the surface of biocarbon, which can be active centres particularly useful in sorption operations.

treatment of cherry stones, sulphur is not observed in the pyrolysates, which indicates that sulphur compounds were removed along with pyrolysis oil or in gas products.

Based on EDS analyses, it is also possible to compare the percentages of the main building elements in waste materials before pyrolysis and in biocarbons obtained by pyrolysis. The examples of the results are summarized in Table 1.

Table 1. The comparison of the relative percentages of carbon and oxygen in the material before and after the pyrolysis of cherry stones

Component	The content of the component in the tested material [% mass]		
	waste before pyrolysis	biocarbon after pyrolysis to temperature $500\text{ }^{\circ}\text{C}$	biocarbon after pyrolysis to temperature $700\text{ }^{\circ}\text{C}$
Carbon	44.91	58.54	69.18
Oxygen	43.60	24.84	6.12

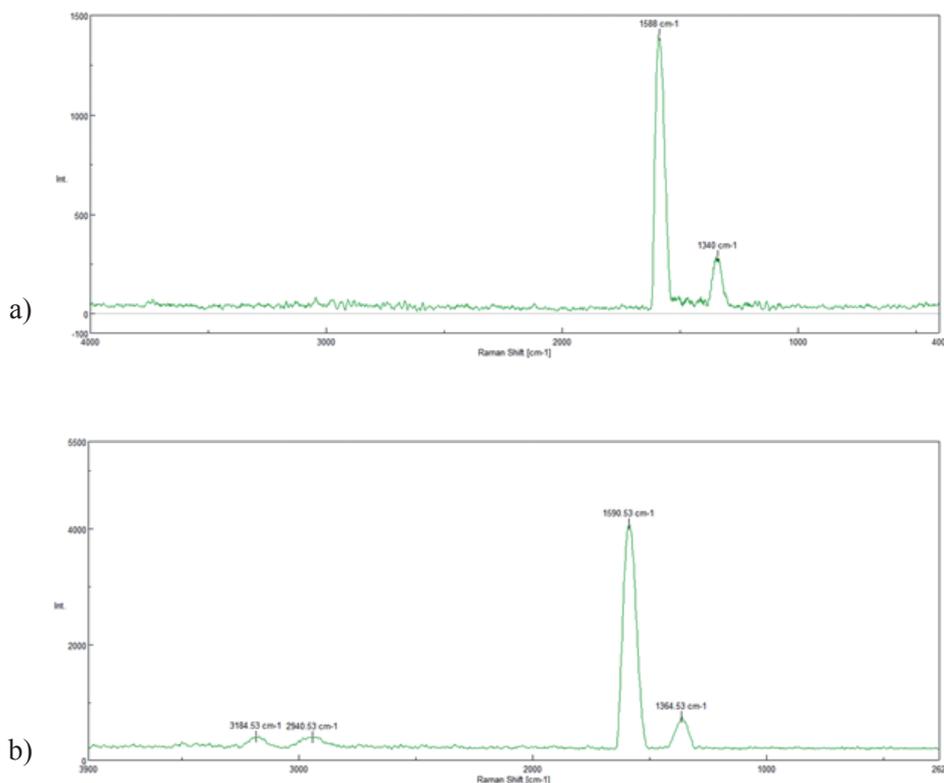
The results obtained (Table 1) indicate that in biocarbons obtained for different process conditions, a carbon content increase is observed compared to the content in the original natural waste. The highest increase in carbon content was observed for products obtained during pyrolysis carried out to a temperature of  $700\text{ }^{\circ}\text{C}$  (10.64% m/m) compared to pyrolysis carried out to a temperature of  $500\text{ }^{\circ}\text{C}$ . The observed changes indicate the destruction of hydrocarbon chains and the removal during the pyrolysis of elements other than carbon in the form of low-molecular chemical compounds, e.g., in the form of low-molecular hydrocarbons, sulphur oxides, carbon oxides, and others. With the increase in carbon

content, a decrease in oxygen content was observed. The greatest oxygen decrease for biocarbons was observed during pyrolysis carried out to a temperature of  $700\text{ }^{\circ}\text{C}$ . The reduction of oxygen content in post-pyrolysis products indicates the breaking of carbon-oxygen bonds in the structures of hydroxyl and glycoside cellulosic wastes, followed by conversion to low-molecular products removed from the pyrolysis chamber. The oxygen determined in biocarbons can come from both the oxygen radicals released during the destruction of plant waste and then built into the biocarbons structure. The resulting functional groups associated with the biocarbons surface can be active centres in selective sorption processes.

The use of X-ray energy dispersion spectroscopy (EDS) as a modern analytical method enables a closer understanding of the surface structure of solids, as well as some of the basic phenomena occurring on them. Therefore, X-ray energy dispersion spectroscopy (EDS) is undoubtedly one of the most important tools used in biocarbon characteristics. The X-ray energy dispersion spectroscopy (EDS) spectra can be used to identify the chemical composition of small sample fragments.

### Research on crystalline and amorphous biocarbon structures

The analysis of the structure of the obtained biocarbon, including the evaluation of the ordering of the crystal structure was possible thanks to research using the Raman spectroscopy. The examples of spectra allowing a comparison of the characteristics of biocarbon obtained at different temperatures are shown in Figure 4.



**Fig. 4. The comparison of Raman spectra of biocarbon obtained during pyrolysis of cherry stones conducted at the temperature of: a) Stone 700°C, b) Stone 500°C**

The spectra of the studied biocarbon contain bands directly related to the vibrations of carbon and hydrocarbon structures. In the case of analysis of the Raman spectra obtained for biocarbon from cherry stones by pyrolysis at 500°C and 700°C, a band size of 1580  $\text{cm}^{-1}$ , otherwise known as the G band, is observed. This band corresponds to stretching vibrations with  $E_{2g}$  symmetry. It comes from tensile vibrations of the  $sp^2$  hybridization of the carbon bond pairs occurring in ring structures. This band occurs in the case of graphite with an ordered structure. An additional band located at the Raman shift above 1340  $\text{cm}^{-1}$  and 1364  $\text{cm}^{-1}$  characterizes the level of amorphousness of carbon structures and indicates a highly disordered biocarbon structure. This band is usually called the D1 defect band. It corresponds to  $A_{1g}$  symmetry and is associated with plane imperfections, e.g., defects and heteroatoms [19, 24, 32].

The Raman spectroscopy is a new technique that has recently been used in many analytical areas. The use of this technique in biocarbons analysis is a new, intensively developed issue. Raman spectroscopy, like infrared spectroscopy, provides information about the structure of the molecule, the interatomic bonds that make it up, as well as about their polarizability. Thus, it can be concluded that Raman spectroscopy is complementary to FTIR spectroscopy and vice versa.

### Conclusion

By using such techniques as X-ray energy dispersion spectroscopy (EDS), infrared spectrophotometry (FTIR), and Raman spectroscopy, one can determine the microstructure, chemical composition, and degree

of ordering of the structure of biocarbons obtained from vegetable waste, which was demonstrated by the example of testing products made from cherry stones on by pyrolysis in two temperature ranges of 500°C and 700°C. The analysis of biocarbons obtained during pyrolysis up to 500°C by infrared spectrophotometry (FTIR) allowed the determination of the occurrence of organo-oxygen groups that may be useful during physicochemical sorbing of polar compounds or chelating metal ions. The biocarbons obtained up to a maximum value not exceeding 700°C, on the other hand, have ether moieties embedded mainly in aliphatic cyclic moieties. By using the X-ray energy dispersion spectroscopy (EDS), it is possible to analyse the elemental composition of biocarbons. Analysis of the obtained charts and tables showed a decrease in oxygen content and an increase in carbon content in biocarbons. The reduction of oxygen content is a result of increasing the temperature of the pyrolysis process. This indicates the possibility of conversion of oxygen functional groups and oxygen removal, e.g., in gaseous products generated during pyrolysis. On the other hand, an increase in the carbon content of pyrolysis products indicates the destruction of hydrocarbon chains and the removal of low-molecular chemical elements during pyrolysis. The Raman spectroscopy analysis helped to obtain information on the degree of biocarbons structure ordering. For the obtained biocarbons, two bands are most characteristic: the G band and the D band. The G band that comes from the stretching vibrations of carbon bond pairs of  $sp^2$  hybridization occurring in ring structures and is closely related to the occurrence of ordered carbon structures. The D band characterizes the level of the amorphousity of carbon structures. The conclusions of the study are complementary and allow one to determine the structure of biocarbons obtained from vegetable waste. The obtained results of the analyses can be used during quality control of commercial products used in various types of process fluids exploitation, in particular, for purifying industrial waters.

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