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Torrefaction of Flax Shives as a Process of Preparation Waste Vegetable Biomass for Energy Purposes

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Keywords:

Vegetable biomass, flax shive, biomass torrefaction, alternative fuel, solid biofuel, biocarbon, combustion heat

Abstract

The use of processed biomass, derived from agricultural crop residues, as a fuel is becoming increasingly important in the energy sector, which additionally allows for the management of excess waste that is a burden on the environment. The aim of this study was to investigate the effect of the torrefaction process conditions in a carbon dioxide atmosphere on the chemical structure of biocarbon and the energy parameters of the produced product, which can be a solid biofuel. The biomass chosen for the experimental work was flax shive. Determinations of the heat of combustion of the produced biocarbon samples were carried out using a KL-10 calorimeter, and identification of the molecular structure of the product and the starting biomass was carried out using infrared spectrometry. It was confirmed that increasing the temperature of biomass torrefaction increases the heat of combustion of the product, with this parameter obtaining the most favourable value for biocarbon obtained during torrefaction at 320°C and for 20 to 30 minutes. The heat of combustion of the biocarbon produced during torrefaction at 320°C and for 30 minutes was 25.92 MJ/kg, with a feedstock mass loss of 41%. Such conditions lead to a significant conversion of the chemical structure of the biomass, with no complete destruction of organic structures.

1. INTRODUCTION

Global use of biomass for energy purposes is steadily increasing and is expected to reach 25-30% of total energy resource consumption by 2050. Current legal regulations allow energy to be obtained from biomass instead of fossil fuels, which is included in the overall balance of energy production from renewable sources. There are several definitions of biomass in both Polish and EU law. In each of the legal acts dealing with biomass, depending on the purpose and legal needs, appropriate nomenclature is used, which may differ from one document to another. For example, in the Act of 7 June 2018 amending the Renewable Energy Sources Act and certain other acts [Journal of Laws 2018 item 1276], biomass is defined as the biodegradable part of products, waste or residues of biological origin from agriculture, including plant and animal substances, forestry and related industries, including fisheries and aquaculture, processed biomass, in particular in the form of briquette, pellet, torrefaction and biocarbon. Biomass also includes the biodegradable fraction of industrial or municipal waste of vegetable or animal origin, including waste from waste treatment installations and waste from water and sewage treatment, in particular sewage sludge, in accordance with waste legislation on the eligibility of the energy fraction recovered from the thermal treatment

of waste. Biomass of agricultural origin, on the other hand, is defined for the purposes of the provisions of the cited law as biomass derived from energy crops, as well as waste or residues from agricultural production and the industry processing its products. On the other hand, biomass is listed as one of the solid fuels in the Act on the System for Monitoring and Controlling Fuel Quality [Journal of Laws 2022, item 1315]. This act applies to biomass obtained from trees and shrubs and vegetable biomass from agriculture. The Regulation of the Minister of Climate and Environment of 24 September 2020 on emission standards for certain types of installations, fuel combustion sources and waste incineration or co-incineration facilities refers to biomass as products consisting of vegetable substances from agriculture or forestry that can be used as fuel in order to recover the energy they contain.

The definition of biomass introduced in the above-mentioned regulation, as well as for the purposes of the regulation of the Minister of Climate and Environment of 7 September 2021 on requirements for emission measurements, is in line with the definitions of this concept adopted in Directive (EU) 2015/2193 of the European Parliament and of the Council of 25 November 2015 on the limitation of emissions of certain pollutants into the air from medium-sized combustion plants and Directive 2010/75/EU of the European Parliament and of

the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control). According to the provisions of the aforementioned directives, biomass can be, in particular, products consisting of vegetable matter from agriculture or forestry that can be used as fuel to recover the energy they contain, as well as vegetable waste from agriculture and forestry.

In contrast, Directive (EU) 2018/2001 of the European Parliament and of the Council of 11 December 2018 on the promotion of the use of energy from renewable sources defines several terms for biomass, such as the biodegradable fraction of biodegradable products, waste or residues of biological origin from agriculture, including vegetable and animal substances, forestry and related industries, including fisheries and aquaculture, as well as the biodegradable fraction of waste, including industrial and municipal waste of biological origin. In addition, agricultural biomass and forest biomass are defined.

It should also be noted that for the statistical purposes of the Central Statistical Office, definitions of solid biomass have been adopted, and types of fuel have been distinguished, including biomass used for heating purposes in households. According to the adopted criteria, solid biofuels (biomass) comprise organic, non-fossil substances of biological origin that can be used as fuel for heat production or electricity generation. The main solid biomass fuels are firewood in the form of logs, roundwood, chips, briquettes, pellets and forestry residues, in particular undersized wood such as branches, poles, chipping, shrubs, brushwood and waste from the wood industry (e.g. shavings, sawdust). A separate group consists of fuels from plantations for energy purposes (fast-growing trees, dicotyledonous perennials, perennial grasses, cereals grown for energy purposes) and organic residues from agriculture and horticulture (e.g. horticultural production waste, animal excrement, straw). The group of solid biofuels also includes biocarbon, understood as solid residues from the pyrolysis of wood and other vegetable substances [CSO 2019]. The separation in the group of solid fuels of biocarbon is in line with other national statutory regulations, in particular the Renewable Energy Sources Act. Hence, it is possible to use agricultural biomass to produce biocarbon, which can be classified as renewable fuels.

The physicochemical properties of biomass depend on its chemical structure and the proportion of lignin, cellulose and hemicellulose in the microstructure. Cellulose contains a large amount of carbon compared to other lignocellulosic components and is largely responsible for the energy parameters of biomass. In contrast, the main function of lignin in lignocellulosic biomass is to act as a binding element for cellulose and hemicellulosic structures [Acharya et al. 2015]. Biomass, due to its physico-chemical properties, i.e. high oxygen content in the chemical structure and moisture content, as well as susceptibility to putrefaction processes, is difficult to store and co-fire with coal, in particular, it interferes with grinding in coal mills, hinders dust feeding into the power

boiler, and has a relatively low calorific value [Ivanovski 2022]. For example, the calorific value of wood is in the range 15.5–16.5 MJ/kg, with a moisture content of 15%. The relationship between the calorific value of wood and its moisture content indicates that it is beneficial to dry the fuel before combustion. The moisture contained in wood constitutes thermal ballast, reducing the value of the wood's combustion heat as well as the efficiency of the entire combustion process [Rybak 2006]. In addition, wood biomass has a high moisture content, i.e. up to 45 %, and a high volatile matter content of about 70 %. Compared to raw biomass, solid fossil fuel (coal) is characterised by a higher calorific value (23–28 MJ/kg), higher energy density (18.4–23.8 GJ/m³), higher bulk density (800–850 kg/m³), lower moisture content (10–15%), and lower volatile matter content, ranging from 15% to 30% by weight [Akbari 2020]. One way to increase the quality characteristics of biomass used for energy purposes is its preliminary torrefaction. Torrefaction is a process of mild pyrolysis carried out at temperatures between 200 and 400°C in an inert gas atmosphere [Abogunde Abdulyekeen 2021]. Biomass torrefaction is usually carried out by stepwise heating consisting of several stages, i.e. preheating, drying, re-drying and intermediate heating, torrefaction and cooling [Wei-Hsin 2021]. It is a method of treating biomass, during which cellulose chains are destroyed (hydroxyl groups are removed, glycosidic bonds are broken), gaseous products (steam, carbon monoxide and dioxide, acetic acid, furans) are generated, in some cases also pyrolysis oil, and, as a consequence, a carbonisate is produced as the main product, characterised by low H/C and O/C ratios, thereby increasing the calorific value of the feedstock and increasing the grindability and storage stability [Wang 2019, Emsley 1994]. For example, the product of rice straw torrefaction at 300°C has a calorific value of 23.57 MJ/kg, which is comparable to that of lignite [Liu 2021]. Another type of biomass is flax shive waste, which constitutes 70–75% of the yield. The energy value of flax shives is approximately 18 MJ/kg. During torrefaction, the energy value increases, and the products co-fire easily with coal. Products of torrefaction are most often obtained from biomass waste, mainly from sawmill production, forestry, fruit and vegetable processing, and agriculture, which causes many problems in storage due to putrefactive processes. During decomposition, greenhouse gases such as methane and carbon dioxide are released. The efficiency of carbonisate formation and the composition of the various by-products (gaseous and liquid) depends on the proportion of cellulose, hemicellulose and lignin in the biomass feedstock. For example during the torrefaction of lignin, small amounts of hydrogen and methane may appear in the gaseous products in addition to the main component, carbon dioxide [Chena 2018]. The Renewable Energy Sources Act defines biochar (a product of torrefaction or pyrolysis) as the renewable fuel that has the greatest potential for reducing carbon dioxide. Each GJ of energy stored in one tonne of biochar can reduce approximately 96 kg of carbon dioxide. This means that

the combustion of biochar with a calorific value of 26 GJ/Mg allows for the reduction of approximately 2.5 tonnes of carbon dioxide produced during the combustion of solid fuels [Wilson 2014].

The aim of this study is to investigate the influence of the torrefaction process conditions (temperature and time) on the chemical structure of the biocarbon and the energy parameters of the produced product, which can be a solid biofuel.

2. MATERIALS AND METHODS

2.1. Study objects and torrefaction methodology

On the basis of previous thermogravimetric studies, waste biomass in the form of flax shive with a moisture content not exceeding 10% was selected. The heat of combustion of this biomass was 17.37 MJ/kg. The elemental composition of biomass was determined using the EDS method (spectrum in Fig. 1).

Flax biomass contains carbon (45.94 % w/w), oxygen (43.09 % w/w), nitrogen, magnesium and calcium. The EDS method does not allow the determination of hydrogen. The structure of the selected flax biomass does not contain sulphur or chlorine. The selected vegetable biomass was subjected to a thermal treatment that included preheating for a period of 30 minutes under temperature rise conditions from 20°C to 200°C, annealing for 5 minutes at 200°C, followed by temperature rise at a rate of 5°/min to the appropriate isothermal torrefaction temperature, viz: 250, 270, 300, 320 or 370°C, which was carried out for 15 min. Isothermal heating temperatures were selected based on literature analysis and the team's experience with the impact of temperature on the quality of pyrolysis products [Thengane et al. 2022, Molenda et al. 2018]. Then,

after turning off the heating, the samples were seasoned in the furnace chamber for 12 h until spontaneous cooling to ambient temperature. The biomass torrefaction process was also carried out at one selected temperature at different times, viz: 10, 15, 20, 30 or 45 minutes. In order to maintain the specified torrefaction time, intensive post-process heat removal was used with a cooling system located in the door to the pyrolytic chamber of the furnace. A carbon dioxide flow rate of 5 dm³/min was used during heating and cooling. The torrefaction processes were carried out on a laboratory bench equipped with a Czylok-type FCF-V12RM chamber furnace.

2.2. Instrumental testing methodology

The biocarbon obtained (see Figure 2 for an illustrative photo) was subjected to instrumental tests to identify its chemical structure and to determine the heat of combustion, which indirectly indicates the energy value of the products obtained.

The biocarbon obtained during torrefaction was subjected to the heat of combustion tests, which were carried out using a KL-10 calorimeter. The measurement consisted of the complete combustion of 1 g of the biocarbon sample, compressed into a tablet. The sample was burned in an atmosphere of oxygen and introduced into a calorimeter bomb at a pressure of 2.5 MPa, which was placed in a water jacket. The temperature rise of the water was recorded, and the heat of combustion was calculated automatically by a computer program. The heat of combustion of the initial biomass not torrefied was also determined for comparison purposes.

Infrared spectra of the waste biomass and the obtained biocarbon were performed with an FTIR 6200 spectrometer (Jasco company) in reflectance mode. A Pike attachment with a diamond crystal was used. Spectral measurements

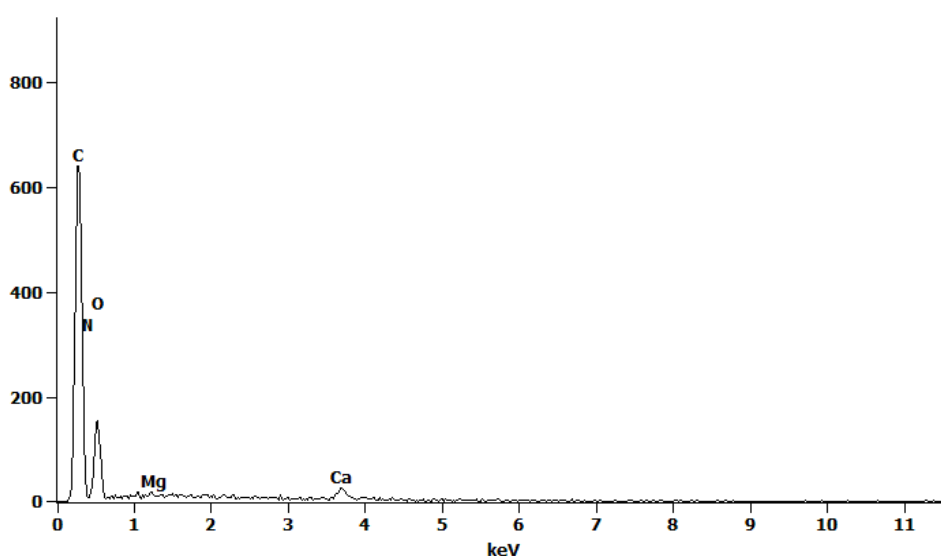


Figure 1. EDS spectrum of flax shive waste biomass



Figure 2. Biocarbon obtained during the torrefaction of flax shive (temperature - 250°C, process time - 10 min)

were made in the range 400-650 cm^{-1} , with a resolution of 4 cm^{-1} , using a TGS detector and averaging spectra from 30 scans.

3. RESULTS AND DISCUSSION

3.1. Influence of biomass torrefaction process parameters on biocarbon energy parameters

Figure 3 shows the variation of the heat of combustion of the torrefaction as a function of process temperature.

Analysis of the results showed the greatest increase in the heat of combustion values of the biocarbon obtained at temperatures of 250-320°C. After exceeding the temperature of 320°C, no further increase in the combustion heat value was found for the biocarbon obtained at 370°C. The greatest increase (56%) in the heat of combustion was found for biocarbon obtained at temperature of 320°C compared to the heat of combustion of the initial biomass.

The torrefaction process made it possible to obtain biocarbons whose mass varied with the process temperature. The smallest mass loss of about 19% was found at a temperature of 250°C, while the largest was 70% at a temperature of 370°C compared to the initial mass of the briquette. Changes in the mass of the torrefaction are shown in Figure 4.

Analysing the results shown in Figure 4, the greatest progression of mass loss was found at temperatures of 250-320°C, which for the product obtained at 320°C was 66% in relation to the initial sample mass. In the next stage of the study, for the temperature 320°C at which the maximum value of the heat of combustion of the biocarbon was recorded, the torrefaction process times were changed in order to determine the minimum process time. On the basis of preliminary tests, the minimum process time was

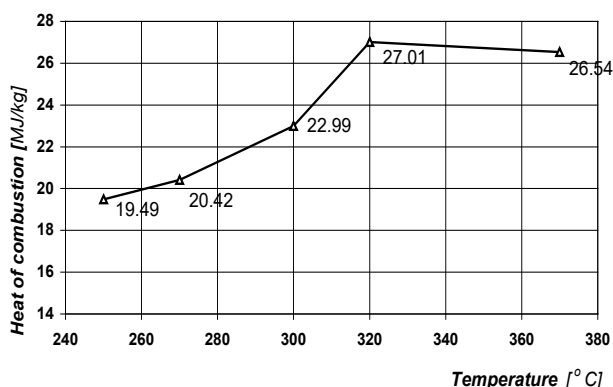


Figure 3. Effect of torrefaction temperature on the heat of combustion of the produced biocarbon (process time - 15 min, protective atmosphere - carbon dioxide)

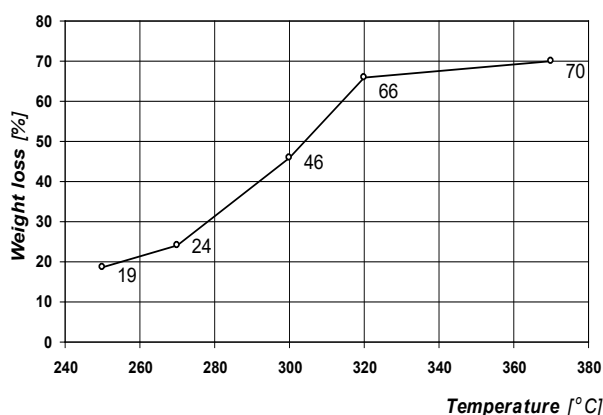


Figure 4. Effect of torrefaction temperature on the mass loss of the initial biomass sample (process time - 15 min, protective atmosphere - carbon dioxide)

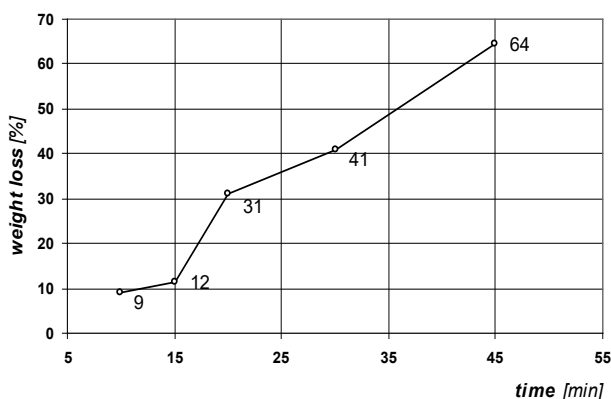


Figure 5. Effect of torrefaction time on the mass loss of the initial biomass sample (process temperature - 320°C, protective atmosphere - carbon dioxide)

set as 10 min, the maximum as 45 min - longer annealing being economically unjustifiable.

The dependence of biomass feedstock loss on the duration of the torrefaction process at 320° C is shown in Fig. 5, and the change in combustion heat in Fig. 6.

Analysis of the results shown in Fig. 5 and Fig. 6 indicates that running the taring process for 30 minutes results in a product with a combustion heat value of 25.92 MJ/kg, while the feedstock mass loss was 41%. The indicated process conditions for thermal treatment of biomass

are therefore sufficient to obtain a feedstock with a combustion heat of twice the value characterising the raw biomass, which was 17.35 MJ/kg. Increasing the duration of torrefaction does not result in a significant improvement in energy parameters but leads to a significant reduction in the amount of product produced. It should be noted that it is possible to run the torrefaction process for less than 30 minutes, which makes it possible to obtain a product with satisfactory energy parameters and less mass loss of the feedstock than in the case of a 30-minute process and can be beneficial in the energy and economic balance of obtaining biocarbon for energy purposes.

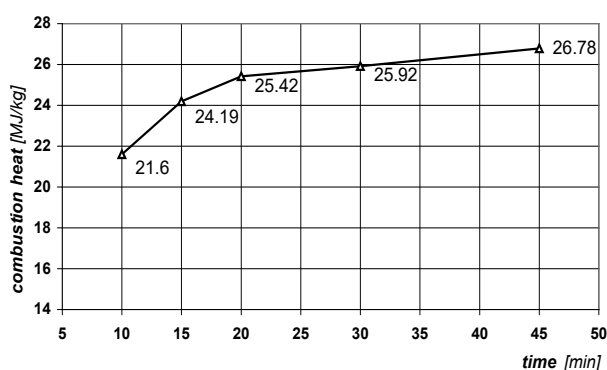


Figure 6. Effect of torrefaction time on the heat of combustion of the produced biocarbon (process temperature - 320°C, protective atmosphere - carbon dioxide)

3.2. Influence of biomass torrefaction process parameters on the chemical structure of biocarbon

A summary of the infrared spectra of the toricates obtained during annealing at different temperatures is shown in Figure 7.

The spectrum of the starting raw material has characteristic signals related to the vibrations of the structural groupings present in the cellulose molecules, and in particular to the stretching vibrations of the oxygen-hydrogen bond in the hydroxyl group (band at wave number 3343 cm⁻¹) and the vibrations of the C-O-C glycosidic grouping (band at wave number 1029 cm⁻¹). The presence of bands associated with vibrations of carbonyl groups (band at 1731 cm⁻¹) should also be noted. Besides, bands of hydrocarbon structures

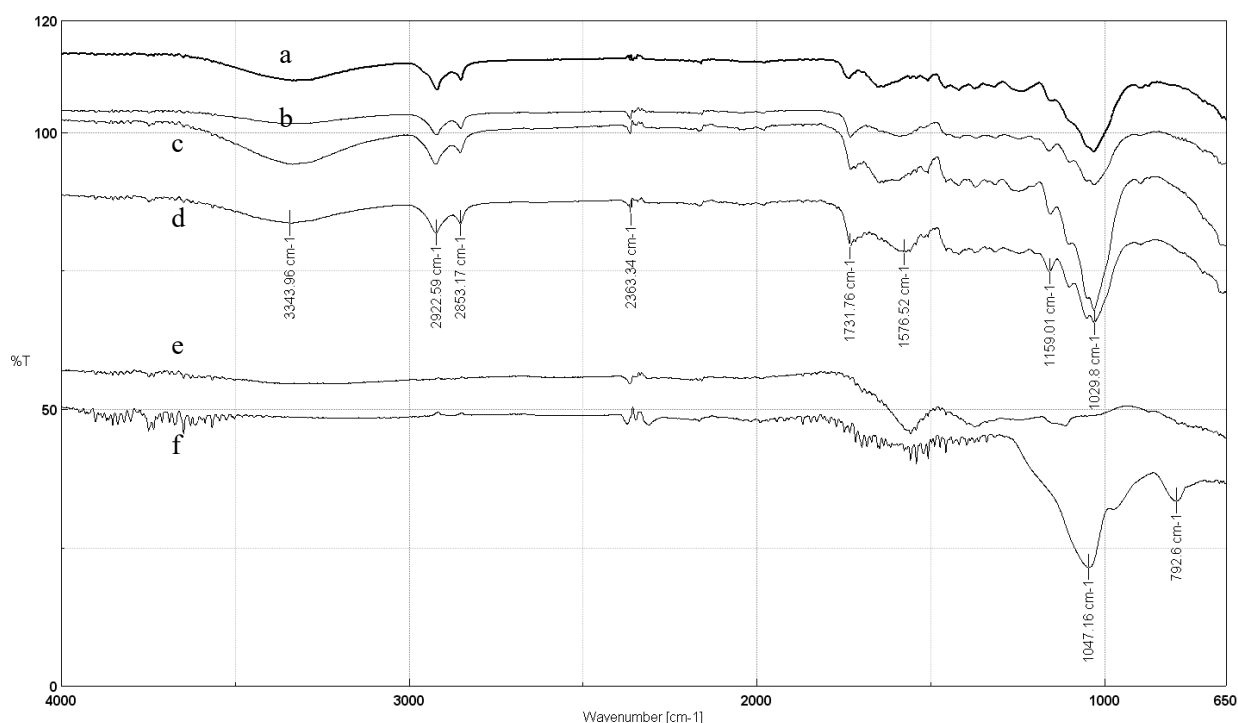


Figure 7. Comparison of the infrared spectra of the starting raw material (a) and the biocarbon obtained at b) 250°C, c) 270°C, d) 300°C, e) 320°C, f) 370°C

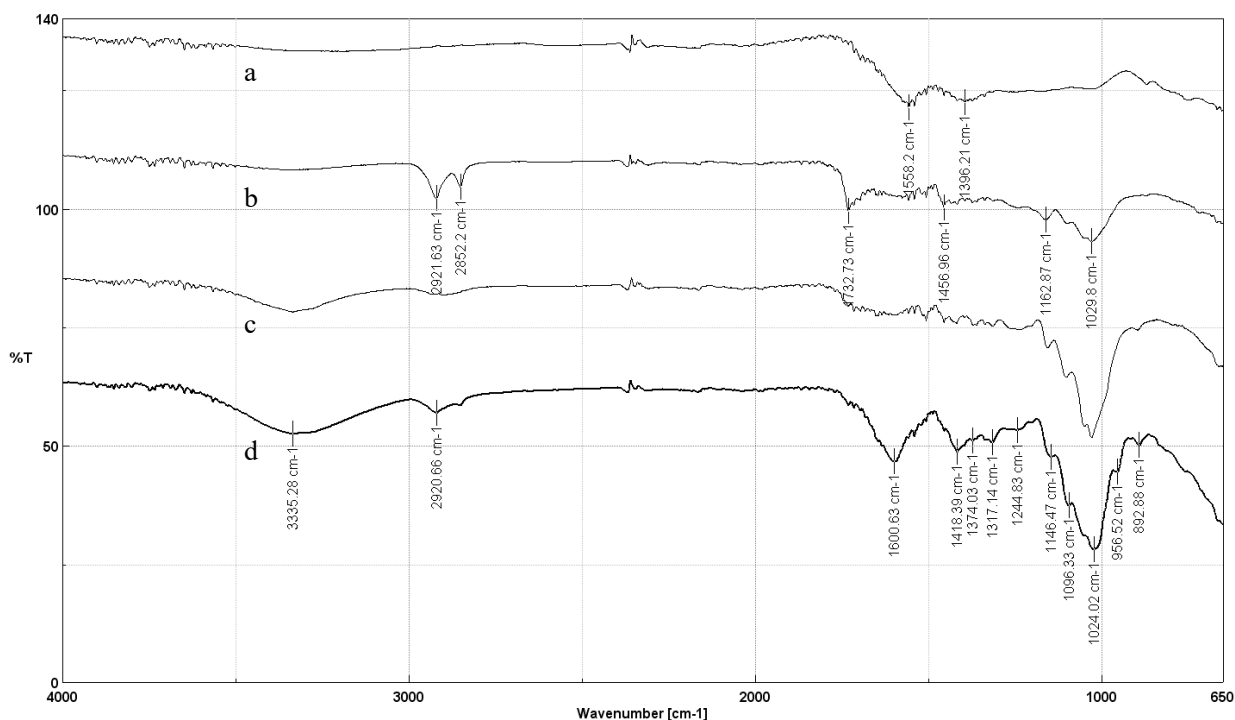


Figure 8. Comparison of infrared spectra of biocarbon obtained at 320°C and at (a) 45 min, (b) 30 min, (c) 20 min, (d) 15 min

are identified, located at wave numbers 2922 cm^{-1} and 2853 cm^{-1} . Comparison of the obtained spectra indicates that up to a temperature of 300°C no clear changes are observed in the structure of the studied torrefaction products, which is due to the analogous shape and position of the bands in the infrared spectra.

Clear differences were only observed in the spectrum of the product obtained at 320°C. At this temperature, the bands of hydrocarbon groups disappear, indicating the breakdown of carbon-hydrogen bonds and, consequently, the removal of hydrogen from the reaction zone together with the gases formed. The intensity of the bands associated with the vibration of the oxyorganic groups (i.e. hydroxyl groups and glycosidic bonds) is also significantly lower. These changes result in a lower hydrogen-to-carbon and oxygen-to-carbon ratio, which significantly increases the calorific value of the biocarbon compared to the initial biomass.

The effect of the torrefaction time at 320°C on the chemical structure of the products was also investigated. A summary of the IR spectra of the resulting torrefaction products is shown in Figure 8.

Analysis of the infrared spectra obtained indicates that increasing the torrefaction time leads to a decrease in the intensity of signals related to the vibrations of hydrocarbon groups (bands at wavenumbers of about 2921 cm^{-1} and 2852 cm^{-1}) and organo-oxygen functional groups (overlapping bands at wavenumbers of about 1024 cm^{-1}). Thus, a loss of hydroxyl groups is observed in the torrefaction product (oxygen loss and O:C ratio changes)

with increasing process time, which affects the calorific value of the product. The course of the IR spectrum of the torrefaction obtained at 370°C is also interesting (Fig. 7) because different signals are observed in the spectrum from those found in both the starting raw material and the torrefaction produced at lower temperatures. This may indicate chemical processes in the annealing zone related to the activity of the generated radicals. In the spectrum, there is a band located at a wavenumber of 1047 cm^{-1} , which may characterise the backbone vibrations of ring ether groups (e.g. in ketals or acetals), as well as a band at a wavenumber of about 792 cm^{-1} , associated with vibrations of oxygen heterocyclic groups.

4. CONCLUSIONS

Flax shavings are a vegetable biomass waste which, according to the Renewable Energy Sources Act and European Union regulations, can constitute a solid biofuel. There is also the possibility of energetic use of this type of waste in the form of torrefaction, which is a product of pyrolytic processing of biomass at temperatures up to 400°C. The thermal treatment of biomass makes it possible to improve the energy parameters of the product. Research work carried out indicates that an increase in the temperature of biomass torrefaction increases the heat of combustion of the product, with this parameter obtaining the most favourable value in the case of biocarbon obtained during torrefaction at a temperature of 320°C

and for a period of 20 to 30 minutes (combustion heat: 25.42-26.92 MJ/kg). Torrefaction increases the energy parameters of biomass fuel. However, this requires heating the raw material. Further work will include an analysis of the energy and economic balance, taking into account the sources of energy needed for the process. Such conditions lead to an advanced conversion of the chemical structure of the biomass, as investigated by

infrared spectrophotometry. During torrefaction, the oxygen-carbon chemical bonds in the cellulose chains, which are the building blocks of the processed biomass, are broken. This results in a loss of organo-oxygen functional groups in the biocarbon compared to the initial raw material and, consequently, an increase in the energy parameters of the product. However, there is no complete destruction of the biomass structure.

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