

Pyrolysis as a method of refining plant biomass residues from poppy (*Papaver somniferum* L.) and buckwheat (*Fagopyrum esculentum*) crops

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Abstract. In recent years, international energy policy has placed great emphasis on increasing the share of renewable energy in gross final energy consumption, which contributes to the growing importance of alternative energy sources and the search for new energy resources. The paper deals with the refinement of plant biomass by pyrolysis of residues from selected agricultural crops for the production of high-enriched biochar materials. In addition, the effect of the length of the pyrolysis process on the basic energy parameters of biochars obtained from buckwheat and low-morphine poppy crop residues was evaluated. Buckwheat husk and poppy residues of poppy plants were subjected to anaerobic thermal modification at 400°C and process times of 2, 4, 6, 8, 10, 12, 14, 16, and 18 min. It was found that the optimal roasting time for the modified biomass is 2 min. For this process variant, the maximum heating values of pyrolysates were 28.52 and 24.7 MJ kg⁻¹ for buckwheat and poppy, respectively. The study also showed that biochar obtained from buckwheat has a significantly higher total carbon content (max. 76.71%) compared to biochar materials obtained from poppy (max. 58.86%). Biochar materials from buckwheat crop residues and low-morphine poppy can be an alternative to other biomass and biochar fuels.

Keywords: poppy, buckwheat, agricultural residues, biochar, pyrolysis, calorific value, biofuels

1. INTRODUCTION

Biomass is considered a renewable energy source because its resources are not limited and its combustion is emission-neutral (Fernández-Dacosta *et al.*, 2019). Biomass is any natural biodegradable organic materials, such as trees, plants, algae, and animal waste. They can be used to produce energy depending on their origin, state of aggregation, and degree of processing. Among the whole range of types of plant biomass, one can distinguish biomass of agricultural origin, which can be agricultural residues and crops to be used for energy purposes (Tripathi *et al.*, 2019). In addition, residues from the forestry industry should be included, which, along with agricultural production, are in the common group of Agro (Bidzińska *et al.*, 2013). Due to the existing shortage of high-grade wood, the amount of harvested wood for energy purposes has been reduced in recent years, and the shortage has been replaced by using waste wood and plantations of energy crops such as Willow (*Salix* L.), Black Locust (*Robinia pseudoacacia* L.), and Poplar (*Populus* L.) (Bidzińska *et al.*, 2013). Grasses and perennials, such as Giant Miscanthus (*Miscanthus giganteus*), Chinese Miscanthus (*Miscanthus sinensis*), and Sida

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Hermaphrodita (*Sida hermaphrodita*), are also used for energy purposes. Global biomass production in the form of biomass pellets is about 40.4 million t, and 45% of this pool is produced within the EU. Poland, on the other hand, ranks the 6th in the EU with an annual production of 1.3 million t (Jerzak *et al.*, 2024).

Poppy is definitely a niche crop; however, it too produces agricultural residues that can be used for energy purposes. Poppy has large amounts of valuable macro and micro elements in its composition and also has such components as riboflavin and niacin. Such a range of health-promoting properties makes poppy cultivation increasingly popular, resulting in an increase in the share of poppy in the food and cosmetics industries. It should be noted that poppy oil contains more than 50% of linoleic acid and about 16% of oleic acid, which disqualifies it for use as biodiesel; however, hot pressing allows it to be used in the paint industry as an ingredient in paints and varnishes (Nijak *et al.*, 2020). After the cultivation is completed, crop residues should be removed from the field by mixing with the soil or collecting (Journal of Laws of 2023, item 1939). According to what is known in the literature, the main yield of poppy is from 0.91 to 1.19 t ha⁻¹, and the by-product yield from low-morphine poppy production can be from 2.3 to 3 t from an area of 1 hectare at a plant density of 2,000,000 plants per hectare of cultivation. This demonstrates the attractiveness of this material for the use of agricultural residues for energy purposes, especially since growers are required to completely dispose of post-production residues after production is completed (Zajac *et al.*, 2010). Buckwheat cultivation is heavily spread and has a high concentration in contrast to the low quantity and poor concentration of poppy crops. It is estimated that the area devoted to buckwheat cultivation in Poland in 2021 was 117288 ha (Statistics Poland, 2023). Such a large crop structure makes Poland one of the leading producers of buckwheat in Europe and the fifth largest worldwide. It should be noted that, of buckwheat production, about 25-30% is a by-product yield in the form of buckwheat husk produced during the process of screening and processing the seeds into food products (Kowalczyk-Juško and Zywer, 2011; Pocienė and Šlinkšienė, 2022). The by-product yield for this crop is estimated at 25 000-30 000 t for energy use in Poland and 450 000 t worldwide (Joka Yildiz *et al.*, 2022). Buckwheat husk is widely used as a component for animal feed, but also has good performance as a component for straw-based pellet mixes and buckwheat husk addition. Buckwheat husk has less chlorine in its composition and a five times lower sulfur concentration, which significantly improves the quality of pellets by reducing corrosion of heating systems. Due to its low moisture content of about 10% and low bulk density of no more than 120 kg m⁻³, buckwheat husk is not suitable as a main raw material for pellet production because the pelletization process is difficult and requires an additional binder (Kulokas *et al.*,

2021). Therefore, it is worth considering the use of buckwheat husk in the pyrolysis process to improve processing parameters as well as its physical and chemical properties.

One method of processing of raw waste biomass that significantly affects the physical and chemical properties of the resulting product is the process of pyrolysis, *i.e.* anaerobic thermal treatment. Pyrolysis is classified as a method of biomass decomposition in aerobic conditions, occurring at temperatures ranging from 350 to 900°C, through a series of complex processes following one another (Fisher *et al.*, 2002; Jahirul *et al.*, 2012; Saffari *et al.*, 2020; Saletnik *et al.*, 2024a). Depending on the temperature and the time of thermal treatment of the material, as well as on the type of biomass, its chemical composition, and the percentage of moisture therein, a variable percentage of pyrolytic oil and solid substance, which is biochar, is obtained (Ghosh *et al.*, 2020; Uddin *et al.*, 2018). Current research shows that plant biomass and organic waste can be successfully converted as a whole product, but also their individual components such as hemicellulose, lignin, and cellulose can be thermally treated, which broadens the spectrum of applications of biomass as a product for the production of high-efficiency biofuels (Kupryaniuk *et al.*, 2023; Zou *et al.*, 2022). Pyrolysis gas is obtained by processing hemicellulose and cellulose, while in order to obtain the more solid fraction (biochar), it is recommended to select biomass with higher lignin content (Wang *et al.*, 2017). Biomass components decompose under the influence of temperature. The first to decompose is hemicellulose, which decomposes in the temperature range of 200-260°C, followed by cellulose, which decomposes when the temperature is increased to the range of 240-350°C; the highest temperature to activate the decomposition is required for lignin, which decomposes when exposed to temperatures in the range of 280-500°C (Gouws *et al.*, 2022; Zou *et al.*, 2022). The above-mentioned elements are parameters that characterize the obtained biofuel in terms of its use in various branches of the energy industry, and are also an elementary component for determining whether a given material after thermal treatment will be characterized by high performance parameters and suitability for use as a fuel or as a product with the ability to improve the quality of soils by binding pollutants contained in soils (Kalina *et al.*, 2022; Saletnik *et al.*, 2019). The pyrolysis process yields a high-quality product with a stable structure that contains organic carbon, aliphatic and aromatic compounds, volatile compounds, and ash (Lehmann *et al.*, 2011).

Many authors define pyrolysis methods according to the temperatures used. The pyrolysis process can be divided into three basic groups: conventional pyrolysis, also known as slow pyrolysis, which takes place in the temperature range of 300-700°C and a roasting time of 600-6 000 s; fast pyrolysis, which takes place in the temperature ranges of 600-1000°C and a final temperature roasting time of 0.5-5 s; and rapid pyrolysis, which takes place in the highest temperature ranges of 800-1000°C and a final temperature

holding time of less than 0.5 s (Fahmy *et al.*, 2020; Holtzer *et al.*, 2016; Li *et al.*, 2013; Mohan *et al.*, 2014). With the choice of pyrolysis parameters, the amount of pyrolysis products obtained can be modulated depending on the needs and the possibility of use; however, it is important to pay attention to the aspect of energy intensity since changing the pyrolysis parameters affects the amount of energy that must be used to obtain the final products.

Biochar can be a form of alternative fuel and, due to its diverse properties, it can also be used in agriculture, food, cosmetic, and medical sectors (Boorboori and Lackóová, 2023; Saletnik *et al.*, 2019). In recent years, biochar has also gained a new application as a material used in the production of super capacitors, among others in electrode manufacturing processes. Studies on super capacitors made with biochar have shown that the maximum number of charging cycles is 10 000, making biochar a very attractive and environmentally friendly raw material in the field of energy (Ahuja *et al.*, 2024).

The steady and rapid economic development in recent years, despite bringing many economic and social benefits, has caused the demand for energy to increase significantly. In addition, most energy is obtained from traditional energy sources, such as fossil fuels, whose resources are depleting and whose exploitation contributes to environmental degradation. As a result, today's society is faced with a growing energy crisis. The search for and the introduction of new green and renewable energy sources to the market has become the answer to this phenomenon. Such sources would be designed not only to meet the growing demand for energy, but also to reduce the negative human impact on the environment. In this context, it is worth considering the production of biochar materials from organic waste and plant biomass, a significant share of which is available in the agricultural sector. Due to the large quantities of good-quality plant biomass created as a byproduct of agricultural production, the biomass energy sector has great potential. However, without adequate technology for its processing, transportation, and storage, this sector may face a number of problems hampering its development. Therefore, it is important to introduce new technologies to optimize the production process of biochar materials.

This work focuses on determining the potential of selected agricultural crop residues as a material for biochar production and on analysing and optimizing the process of biochar production by pyrolysis. This can allow the selection of the optimal technology and raw materials for the production of a renewable and environmentally friendly solid fuel, such as biochar. Ongoing research can contribute to the available scope of knowledge in the field of production and use of present raw materials. Therefore, the purpose of this study was to determine the feasibility of using biomass residues from buckwheat and poppy crops to produce biochar by pyrolysis. An additional goal was to

optimize the manufacturing process of biochar materials by modifying the parameter of the sample holding time at the final temperature.

2. MATERIALS AND METHODS

2.1. Research object

Waste plant biomass in the form of buckwheat (*Fagopyrum esculentum*) and poppy residues (*Papaver somniferum* L.) were used to conduct a study on the possibility of using residues from selected agricultural crops to produce biochar (Fig. 1). The poppy residues consisted mainly of seed heads, and in the case of buckwheat it was only the husk.



Fig. 1. Residues of agricultural crops. A – buckwheat husks, B – post-production material from poppy (seed heads).

The material for the study was collected during the 2022/2023 crop season from an individual farm specializing in poppy and buckwheat cultivation since 2020, located in Hosznia Ordynacka, Lublin Province, Poland. Plants were taken at random from an area of 1 ha, and then they were transported to the laboratory. The material intended for testing was dried to a moisture level of less than 10% and then crushed to a fraction of less than 10 mm.

2.2. Pyrolysis process

The pyrolysis process was carried out with the use of a retort furnace FCF 2R designed for heat treatment in the atmosphere of inert gas and equipped with a post-process gas cooler with a water well (CZYŁOK, Jastrzębie-Zdrój, Poland).

Pyrolysis tests of the test samples were performed in a nitrogen atmosphere of 99.99% purity with a gas flow of 10 l min⁻¹ at temperatures of 400, 450, and 500°C, respectively, and in time of 2, 4, 6, 8, 10, 12, 14, 16, and 18 min (Figs 2-3). A sieve with a diameter of holes equal to 1 mm was then used to sift through the obtained pyrolysates. The samples were rinsed several times with distilled water and then dried for 12 h (at 80°C) in order to remove potential contaminants.

2.3. Analysis of samples

The materials were analysed with the aim to determine basic physical and chemical parameters, *e.g.* the total content of carbon, ash, nitrogen, hydrogen, and volatile

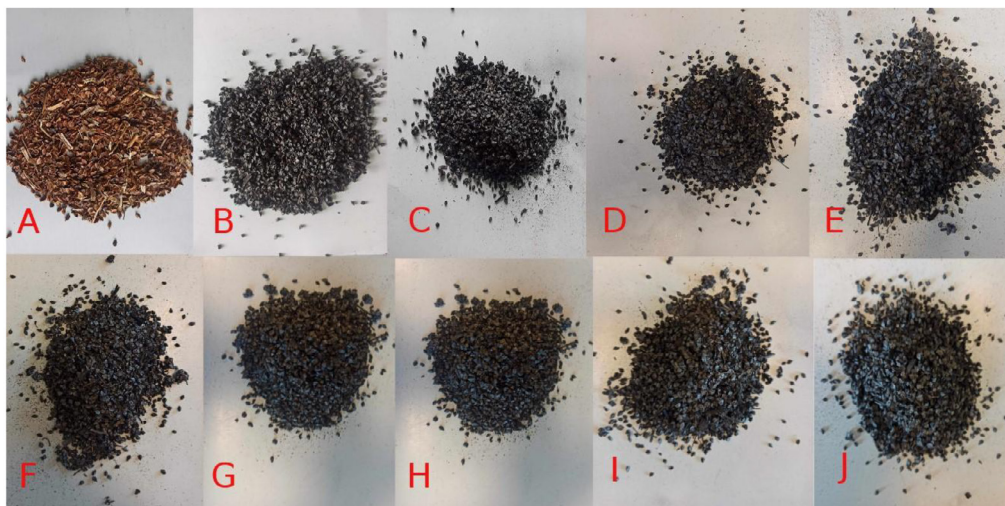


Fig. 2. Pyrolysates prepared from buckwheat post-production residues. A – non-heat-treated material; B – pyrolysis (400°C, 2 min); C – pyrolysis (400°C, 4 min); D – pyrolysis (400°C, 6 min); E – pyrolysis (400°C, 8 min); F – pyrolysis (400°C, 10 min); G – pyrolysis (400°C, 12 min); H – pyrolysis (400°C, 14 min); I – pyrolysis (400°C, 16 min.); J – pyrolysis (400°C, 18 min).

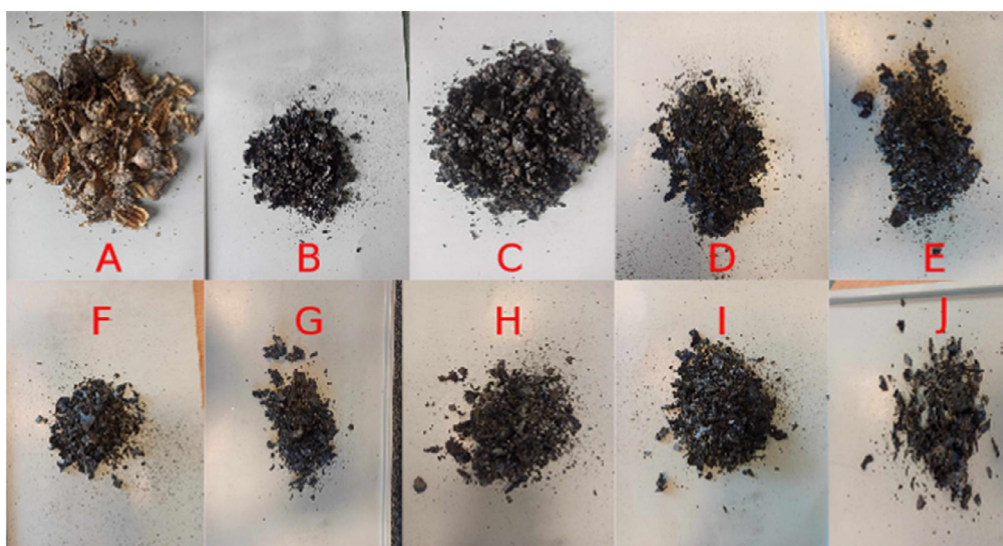


Fig. 3. Pyrolysates prepared from poppy post-production residues. Explanations as on Fig. 2.

Table 1. Parameters analysed with research methods

Parameter		Research method
Content of carbon, nitrogen and hydrogen	PN-EN ISO 16948:2015-07	Solid biofuels – Determination of total carbon, hydrogen and nitrogen content
Ash content	PN-EN ISO 18122:2023-05	Solid biofuels – Determination of ash content
Volatile matter	PN-EN ISO 18123:2023	Solid biofuels – Determination of volatile matter
Calorific value	PN-EN ISO 18125:2017-07	Solid biofuels – Determination of calorific value

substances and the calorific value. The thermogravimetric method with use of TGA 701 apparatus from LECO (LECO Corporation, Saint Joseph, MI, U.S.A.) was employed to analyse the contents of ash and volatile substances in the samples. The TrueSpec CHN analyser from LECO (LECO Corporation, Saint Joseph, MI, U.S.A.) was used to test the contents of total carbon, hydrogen, and nitrogen. The

AC500 calorimeter from LECO (LECO Corporation, Saint Joseph, MI, U.S.A.) was used to determine the calorific value of the analysed materials.

Samples of biomass and biochars were subjected to laboratory analyses using current analytical standards (Table 1).

2.4. Names of tests

In order to conduct further identification, the biomass samples were described with the use of symbols depending on the type of material and duration of the pyrolysis process (Table 2).

2.5. Statistical analysis

Analysis of variance (ANOVA) with use of Duncan’s test was performed in order to examine the effects of experimental factors reflected by the relevant parameters and the relationships between them. In order to compute statistical analyses, Statistica 12 software was used. A significance threshold of ≤ 0.05 was set in the case of all analyses. For each type of materials, the data were analysed separately.

3. RESULTS

All the biochar samples tested showed an increase in the ash content compared to the unrefined materials. The ash content in the thermally untreated samples (poppy residues) was 9.34% and increased with the longer process time. The highest percentage ash content of 26.72% was measured for the sample subjected to the longest pyrolytic treatment. There was also a positive correlation between the length of the pyrolysis time and the decrease in the volatile content. For the poppy materials, the highest proportion of volatile substances of 77.95% was recorded for the control sample, and the lowest level of 33.23% was recorded for the P-400/18 sample. The nitrogen content was recorded in all the materials tested, the concentration of which initially increased and then decreased as the time the sample was held at the final temperature increased. The nitrogen content in the control sample, *i.e.* in the non-thermally processed poppy residues, was at the level of 2.67%. In contrast, the highest nitrogen concentration was recorded for the P-400/6 sample and it was at the level of 3.22%. The

Table 2. Test parameters

Duration of the Pyrolysis (min)	Symbol to residues from	
	poppy cultivation	buckwheat cultivation
–	P-0/0	B-0/0
2	P-400/2	B-400/2
4	P-400/4	B-400/4
6	P-400/6	B-400/6
8	P-400/8	B-400/8
10	P-400/10	B-400/10
12	P-400/12	B-400/12
14	P-400/14	B-400/14
16	P-400/16	B-400/16
18	P-400/18	B-400/18

biochar materials obtained from the poppy crop residues had the highest carbon content at 58.86% (sample P-400/2), which had a holding time of 2 min at the final temperature. Thus, there was an increase of 15.56% compared to the “raw” biomass, whose total carbon content was 43.30%. In contrast, the lowest carbon content in the resulting pyrolysates was recorded for the P-400/18 sample, which had a percentage of 53.79%. For all the biochar materials tested, there was a decrease in the hydrogen content compared to the control sample. The lowest hydrogen content of 5.04% characterized the sample exposed to 12 min pyrolysis (Table 3).

For the buckwheat crop residues, an ash content of 2.45% was recorded and, as with the earlier material, the proportion of ash in the prepared pyrolysate increased with the increasing holding time at the final temperature. The highest ash content of 8.28% was recorded for sample B-400/18, which had a holding time of 18 min at the final temperature. The highest concentration of volatile parts of 76.82% was recorded for the agricultural residues, *i.e.*

Table 3. Content of general nitrogen, total carbon, hydrogen, ash and volatile substances in the residues of poppy crops and biochars depending on the duration of the pyrolysis process

Sample	General nitrogen	Total carbon	Hydrogen	Ash	Volatile substances
	Residues from poppy cultivation (%)				
P-0/0	2.67 ^{ab} ± 0.06	43.30 ^a ± 0.08	7.23 ^c ± 0.02	9.34 ^a ± 0.11	77.95 ^c ± 0.19
P-400/2	2.94 ^{bc} ± 0.04	58.86 ^b ± 0.08	5.14 ^a ± 0.01	20.12 ^b ± 0.07	38.97 ^b ± 0.28
P-400/4	2.84 ^{bc} ± 0.03	55.84 ^b ± 0.09	5.41 ^{ab} ± 0.01	20.15 ^b ± 0.11	37.05 ^b ± 0.06
P-400/6	3.22 ^c ± 0.58	56.93 ^b ± 0.10	5.86 ^b ± 0.02	20.39 ^b ± 0.08	37.61 ^b ± 0.08
P-400/8	2.72 ^{ab} ± 0.08	56.4 ^b ± 0.11	5.42 ^{ab} ± 0.06	21.06 ^{bc} ± 0.13	37.37 ^b ± 0.11
P-400/10	2.82 ^b ± 0.03	55.33 ^b ± 0.10	5.53 ^{ab} ± 0.03	21.66 ^{bc} ± 0.07	37.73 ^b ± 0.15
P-400/12	2.89 ^{bc} ± 0.06	54.94 ^b ± 0.10	5.04 ^a ± 0.06	22.56 ^{bc} ± 0.08	36.36 ^{ab} ± 0.20
P-400/14	2.81 ^b ± 0.03	56.81 ^b ± 0.15	5.13 ^a ± 0.01	22.85 ^c ± 0.14	33.52 ^a ± 0.10
P-400/16	2.56 ^a ± 0.04	54.19 ^b ± 0.10	5.13 ^a ± 0.03	23.18 ^c ± 0.09	33.33 ^a ± 0.12
P-400/18	2.67 ^{ab} ± 0.05	53.79 ^b ± 0.06	5.14 ^a ± 0.02	26.72 ^d ± 0.07	33.23 ^a ± 0.09

Statistically significant differences marked by different letters ($p \leq 0.05$). Differences between average values marked with the same letters are not statistically significant at the level of $p \leq 0.05$ according to the Duncan test. The data were analysed separately for each type of materials.

Table 4. The content of general nitrogen, total carbon, hydrogen, ash and volatile substances in buckwheat crop residues and biochars depending on the duration of the pyrolysis process

Sample	General nitrogen	Total carbon	Hydrogen	Ash	Volatile substances
	Residues from buckwheat crops				
	(%)				
B-0/0	1.91 ^a ± 0.02	44.04 ^a ± 0.07	6.57 ^c ± 0.02	2.45 ^a ± 0.06	76.82 ^c ± 0.11
B-400/2	3.16 ^b ± 0.02	74.28 ^b ± 0.09	5.93 ^{bc} ± 0.03	6.83 ^b ± 0.10	29.37 ^b ± 0.10
B-400/4	3.16 ^b ± 0.01	74.50 ^b ± 0.05	5.21 ^a ± 0.01	7.55 ^{bc} ± 0.14	28.33 ^b ± 0.08
B-400/6	3.16 ^b ± 0.04	76.32 ^b ± 0.11	5.36 ^{ab} ± 0.01	7.92 ^c ± 0.05	27.48 ^{ab} ± 0.07
B-400/8	3.13 ^b ± 0.01	76.10 ^b ± 0.08	5.34 ^{ab} ± 0.02	7.81 ^c ± 0.04	26.92 ^{ab} ± 0.06
B-400/10	3.17 ^b ± 0.03	76.13 ^b ± 0.06	5.24 ^a ± 0.04	8.10 ^c ± 0.06	26.79 ^{ab} ± 0.09
B-400/12	3.27 ^b ± 0.04	76.22 ^b ± 0.04	5.37 ^{ab} ± 0.02	8.16 ^c ± 0.06	25.72 ^{ab} ± 0.14
B-400/14	3.11 ^b ± 0.02	76.44 ^b ± 0.10	5.35 ^{ab} ± 0.02	7.77 ^c ± 0.08	25.55 ^{ab} ± 0.07
B-400/16	3.29 ^b ± 0.01	76.65 ^b ± 0.14	5.27 ^a ± 0.01	8.10 ^c ± 0.08	25.50 ^a ± 0.08
B-400/18	3.37 ^b ± 0.02	76.71 ^b ± 0.11	5.18 ^a ± 0.01	8.28 ^c ± 0.04	25.25 ^a ± 0.12

Explanations as in Table 3.

buckwheat husks not subjected to pyrolysis. In contrast, the lowest volatile content of 25.25% was recorded for sample B-400/18. There were statistically significant differences in the nitrogen content between the biochar material made from buckwheat with the use of the 18 min pyrolysis process and the non-thermally processed sample (control sample – 1.91%, biochar B-400/18 – 3.37%). The biochar formed from the buckwheat crop residues had a maximum carbon content of 76.71% (sample B-400/18). There was an increase of 32.7% compared to the raw biomass, whose general carbon content was 44.04%. All the pyrolysates produced were statistically significantly different from the control sample with respect to this parameter. It should be noted, however, that increasing the duration of the pyrolysis process at 400°C did not affect statistically significant changes in the concentration of total carbon in individual pyrolysates. The thermally non-processed buckwheat husks had an ash content of 6.57%. On the other hand, a decrease in the hydrogen content of the biochar from 5.93 to 5.18% was observed with an increase in the duration of the pyrolysis process (Table 4).

The agricultural residues resulting from poppy cultivation had a high calorific value of 17.16 MJ kg⁻¹. The use of the pyrolysis process resulted in a statistically significant increase in the calorific value in most variants. The highest calorific value was recorded for pyrolysates obtained from poppy by pyrolysis with a holding time of 2 min at the final temperature, *i.e.* 400°C. This sample had a calorific value of 24.70 MJ kg⁻¹, which was an increase of nearly 44% compared to the sample not subjected to the pyrolysis process. Subsequent materials, in which the holding time at the final temperature was increased, were characterized by a decrease in the calorific value, where the lowest value for biochar materials was obtained by the P-400/18 sample, whose calorific value was 18.73 MJ kg⁻¹. It should be noted, however, that there were no statistically significant

changes in the calorific value of the pyrolysates obtained in the pyrolysis tests lasting 4 and 18 min. The optimal time to keep the sample at the final temperature was 2 min, and the calorific value in this case was statistically significantly different from all the other samples tested (Fig. 4).

The highest calorific value for biochar materials made from buckwheat husk was obtained in the pyrolysis process whose holding time at the final temperature was 2 min. In contrast, it is worth noting that the other pyrolysates had similar values and no statistically significant differences were noted among them. For the B-400/2 sample, a value was obtained at a level equal to 28.52 MJ kg⁻¹, giving an increase of 72% compared to that for the materials not subjected to pyrolysis (16.55 MJ kg⁻¹). All the biochars produced differed statistically significantly in their calorific value from the control sample. Taking into account the required energy input for the preparation of biochar and the calorific value obtained, the most favorable variant of the pyrolysis process was a holding time of 2 min at the final temperature (Fig. 5).

4. DISCUSSION

Currently, there are many methods and processes for refining biomass to give it better parameters as a raw material for energy purposes. Most of these processes are necessary because biomass, as a material of organic origin, is characterized by high water content and low bulk density which, combined with its relatively low calorific value, makes it an unattractive material for direct combustion. In addition, unprocessed biomass is prone to biological decomposition during storage. For this reason, various methods of its conversion are used, including pelletization, pyrolysis, and torrefaction to reduce its water content and increase its bulk density and calorific value (Jerzak *et al.*, 2024; Kaczor *et al.*, 2020; Saletnik *et al.*, 2024b). The literature on the subject also contains information on the possibility of using

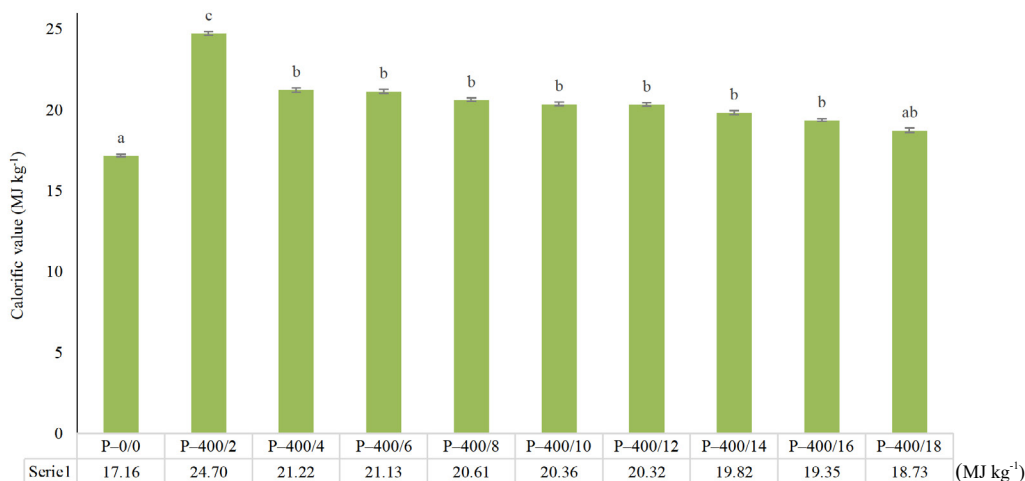


Fig. 4. Calorific value of residues from poppy crops and biochars depending on the duration of the pyrolysis process. Explanations as in Table 3.

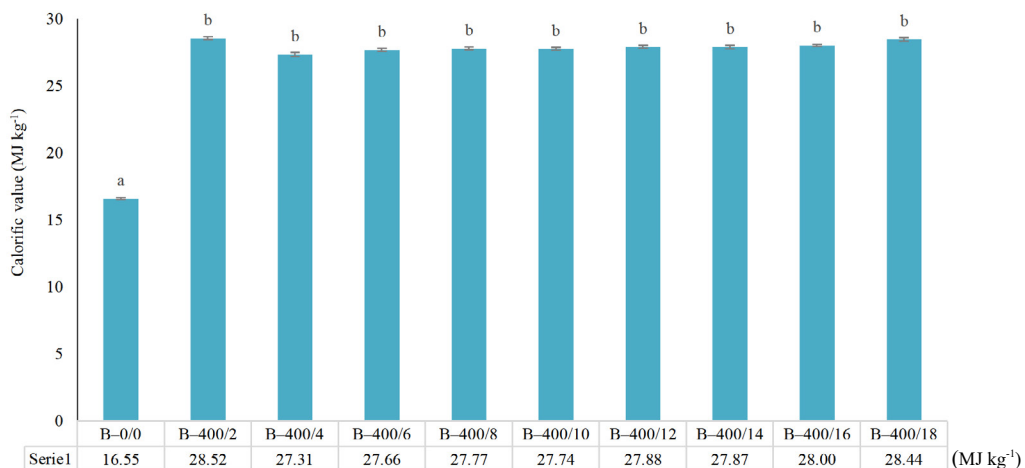


Fig. 5. Calorific value of residues from buckwheat crops and biochars depending on the duration of the pyrolysis process. Explanations as in Table 3.

discrete element method simulations to describe the compaction process and the mechanical reaction of the pellets to compression. The discrete element method (DEM) and the parallel bonded particle model (BPM) appear to be very useful in providing a particle scale insight into the bonding mechanisms (Horabik *et al.*, 2023).

Biochar materials that are the product of pyrolysis must meet a number of standards to be counted as renewable energy sources. Raw materials used for the production of biochars from the agriculture sector often contain very high amounts of chlorine and other corrosive elements, which is caused by fertilization with agents rich in NH₄Cl (Ishikawa *et al.*, 2015). Pyrolysis of agricultural materials fertilized with ammonium chloride yields biochar with high nitrogen content, which in turn can be used in agriculture. This material can improve soil structure by increasing the pH and sorption capacity of soils (Saletnik *et al.*, 2019). Biochar can also affect water hydraulics, retention, repel-

lency, and soil texture (Faloye *et al.*, 2022). In addition, biochar can contribute to reducing greenhouse gas emissions in agricultural soil, to varying degrees depending on such parameters as the soil type, biochar properties, or pyrolysis type (Walkiewicz *et al.*, 2023). It can also be used as an absorbent for the disposal of heavy metals and agricultural chemical residues (Kasera *et al.*, 2022; Leng *et al.*, 2020). In the present research, the biochar materials obtained from poppy and buckwheat crop residues were characterized by a nitrogen content of 2.5-3.5%; a similar result was also obtained by other authors in their study of thermal processing of biomass (Joka Yildiz *et al.*, 2022) due to low bulk density and low susceptibility to compaction, it is beneficial to use them in the form of co-pellets. The study presents comprehensive research detailing buckwheat husks' potential for co-pelletization with oily (peanut husks). However, it is important to emphasize the fact that the chemical composition of the samples, and especially

the nitrogen and chlorine content, can be defined by the method and intensity of fertilization (Ishikawa *et al.*, 2015). In contrast, studies conducted by Saletnik *et al.* (2024a) on pyrolysates produced from tobacco crop residues did not show the share of nitrogen in the samples tested. This may be due to the level of fertilization and the specification of the plants, which lacked nitrogen in the residues after harvest.

Research and development of methods for processing post-production raw materials from agriculture are part of the decarbonization process aimed at reducing net carbon emissions to the atmosphere (Jerzak *et al.*, 2023). A very important factor in the production of biochar is the optimal selection of the raw material for its production because the percentage of lignin, cellulose, and hemicellulose will determine such parameters as carbon, nitrogen, and hydrogen content and the amount of volatile substances (Saletnik *et al.*, 2024a; Wang *et al.*, 2017; Zou *et al.*, 2022). Nevertheless, another important factor in the production of biochar is the optimal selection of the method and parameters of the process of refining the raw material. The combination of these two aspects can make it possible to produce a material with very good parameters, such as carbon content above 50%, water content below 15%, and the proportion of volatile substances below 40% (Saletnik *et al.*, 2024a). The pyrolysates prepared in our study were characterized by carbon content at the level of 55.91% on average for all the tested samples made from poppy and 75.93% for the materials made from buckwheat. For all the samples tested, the biochar materials had an average volatile fraction of 26.77% for buckwheat and 36.13% for poppy residues. The poppy pyrolysates had a significantly higher proportion of ash of 21.97% compared to the buckwheat materials, whose average proportion of ash content for all the samples was 7.84%.

In many countries, poppy cultivation is hampered by restrictive laws limiting and regulating cultivation areas, which is why poppy accounts for a small percentage of sowings, compared to other crops. It is estimated that 27 773 ha of poppies are grown worldwide. This information is not accurate because it does not include many countries where data on the sown area is not reported to other institutions and is difficult to obtain. This is the situation in Poland, for example, where sowing data is held by provincial marshal offices. According to the data on various official sites, it is possible to estimate the area of poppy cultivation at about 2 500 ha. In the scientific literature, there is a lack of information on detailed analyses of poppy by-product yields and the possibility of producing biochars; hence, it is worth highlighting the idea of research to use such raw materials. Cultivation of buckwheat is a serious branch of the agricultural market; it is estimated that the area devoted to its cultivation was 2 million 200 thousand ha, of which 114 thousand ha were cultivated in Poland, and about 100 000 t of raw material was harvested on average per year in 2010-

2020 (FAO, 2024.). These figures indicate the possibility of processing between 25 000 and 30 000 t of agricultural by-products for energy purposes in Poland and 450 000 t globally. However, such quantities of post-production materials can be troublesome to burn directly due to their low bulk density value. Pellet production based solely on raw material is also hampered by poor compaction susceptibility (Joka Yildiz *et al.*, 2022) due to low bulk density and low susceptibility to compaction, it is beneficial to use them in the form of co-pellets. The study presents comprehensive research detailing buckwheat husks' potential for co-pelletization with oily (peanut husks. According to studies conducted by Kazimierski *et al.* (2022), the global energy potential of buckwheat husk is estimated at 14.21 PJ, demonstrating the enormous potential of this material, especially when subjected to the refining process (Kazimierski *et al.*, 2022).

Authors involved in research on buckwheat husk processing point to the great potential of the husk as a component for the production of pellets or other products to be burned after compaction. In addition, Joka Yildiz *et al.* (2022) showed in their study that buckwheat husk has a high calorific value and trace amounts of chlorine and sulfur, making it a very attractive raw material for improving the quality of pellets made from raw materials with high sulfur and chlorine content. The present research showed that the calorific value of buckwheat husk is 17.16 and is by 0.61 MJ kg⁻¹ lower than that of the thermally non-processed residues from poppy crops. The use of pyrolysis at 400°C and a holding time of 2 min allowed an increase in the calorific value by 72.3% compared to the original value of the unprocessed buckwheat raw materials. In contrast, for the poppy materials in this process variant, there was an increase of 43.9% in comparison to the original value of 17.16 MJ kg⁻¹. Other authors in their studies also highlight the suitability of buckwheat husk biochar materials for tar cracking, citing economic arguments and describing that buckwheat husk is more environmentally friendly than biochar materials based on wood biomass (Villot *et al.*, 2023). Gendek *et al.* (2023) analysed the possibility of producing good quality pellets from a mixture of such materials as ground walnut shells and coniferous tree cones as well as their three mixtures. The authors obtained biofuels characterized by an average calorific value of about 19 MJ kg⁻¹ (Gendek *et al.*, 2023). In turns, in their research on the possibility of using alternative fuels from biomass (corn straw) and plastics, Domański *et al.* (2020) found that the calorific value of the obtained pellets in the working condition was 24.513 MJ kg⁻¹ (Domański *et al.*, 2020). Pena *et al.* (2020) showed in their study of biochar materials that buckwheat husk consists mostly of lignin, with the carbon content close to 47.5% and the calorific value of 18.3 MJ kg⁻¹. In a further study, the authors showed that the biochar materials obtained at 500°C contained 78.4% of carbon and had a calorific value of 28.1 MJ kg⁻¹. The

Table 5. Basic physicochemical parameters of selected vegetable raw materials, conventional fuels and biochars

Material	Volatile substances	Ash	Total carbon	Calorific value (MJ kg ⁻¹)	Sources
	(%)				
Raw buckwheat husk	63.75-76.82	0.94-9.34	42-50.88	16.55-18.3	Joka Yildiz <i>et al.</i> (2022) Kazimierski <i>et al.</i> (2022), Pena <i>et al.</i> (2020)
Raw poppy post-production material	76.07-77.95	9.34-12.80	11.3-43.30	17.16	Hopa <i>et al.</i> (2019)
Biochar from poppy (550°C)	38.97	25.72	35-58.86	24.70	
Biochar from buckwheat (500°C)	28.7-29.37	5.7-8.28	76.71-78.4	28.1-28.52	Pena <i>et al.</i> (2020)
Biochar from sunflower	13.4	28.9	63.4	20.5	Malińska (2012)
Natural gas	100	0.0	75	48	
Sunflower husk	66.6	1.6	50.5	17.68	Zajemska and Musiał (2013)
Lignite	6-46.6	4.1-5.7	60-60.97	22.93-25	Werle (2021) Zajemska and Musiał (2013)
Hard coal	35	5.7	87.52	20-30	Fabiańska <i>et al.</i> (2013)
Tobacco stalks	76.07	5.04 5.49	40.96 43.97	16.16 18.4	Berbeć and Matyka (2020) Mijailovic <i>et al.</i> (2014), Pesevski <i>et al.</i> (2010), Saletnik <i>et al.</i> (2024a)
Untreated oak wood	79.24	2.11	49.87	18.38	Saletnik <i>et al.</i> (2022)

percentages of hydrogen and nitrogen in the biochar varied in the range of 5.8-3.1 and 2.3-1.3%, respectively, due to the release of these elements in the pyrolysis process in the form of tar and gas (Pena *et al.*, 2020; Yahya *et al.*, 2015). Thanks to the pyrolysis thermal processing, it has been possible to obtain calorific values comparable to other conventional energy sources currently known and used by the power industry. The biochars obtained from buckwheat and poppy crop residues had higher calorific values compared to biochars from sunflower, tobacco stalks, and materials obtained from coal and lignite commonly used in the power industry. Additionally, biochars from buckwheat hulls and poppy residues had a higher proportion of total carbon compared to conventional materials, such as oak wood or coal (Joka Yildiz *et al.*, 2022; Kazimierski *et al.*, 2022; Pena *et al.*, 2020; Saletnik *et al.*, 2022, 2024a).

Studies of the pyrolysis process of buckwheat and poppy crop residues have shown that the optimal time in terms of energy balance and, above all, calorific value is when the residues are kept by 2 min at a final temperature. This may be due to the high lignin content, which disintegrates and, as the time increases, the ash content in the samples also increases, which affects the total carbon content and calorific value (Pena *et al.*, 2020).

In Table 5, the basic physicochemical parameters for selected vegetable raw materials, conventional fuels, and biochars are summarized.

5. CONCLUSIONS

This article presents the possibility of using residues from poppy and buckwheat crops in the pyrolysis process to improve energy performance and to use materials that are treated as waste. The produced biochars had significantly higher heating values and higher carbon content than the untreated material. The highest carbon content in the prepared pyrolysates from the buckwheat and poppy residues was 76.71 and 53.79%, respectively. In contrast, the maximum calorific values of the pyrolysates were 28.52 and 24.7 MJ kg⁻¹ for buckwheat and poppy, respectively. The biochars made from buckwheat husk were characterized by lower content of ash and volatile substances and by higher calorific value and carbon content in the samples than the poppy product, which, combined with similar parameters such as hydrogen and nitrogen, makes biochars obtained from buckwheat a much more attractive material for use in commercial power generation. All the biochars tested were characterized by a decrease in the volatile content, which is of great importance in terms of work safety and material storage, because as the proportion of volatile substances decreases, the risk of dust explosion is lower. The duration of the pyrolysis process had a statistically significant

effect on the ash content, which increased with the process duration, while the content of volatile substances decreased with the extension of the pyrolysis time.

While modifying the parameter of the time of holding the sample at the final temperature during the pyrolysis process, a time of 2 min was determined as optimal. Thus, the present research has contributed to an increase in the knowledge concerning the production of alternative materials with high energy potential from products considered as residues or waste. Nevertheless, it seems necessary to expand research in the area of utilization and modification of residual buckwheat and poppy crops. It was found that biochars obtained from the post-production residues of poppy and buckwheat cultivation have high energy potential and can be an alternative to substrates for fuel production. It is required to develop appropriate post-treatment and modification schemes in respect to the use of post-production waste in order to unlock the large energy potential from the agricultural production sector. The use of agricultural residues for the preparation of alternative biochar materials therefore seems to fit perfectly into a closed-loop system, clean energy production, sustainable development, reduction of CO₂ emissions into the atmosphere, and promotion of green fuels.

Conflicts of Interest: The Authors do not declare any conflict of interest.

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