TÉCNICO LISBOA

Evaluation of slow pyrolysis of kitchen and garden biowaste to produce biochar – Experimental study

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Abstract

Biowaste, which includes food and garden waste, represents a significant part of municipal waste. The present work aimed to determine the properties of three types of households biowaste and the possibility of using them as feedstock in slow pyrolysis to obtain biochar, as well as to determine the characteristics of the biochar obtained. The slow pyrolysis process of the biowaste was carried out in an electrically heated Horizontal Tube Furnace (HTF) at temperatures of 400^{o}C, 500^{o}C and 600^{o}C under a nitrogen atmosphere. The properties of kitchen and garden biowaste differed significantly. In addition, the properties of the tested kitchen biowaste proved to be similar to those of other food wastes tested in other regions of the world, and to those of biomass feedstocks used in slow pyrolysis processes. For all biowaste studies, it was shown that as the pyrolysis temperature increases, the biochar yield decreases. Compared to biowaste before pyrolysis, biochar obtained from kitchen biowaste had a high carbon content, fixed carbon and higher HHV, while biochar obtained from garden biowaste had a lower carbon content and lower HHV.

Keywords: biowaste, household waste, food waste, garden waste, slow pyrolysis, biochar

Resumo

Os bio-resíduos, que incluem resíduos alimentares e de jardim, representam uma parte significativa dos resíduos urbanos. O presente trabalho teve como objetivo determinar as propriedades de três tipos de resíduos biológicos domésticos e a possibilidade de os utilizar como matéria-prima na pirólise lenta para obtenção de biochar, bem como determinar as características do biochar obtido. O processo de pirólise lenta dos resíduos biológicos foi realizado num forno tubular horizontal (HTF) aquecido eletricamente a temperaturas de 400ºC, 500ºC e 600ºC sob uma atmosfera de azoto. As propriedades dos resíduos biológicos de cozinha e de jardim diferiram significativamente. Além disso, as propriedades dos resíduos biológicos de cozinha testados revelaram-se semelhantes às dos resíduos alimentares testados noutras regiões do mundo e às das matérias-primas de biomassa utilizadas em processos de pirólise lenta. Para todos os resíduos biológicos estudados, foi demonstrado que à medida que a temperatura de pirólise aumenta, o rendimento de biochar diminui. Em comparação com os resíduos biológicos antes da pirólise, o biocarvão obtido a partir de resíduos biológicos de cozinha tinha um elevado teor de carbono, carbono fixo e um valor de aquecimento mais elevado, enquanto o biocarvão obtido a partir de resíduos biológicos de jardim tinha um teor de carbono mais baixo e um valor de aquecimento mais baixo.

Palavras-chave: resíduos biológicos**,** resíduos domésticos**,** resíduos alimentares**,** resíduos de jardim**,** pirólise lenta**,** biochar

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1. Introduction

According to European Commission data, biowaste represents on average 30-40% of municipal solid waste (values can vary between EU Member States and range from 18% to 60%). In the European Union, biowaste generation ranges from 118 to 138 million tons per year, with more than two-thirds of that being municipal biowaste and the remainder coming from the food industry [1].

In compliance with the Waste Framework Directive biowaste has been defined as "biodegradable garden and park waste, food and kitchen waste from households, offices, restaurants, wholesale, canteens, caterers and retail premises and comparable waste from food processing plants" [2]. Based on this description, there are two major fractions that may be distinguished: the first is garden and park waste, and the second is food and kitchen waste [3]. Therefore, household biowaste can be considered a mixture of kitchen and garden waste [4]. Additionally, food waste can be divided into edible and inedible or avoidable and unavoidable [5]. Edible (avoidable) food waste is all the food that was originally intended to be eaten but was thrown away, e.g. spoiled products, incorrectly prepared food, expired date products, and food leftovers on a plate. Inedible (unavoidable) food waste is parts of food that were never intended to be eaten, e.g. inedible parts of fruits and vegetables, coffee grounds and bones [6], [7].

According to estimates from the United Nations Food and Agriculture Organization (FAO), around one third of the edible food produced for human use is either lost or wasted globally [8]. Based on data from across Europe, Stenmarck et al. [9] estimated that in 2012, the amount of food waste in the EU-28 was 88 million tonnes which corresponds to 173 kilograms of food waste per person. Food waste is generated at various stages of the food supply chain [10]. However, the household sector generates the most food waste with 47 million tonnes (53%), followed by the processing sector with 17 million tonnes (19%). The remaining sectors generate respectively: food service - 11 million tonnes (12%), primary production - 9 million tonnes (11%) and wholesale and retail - 5 million tonnes (5%) [9].

In line with the circular economy, biowaste can be treated as a source of valuable resources such as nutrients, organic matter and energy [11]. Despite the enormous recycling potential of this organic material, most of the biowaste produced each year in Europe is still lost through landfilling and incineration [5].

Landfilling of biowaste has a very high negative impact on the environment. In landfills, biodegradable waste decomposes and produces greenhouse gas, which consists mainly of methane, carbon dioxide and hydrogen sulphide [12]. According to the European Environment Agency, a significant source of greenhouse gas emissions from landfills is biodegradable waste, including biowaste, which accounts for approximately 3% of all greenhouse gas emissions in the EU [13]. For this reason, it is important to collect biowaste that cannot be prevented and to choose a treatment option that is sustainable [5].

Up to now, the treatment of biowaste has been studied using biological and thermochemical processes [12]. Currently, two biological treatment methods for biowaste are most used: composting (treatment in the presence of oxygen) and anaerobic digestion (treatment in the absence of oxygen).

These methods can be considered as recycling when the compost or digestate produced is of good quality and can be used as a soil improver or fertilizer. This results in agricultural benefits or ecological improvements [11]. Anaerobic digestion also produces biogas, which can be used to produce heat and electricity or converted to low-carbon biofuel. The preferred treatment technique depends on the composition of the biowaste and the characteristics of the separate collection system. Separation of biowaste at source is an essential prerequisite for high-quality products [4].

Biowaste that is not collected separately and is part of municipal solid waste (MSW) is usually incinerated. Incineration can be considered energy recovery or disposal depending on energy efficiency. Incineration efficiency is reduced by wet biowaste, therefore it may be beneficial to remove biowaste from municipal waste and treat it separately [11].

Due to the high moisture content of biowaste (> 60%), thermochemical processing such as pyrolysis or gasification was less popular for biowaste treatment. Waste treated by thermal processes must be relatively dry. Therefore, in the case of biowaste, it must be dried before thermochemical processing, which consumes a lot of energy [12].

However, pyrolysis of biowaste is an efficient and sustainable way to create large amounts of renewable bioenergy, such as biochar and bio-oil while reducing greenhouse gas emissions and additional pollutants [14]. The main advantage of the pyrolysis process is that it allows the conversion of low-energy-density materials into high-energy-density biofuels [15].

Special consideration should be given to biochar, which is a stable, porous carbon-rich substance. It is produced by pyrolysis of biomass at a low heating rate and relatively low temperature (400-700^{o}C) [16]. Biochar can be used in a wide range of applications. The use of biochar for soil improvement and water treatment has been most studied [17]. It can also be used as a fuel [18] or energy storage material [19]. Additionally, the use of biochar made from organic waste has implications for mitigating greenhouse gas emissions, climate change, and can contribute to carbon sequestration [17].

1.1. Objectives and scope of work

This report focuses on kitchen (food) and garden biowaste (collected in spring and autumn) from Polish households and the potential to produce biochar from this biowaste using slow pyrolysis technology.

As part of the experimental study, the slow pyrolysis process of the tested biowaste was carried out in an electrically heated Horizontal Tube Furnace (HTF) at temperatures of 400^{o}C, 500^{o}C and 600^{o}C. Furthermore, the properties of the tested biowaste and the obtained biochar were determined.

The main objectives of this work include:

- determination of the characteristics of the studied biowaste (kitchen, spring garden and autumn garden biowaste),
- determination of the effect of the temperature at which the slow pyrolysis process was carried out on the yield and physicochemical properties of the biochar obtained,
- determination of the characteristics of the obtained biochar.

2. Literature review

2.1. Overview of biowaste

Typical household biowaste consists of a variety of organic materials. Determining the characteristics of biowaste will influence the choice of an appropriate treatment method and allow for better management of biowaste [11].

2.1.1. European biowaste policy

Biowaste is one of several important waste streams that are progressively addressed by European circular economy and waste legislation. These include mandatory separate biowaste collection as well as new goals for municipal waste recycling and preparation for reuse. The main legal documents that take biowaste into account are the 2018 revised Waste Framework Directive (WFD) [2], the European Commission's monitoring framework of indicators for the circular economy [20], the EU's circular economy action plan [21] and Sustainable Development Goals [22].

The Waste Framework Directive (WFD) [2] specifies that:

- from 31 December 2023, all EU Member States will be obliged to separately collect biowaste or ensure recycling at source,
- without proper management of biowaste, it seems unlikely that the new targets for preparing for reuse and recycling of municipal waste (by weight, at least 55% by 2025, 60% by 2030 and 65% by 2035) will be met while at the same time reducing landfilling of municipal waste,
- according to Sustainable Development Goal 12.3 [22], by 2030 food waste should be reduced by half, therefore the European Commission is to propose a binding target for food waste reduction by the end of 2023,
- from 2020 the EU Member States are required to measure and report food waste generation annually and to adopt special programs to prevent food waste.

Food waste is also included in the European Commission's monitoring of indicators for the circular economy [20]. In addition, the EU's circular economy action plan includes the use of biowaste as a resource [21].

2.1.2. Types of biowaste collection

Favoino et al. [23] described in detail methods of biowaste separation in individual EU countries. They showed that the total potential generation of biowaste (food and garden waste) in European Union countries is 222 kg/person/year. Whereas the capture of this waste in 2017 was 71 kg/person/year.

There are two basic ways of collecting biowaste: separately collected biowaste and biowaste present in residual municipal waste. The amount of biowaste treated by each method varies and depends on the efficiency of separation. Each system has an appropriate infrastructure for the collection and treatment of biowaste. It is worth noting that usually, these two systems operate in parallel. Separately collected biowaste is separated at the source by residents and treated as a specific stream.

Biowaste can also be collected traditionally as a door-to-door collection [4] or in a more advanced way, e.g. by an underground pneumatic system [24]. Nowadays, biowaste collected in this way is transported to composting plants or digesters [4]. In Poland, food and garden biowaste are mainly collected together as biowaste in one container [25]. For the separate collection of garden and food biowaste, municipalities in Flanders (Belgium), the Netherlands, Austria and Germany use wheelie bins called 'biobins' (or 'biotonnen') [26].

Biowaste present in residual municipal waste in developing countries is usually landfilled. In contrast, in countries with developed waste management systems, the preferred option is to incinerate this waste with heat recovery called Waste-to-Energy [4].

Recent studies indicate that food and garden biowaste, due to their different properties, should have different collection and treatment methods. Wanderley et al. [26], based on an analysis of systems in different regions, showed that there are some operational problems associated with the collection of garden waste and food waste at the same time. Compared to door-to-door collection of food waste, collecting both types of waste at the same time increases costs due to the need for larger trucks with a compaction system.

Biowaste collection systems focused mainly on food biowaste have been introduced in Milan (Italy), Wales (UK) and Catalonia (Spain). Garden biowaste in these regions is collected separately in specific collection rounds, which are carried out much less frequently than the collection of food biowaste. An additional solution in some regions involves residents delivering garden biowaste to 'drop-off' points [26].

Nevertheless, researchers agree that to increase the quality and quantity of biowaste collected, the best options are individual separate collection of garden and food waste, as well as separate collection of both types of biowaste at the same time [4], [26].

2.1.3. Variability in the composition of biowaste from households

The composition of household biowaste can vary over time (multi-year, year, season) and can also vary according to the place of generation (e.g. rural, urban). The waste's composition, particularly its carbon and nutrition content, determines the best biowaste treatment technology to use. The best balance of nutrients and carbon may require adjusting the composition of the treated biowaste with additions due to seasonal fluctuations in the composition of biowaste. To choose the best treatment technology, it can be important to understand how the content of biowaste changes throughout the year [27].

Hanc et al. [27] decided to look at the variations in biowaste from Czech households during the four different climatic seasons. The composition of biowaste from urban settlements was almost constant during these seasons. The main fraction of biowaste from urban settlements was fruit and vegetable residues (58.2%). In contrast, the composition of biowaste from single-family houses varied from season to season because in this case, the biowaste consisted mainly of seasonal garden ingredients. A similar study, also in the Czech Republic, was conducted by Stejskal et al. [28]. The team of researchers obtained results comparable to Hanc et al. [27].

Ilakovac et al. [29] analysed the composition of food waste generated in households. The data analysis showed that, irrespective of the country, the largest share of biowaste was vegetables and/or fruit (46%). Another large fraction (12%) consists of non-edible parts of food such as eggshells, tea leaves and coffee grounds. Following this are bread and bakery products (9%), potatoes (8%), meat (7%), pasta and rice (4%), milk and dairy products (4%), fish (3%) and ready meals (3%), cakes and biscuits (2%) and fruit and vegetable preparations (2%).

2.1.4. Characteristics of biowaste as a feedstock

Determining the thermal properties of biowaste by performing proximate analysis, ultimate analysis and determining the higher heating value (HHV) makes it possible to predict the behaviour of biowaste and assess the feasibility of using it for energy purposes [30].

2.1.4.1. Proximate analysis

The proximate analysis determines the moisture, volatile matter, fixed carbon, and ash content of the biowaste [31].

Moisture content (MC) represents the amount of water in the analyzed material. Total moisture content can be divided into transient moisture and bound moisture. Transient moisture represents the part of the water contained in the fuel that is lost by the biomass during drying in air at ambient temperature, reaching a state of sorption equilibrium with the humidity of the air. The bound (hygroscopic) moisture content determines the water content of the fuel that remains after the removal of transient moisture. The moisture content has a negative effect on fuel properties. It reduces the heating value and complicates ignition [31]. Biowaste is characterized by a high content of total moisture [32]. Therefore, it is necessary to design appropriate drying and storage facilities for biowaste. In addition, high moisture content increases the weight of biowaste which affects the higher cost of transporting such materials [33].

Volatile matter (VM) includes components such as hydrocarbons, hydrogen, and water vapour from chemically bound water. These are separated from the waste and fuels in the degassing process (based on heating the sample without oxygen). The volatile content facilitates the ignition of the combustible substance and affects the speed of the combustion process [34]. Biowaste is characterized by a high content of volatile parts [31].

Ash (A) is the inorganic solid residue from the complete combustion of fuel. The main components of ash are silica, aluminium, iron and calcium. Ash may also contain small amounts of magnesium, titanium, sodium and potassium [33]. Ash content, similar to moisture content, has a negative effect on heating value and ignition temperature [31]. The ash content does not reflect the original inorganic mineral matter in the fuel, since some ash components can be oxidized during combustion. The quantity and quality of ash produced during thermal utilization of biowaste depends on its type and the treatment technology [33].

Fixed carbon (FC) represents the solid carbon in the biomass remaining after the determination of moisture, volatile matter and ash content [18], [33]. The fixed carbon content depends on the volatile content, which changes with the heating rate, which is why fixed carbon is not a fixed quantity and is determined indirectly. The fixed carbon content, measured under standard conditions, gives a useful fuel evaluation parameter [33].

2.1.4.2. Ultimate analysis

The ultimate analysis determines the content of organic matter forming elements in the biowaste, such as carbon, hydrogen, oxygen, nitrogen, sulfur and chlorine [33].

Carbon (C) and hydrogen (H) are the main combustible chemical elements of solid fuels. The carbon and hydrogen content has a positive effect on the higher heating value (HHV). Due to the formation of water, hydrogen also has an impact on the lower heating value (LHV) [35]. The main product of complete combustion of carbon is carbon dioxide (CO_2). However, if a sustainable use is considered, CO_2 emissions from the combustion of biomass are viewed as CO_2-neutral with reference to the greenhouse gas effect. On the other hand, incomplete combustion can release unburned carbon pollutants such as carbon monoxide, hydrocarbons, polycyclic aromatic hydrocarbons, tar, and soot into the atmosphere [35].

Oxygen (O) is one of the main components of solid biofuels. The higher heating value (HHV) is negatively impacted by the oxygen content [35].

Nitrogen (N) is the main component that contributes to the formation of the peptide bonds seen in biomass proteins [36]. The nitrogen content of biofuel results in the formation of NO_x, the emissions of which have a negative impact on the environment [35].

The sulphur (S) contained in solid biofuel during combustion mainly creates gaseous SO_2 to some extent also SO_3 and alkali as well as earth-alkali sulphates. Also, sulphur is responsible for the formation of deposits and corrosion of the installation [35].

The chlorine (Cl) contained in solid biofuel during combustion produces mainly gaseous HCl, Cl_2 or alkali chlorides like KCl and NaCl. The chlorine content affects the corrosion of the installation [35].

2.1.4.3. Heating value

Higher heating value (HHV) is also called gross calorific value (GCV) or heat of combustion [37]. According to the definition, higher heating value (HHV) is the amount of heat released when a unit mass or volume of fuel with an initial temperature of 25°C is completely and entirely burned and the products of combustion are cooled to an ambient temperature of 25°C, assuming that the water vapor contained in the flue gas is condensed [33], [37], [38]. This includes the latent heat of vaporization of water [37].

Lower heating value (LHV) is also called net calorific value (NCV) or calorific value [37]. The lower heating value (LHV) of a solid fuel is the heat of combustion reduced by the heat of vaporization of water separated and formed during the combustion of the fuel sample [38].

According to the definition, the lower heating value (LHV) is the amount of heat released when a unit mass or volume of fuel with an initial temperature of 25°C is completely and totally burned and the products of combustion are cooled to an ambient temperature of 25°C, assuming that the water vapor contained in the flue gas does not condense [33], [37], [38].

The difference between the higher heating value and the lower heating value is the latent heat of condensation of the water vapor produced during the combustion process. The higher heating value assumes that all the water vapor produced during the combustion process is completely condensed. In contrast, a lower heating value assumes that water is removed with the combustion products but is not condensed [37]. The values of higher and lower heating value can be obtained experimentally using a calorimeter or numerically using empirical equations [18], [38].

2.1.5. Garden and kitchen biowaste

Garden and park waste as well as food and kitchen waste are the two main fractions of biowaste as it is defined in the revised Waste Framework Directive [2]. It should not be confused with the more general phrase "biodegradable waste," which also includes other biodegradable materials including wood, paper, cardboard, and sewage sludge. Additionally, it excludes residues from forestry and agriculture [32].

Garden and park biowaste, also known as yard waste, have a high moisture content (50 - 60%) and high wood content (lignocellulose). It is characterized by low density and low degradability. Garden waste is seasonal, meaning that the rate of production and its composition varies throughout the year. For instance, compared to the winter months, significantly more garden waste is generated in autumn (fallen leaves) and summer (cut grass) [26], [32]. Furthermore, the production of garden waste is also geographically diverse [32].

Food and kitchen biowaste, compared to garden waste, has an even higher moisture content (up to 80%) [32] and it has a high density [26]. Food biowaste is unstable and inconvenient due to odour and percolation. In addition, household food biowaste often has contaminants that are difficult to remove [32]. The characteristics of selected green and food biowaste are presented in Table 1.

Yang et al. [39] studied the properties of an organic fraction of municipal waste that was delivered in winter by a local municipal waste treatment facility in Leicester, UK. The waste was collected from local households. Due to the presence of biologically degraded food waste, the waste had a high moisture content. In addition, small pieces of inorganic materials were present in the waste, which could not be removed at the sorting stage therefore the waste had a high ash content. The results of the analysis of this biowaste are presented in Table 1.

Chhabra et al. [40] studied the properties of mixed municipal waste collected in the Mumbai Metropolitan Region. The waste was collected from a waste site and then manually segregated. Among the main fractions of this waste, the researchers distinguished yard waste and food waste. The results of the analysis of this biowaste are presented in Table 1.

Table 1. Proximate and ultimate analysis of specific biowaste

biowaste type	proximate analysis, wt.%				ultimate analysis, wt.%						HHV, MJ/kg	Ref.
	MC	VM	A	FC	C	H	N	S	O	Cl		
	(wet basis)	(dry basis)			(dry basis)						(dry basis)	
organic fraction of MSW, Leicester, UK (winter)	42.90	51.60	44.30	4.10	34.50	4.70	1.60	0.40	14.40	-	-	[39]
food waste from canteen, University of Mauritius	92.36	71.32	10.24	18.44	41.70	7.47	3.49	-	37.09	-	15.08	[41]
food waste fraction of MSW, Mumbai Metropolitan Region	-	70.70	10.80	18.50	46.10	5.54	1.02	-	36.55	-	-	[40]
yard waste fraction of MSW, Mumbai Metropolitan Region	-	72.10	10.20	17.70	47.15	6.13	1.15	-	35.29	-	-	[40]
yard waste fraction of MSW, Mumbai Metropolitan Region (2nd sample)	-	52.80	39.20	8.00	28.67	3.31	2.43	-	26.39	-	-	[40]
grass, in general	-	-	7.00	-	45.57	5.86	1.30	0.19	39.99	0.74	-	[35]
grasses	-	-	-	-	48.30	5.70	0.80	-	39.40	-	-	[42]
shredded green waste	-	77.60	1.00	15.30	47.20	5.66	0.20	0.03	45.91	-	18.12	[43]
garden waste	50.00	84.50	1.00	14.50	50.12	6.40	0.14	0.08	42.26	-	-	[44]
lawn grass	-	82.60	3.85	13.55	42.85	7.25	2.68	0.00	43.37	-	-	[45]

Rago et al. [41] investigated the properties of food waste collected from the University of Mauritius canteen. The biowaste was composed mainly of raw vegetables, fruits, and peels. The results of the analysis of this biowaste are presented in Table 1.

2.2. Biowaste treatment technologies

Biowaste can be used in energy recovery processes in the form of electricity and/or heat, which are referred to as Waste-to-Energy processes [46]. Additionally, employing diverse conversion pathways, biowaste can be used to synthesize a variety of relevant products. Two main treatment methods for biowaste can be distinguished: biochemical decomposition using microorganisms and thermochemical conversion [14]. Biochemical processes include aerobic digestion, anaerobic digestion, and fermentation, while thermochemical processes mainly include combustion, pyrolysis and gasification [33].

2.2.1. Biochemical conversion

In biochemical conversion, microorganisms or enzymes break down organic compounds into smaller molecules. Biological processes compared to thermochemical conversion are much slower but do not require a large amount of external energy [33].

2.2.1.1. Aerobic digestion

Aerobic digestion, also called composting, is a process carried out in the presence of oxygen. The process is usually carried out in open-air windrows or vessels [15]. The process consists of three phases: a mesophilic phase, a thermophilic phase and a final phase which is a cooling and maturation [47]. Various types of microorganisms are used to decompose organic matter, accessing oxygen from the air to produce carbon dioxide, heat and a solid digestate [33]. The main product of the aerobic digestion process is the solid digestate, also known as humic matter [15]. It can be used as a fertiliser, soil improver or as a component of a growing medium. The balance between easily degradable, moist organic materials, like food waste, and organic matter that reinforces structure, like garden waste, is what allows aerobic digestion to take place most effectively [15], [48].

2.2.1.2. Anaerobic digestion

Anaerobic digestion is the conversion of organic matter under the influence of microorganisms into methane-rich biogas. The process is carried out in closed vessels without access to oxygen [15]. Anaerobic digestion consists of four separate phases: hydrolysis, fermentation, acetogenesis and methanogenesis. Each phase produces specific end products. The transformations occurring during the last phase (methanogenesis) produce biogas, the main components of which are methane (about 60%) and carbon dioxide (about 39%). The remaining gases are mainly hydrogen sulphide, ammonia, nitrogen and hydrogen [49]. Produced biogas, can be used to generate electricity or heat, or upgraded to fuel. In addition, the process produces a solid residue, called digestate, which can be used as an organic fertiliser or soil improver [15].

A variety of organic input materials can be used for the anaerobic digestion process, but it is important to note that this process does not break down lignin, which is a main component of wood [15], [48]. Czekała et al. [49] described various essential technological solutions for conducting the anaerobic digestion process. Concerning the dry matter content, a distinction can be made between wet anaerobic digestion, where the dry matter content is less than 15%, and dry anaerobic digestion, where the dry matter content is between 15% and 40%. The anaerobic digestion process can be a single-stage or two-stage procedure. In single-stage installations, all stages of the anaerobic digestion process take place in a single reactor. In a two-stage process, the first two phases, are separated from the other two.

2.2.1.3. Fermentation

The fermentation process uses acids or enzymes to convert part of the biomass into sugars. Then, using yeast, the created sugars are converted into bioethanol or other chemicals [33]. Fermentation consists of three steps: acid or enzymatic hydrolysis, fermentation of the sugars to ethanol using microorganisms (mainly yeast) as well as separation and concentration of the ethanol produced by distillation-rectification-dehydration. If lignocellulosic feedstock is used in the fermentation process, it requires a pretreatment stage named delignification. This step makes the cellulose and hemicellulose contained in the raw material more available for subsequent stages of the fermentation process [47]. This is a difficult and expensive process, therefore fermentation of cellulosic biomass feedstocks is not widely used [33]. Nevertheless, the fermentation of feedstocks with starch and sugar content (such as sugar cane and maize) is a completely commercial technique to produce bioethanol. Bioethanol (ethyl alcohol) is considered the primary biofuel. Additionally, bioethanol and gasoline mixes are promoted as a fuel that is environmentally friendly and decreases car emissions [47].

2.2.2. Thermochemical conversion

To extract and produce energy carriers as products, thermochemical conversion processes use heat to trigger chemical reactions. Thermochemical conversion processes are faster than biochemical processes but require significant energy input [47].

2.2.2.1. Combustion

Biowaste incineration is the most common thermochemical process [14]. From a chemical point of view, combustion is an exothermic reaction between oxygen and hydrocarbons in biowaste, resulting in the oxidation of biowaste to two main stable compounds, H_2O and CO_2 [33]. The heat released in the reaction is often used to turn steam turbines to generate electricity and/or for heat exchangers in industry or district heating. Food biowaste contains high levels of moisture and inert components therefore can reduce the calorific value of the burned residue. In addition, due to the need for a pre-drying step to evaporate water, biowaste can have a negative impact on the energy balance of the combustion process. A way to thermochemical process biowaste is to co-fire it with other drying materials, which can potentially increase net energy recovery. In addition, heat losses from incinerators can be used to dry biowaste. The incineration of biowaste is associated with SO_x and NO_x emissions, so the installation of advanced flue gas cleaning equipment is required. Additionally, it has been shown that biowaste can acidify flue gases [14].

2.2.2.2. Pyrolysis

In contrast to combustion, pyrolysis takes place in the complete absence of oxygen and is not an exothermic process [33]. In pyrolysis, biomass is broken down at high temperatures without oxygen [15]. The consequence is that the organic material is mainly converted into biochar, bio-oil, and pyrolysis gas, which contains varying concentrations of CO_2, CO, CH_4, H_2, C_2H_6, and C_2H_4 [14]. The conventional pyrolysis process is irreversible. The slow decomposition of organic material is typically used to produce biochar [14], while the fast decomposition of organic material mainly produces a liquid fuel such as bio-oil [33]. For the pyrolysis process, a variety of raw materials, including domestic and industrial waste, can be used. The advantage of pyrolysis is that it produces high-energy-density biofuels from low-energy-density materials [48].

2.2.2.3. Gasification

To convert organic materials, the gasification process uses high temperatures and a limited oxidizing agent [14]. Gasification consists of four stages: drying of the material, removal of volatile parts (pyrolysis), oxidation and reduction [47]. The product of gasification is a combustible gas containing mainly CO and H_2 (syngas) [14]. Syngas is used as a fuel or in the production of chemicals [15]. The gasification process releases little emissions and can be used to process a variety of materials, including biowaste [14], [48]. The main challenge of gasification is to find solutions to deal with heterogeneous feedstocks, such as household biowaste [15].

2.3. Overview of pyrolysis process

Pyrolysis is a thermochemical process that decomposes biomass into useful products under the influence of heat and without the presence of oxygen. The process results in solid, liquid and gaseous products [33]. Product composition depends on factors such as residence time, temperature and heating rate [50]. Pyrolysis involves temperatures in the range of 300-650°C [33]. Pyrolysis has been practised for thousands of years and was used in the production of charcoal, metallurgy, boat sealing, and embalming (in ancient Egypt) [47]. Based on pyrolysis, fast pyrolysis was developed in the 1840s, which produced kerosene and contributed to a revolution in lighting and ecology [33].

2.3.1. Stages of the pyrolysis process

Pyrolysis is a complex process, during which many reactions occur in parallel and in series, resulting in the production of many intermediate products. Therefore, the exact mechanism of decomposition and the reaction pattern of biomass conversion to gaseous, liquid and solid fractions are not fully understood [47].

According to temperature, the pyrolysis process can be divided into four stages, which are partially overlapping [33].

a) The first stage of pyrolysis is drying, which occurs at a temperature of about 100°C. In this stage, moisture and loosely bound water are released during the heating of the biomass by evaporation [33]. Evaporation occurs at a constant temperature which means that the temperature of the biomass is constant and does not depend on the outside temperature of the reactor. Due to the high latent heat of water, this stage has the highest energy consumption. This is especially relevant for biomass with a high initial moisture content. Therefore, to reduce heat loss before introducing raw biomass into the reactor, it is recommended to pre-dry it in the sun [18].

b) The second stage of pyrolysis is the initial stage and occurs in a temperature range of about 100 to 300°C [33]. After drying, the temperature of the biomass increases causing exothermic dehydration, during which water molecules bound inside the fibers and light volatiles such as CO and CO_2 are released. At this stage, torrefaction also occurs at 200-300°C, which starts the decomposition process [18], [33].

c) The third stage of pyrolysis is the intermediate stage and occurs at temperatures above 200°C. At this stage, primary pyrolysis occurs at temperatures between 200 and 600°C, producing most of the vapour or precursors of bio-oil. During this stage, large biomass particles are decomposed into char (primary char), condensable gases (vapour and liquid precursors) and non-condensable gases [33].

d) The fourth stage is the final stage, occurring in the temperature range from about 300 to 900°C. At this stage, the secondary breakdown of volatiles into char and non-condensable gases takes place. Condensing gases of relatively high molecular weight, which remain in the biomass long enough, can break down to form additional (secondary) char and gases. However, if the condensable gases are quickly removed from the reactor will be condensed as tar or bio-oil [33].

2.3.2. Products of pyrolysis

Three main products of pyrolysis can be distinguished, occurring in three phases [33]:
- solid: char (biochar),
- liquid: condensing vapors (bio-oil, tars, water),
- gaseous: gases, which consists of various amounts of CO_2, H_2O, CO, C_2H_2, C_2H_4, C_2H_6, C_6H_6.

2.3.2.1. Biochar

Biochar is a solid product obtained by pyrolysis. The potential use of biochar depends on its physical, chemical and mechanical properties, which in turn depend on the type of feedstock and the conditions under which the pyrolysis process was carried out [47]. Biochar consists mainly of carbon, while it may contain some oxygen and hydrogen [50]. The higher heating value of biochar ranges from 20 to 36 MJ/kg [47]. The main characteristic of biochar is that it has a large pore surface area [33].

Biochar is an environmentally friendly alternative to burning biomass, helping to sequester carbon dioxide [51]. In many regions, biochar is still the primary cooking fuel [47].

Currently, research is being conducted on the use of biochar as a fuel [50], a soil additive [52] or a precursor for the production of catalysts and adsorbents for pollutants [53]. In addition, biochar can be used as a feedstock for direct gasification. Compared to the gasification of raw biomass, the gasification of biochar yields gaseous products with lower tar content. This is because the volatile content was reduced during pyrolysis [54].

2.3.2.2. Bio-oil

Bio-oil, also referred to as pyrolytic oil, is a liquid product produced by pyrolysis. It typically ranges in color from dark reddish-brown to almost black, has a distinct smoky odor and can irritate the eyes [50]. Bio-oils are complex mixtures containing 15 to 35% water [30] and more than 300 organic compounds [47]. Maximum liquid yields are achieved by fast pyrolysis at temperatures around 500°C, at atmospheric pressure, high heating rates and very short residence times [55].

High moisture and acid content have a negative impact on the properties of bio-oil, making it unstable, corrosive, viscous, low energy density and difficult to ignite. The higher heating value (HHV) of bio-oil is 15 to 20 MJ/kg [47]. Nevertheless, bio-oil has been tested as a fuel for combustion to generate electricity and heat [50]. However, to increase the utility of bio-oil, it needs to be improved through chemical methods. To use bio-oil as a transportation biofuel, it is necessary to reduce its volatility, increase its thermal stability, reduce its viscosity by removing oxygen, and reduce the molecular weight of the bio-oil [47].

2.3.2.3. Gas

A mixture of gases, also known as pyrolytic gas, contains gases that do not condense during cooling under standard conditions (temperature 25°C, pressure 1 bar). These include gases such as carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), ethane (C_2H_6) and ethylene (C_2H_4) [33]. The LHV of pyrolytic gases ranges from 10 to 20 MJ/Nm^3 [47]. Gases can be used directly to produce electricity or heat. Also, it can be used to produce individual gas components, e.g. CH_4 or H_2 or to produce biofuels by synthesis [56].

2.3.3. Types of pyrolysis

Pyrolysis processes can be divided according to the conditions under which the process is carried out. The main division considers parameters such as heating rate, the residence time of the solid and temperature. Based on this, a classification can be made between slow pyrolysis and fast pyrolysis [33]. In pyrolysis processes, heating rates range from less than 1°C/s to more than 1000°C/s. The residence time can range from less than 1 second to hours and the temperature is in the range of 300 to 700°C or more. Depending on the conditions of the pyrolysis process, different proportions of the three types of products (biochar, bio-oil and gas) are obtained [30].

2.3.3.1. Slow pyrolysis

The slow pyrolysis process occurs at a low heating rate, which ranges from 0.1 to 0.8°C/s. The process is carried out in the temperature range of 300 to 550°C and has a longer residence time of 5-30 min or even 25-35 h.

These slow pyrolysis conditions are designed to produce the maximum amount of biochar, which consists of both primary and secondary char. The slow pyrolysis process typically results in yields of biochar of 35 wt.%, bio-oil of 30 wt.% and gas of 35 wt.%. It is worth mentioning that to obtain biochar when fast heating rates are not required, biomass with large particle sizes, from 5 to 50 mm, can be used for the slow pyrolysis process [30].

2.3.3.2. Fast pyrolysis

The fast pyrolysis process occurs at a high heating rate, which varies from 10 to 1000°C/s. The process is carried out in the temperature range of 450 to 550°C and has a short residence time, being between 0.5 and 2 s [30]. These fast pyrolysis conditions aim to produce the maximum amount of bio-oil [33]. The fast pyrolysis process typically produces bio-oil yields of 60-70 wt.%, biochar yields of 12-15 wt.% and gas yields of 13-25 wt.% [56].

Depending on what product is desired, the fast pyrolysis process can be influenced by heating rate, residence time and the choice of the appropriate feedstock [50]. For higher bio-oil yields, the fast pyrolysis process should be carried out in the temperature range between 425 and 600°C, while the peak pyrolysis temperature should be below 650°C. On the other hand, to obtain higher yields of gaseous products, the pyrolysis peak temperature can be up to 1000°C [33]. Due to the high reaction rate in fast pyrolysis, the yield of biochar is low, as only primary char is produced [30].

It should be noted that in fast pyrolysis, biomass particle sizes affect the yield of the products obtained. To obtain maximum bio-oil yields, a small particle size, typically less than 1mm, should be used. Small particle size, results in high heat transfer rates at high heating rates. To obtain sufficiently small particles and to minimize the water content of the bio-oil, biomass with a low moisture content (< 10 wt.%) is used for fast pyrolysis [30].

2.3.4. Reactor types used for pyrolysis

Based on the mode of gas-solid contact, reactors used in pyrolysis can be divided into fixed bed reactors and fluidized bed reactors [50].

2.3.4.1. Fixed bed reactor

The fixed bed reactor is the oldest type of reactor used for the pyrolysis process [33]. The heat required for the thermal decomposition of biomass is supplied to the reactor by external heating via an electric tube furnace [57] or internal heating via fire tubes containing an insulated electric coil [58]. The formed biochar remains in the reactor, while the gaseous products are removed from the reactor. The gases flow out either spontaneously or using an inert and oxygen-free gas. Due to its relatively slow heating rate and long residence time, the fixed bed reactor is used to conduct a slow pyrolysis process. The main product obtained in this reactor is biochar [33].

2.3.4.2. Fluidized bed reactor

Two types of Fluidized Bed Reactors can be distinguished which are Bubbling Fluidized Bed and Circulating Fluidized Bed (CFB). Both reactors are used for fast pyrolysis [42].

- **Bubbling Fluidized Bed**

  Bubbling fluidized beds are the most used reactor type for fast pyrolysis due to their simplicity, efficient temperature control and excellent heat transfer to the biomass particles. In a bubbling fluidized bed system, ground biomass between 2 and 6 mm in size is mechanically transferred to a vertical tank filled with a hot sand bed [33]. The fluidized gas is injected at the base through a perforated steel manifold plate, ensuring thorough mixing and efficient heat transfer. A hot gas filter at the gas outlet prevents solids (sand and char) from being carried away. The reaction takes place at temperatures between 450°C and 600°C, using nitrogen for fluidization and as a feed gas. Char particles in the product gas are removed using cyclones [50]. The heat supplied to the reactor can come from the combustion of the gas produced in the bed or the combustion of solid char in a separate chamber and the transfer of this heat to the bed of solids. The resulting pyrolysis product is about 70-75% liquid [33].

- **Circulating Fluidized Bed (CFB)**

  A circulating fluidized bed (CFB) reactor works similarly to a bubbling fluidized bed, while the bed is highly expanded, and the solids are continuously recycled around an outer loop consisting of a cyclone and an outer loop seal. This configuration provides good temperature control and uniform mixing throughout the unit. The CFB reactor has a higher gas velocity and can process large amounts of biomass. It is worth noting that biochar entrained in the reactor can be easily separated and burned in an external fluidized bed, transferring heat to the recovered inert solids through the loop seal [33].

2.3.4.3. Auger reactor

An auger reactor, also known as a screw reactor, uses a rotating auger, resembling a screw, to continuously transport and mix feedstock through an oxygen-free heated tube. Tubes with smaller diameters can be heated by applying heat to the outside of the tube, while a solid heat transfer carrier (steel or ceramic pellets) that is fed with the biomass is used to heat larger-diameter tubes [59]. Passing through the tube raises the feedstock to the desired pyrolysis temperature in the range of 400^{o}C to 800^{o}C, resulting in its devolatilization and degassing [50]. The vapours produced during pyrolysis go to a condenser where condenses as bio-oil, while the gas is collected separately. The produced biochar is transported through the auger to a collection vessel. When a solid heat carrier was used, it was separated from the biochar by a sieving system [59]. The continuous feeding mechanism in the auger reactor, along with efficient mixing, increases the overall efficiency of the pyrolysis process. Auger reactors can be used for both slow and fast pyrolysis, depending on the specific design and operating conditions [60].

2.3.5. Operating conditions of the pyrolysis process

The yield of pyrolysis products depends on the reactor design, the physical and chemical properties of the material used in the process, and operational parameters such as pyrolysis temperature, residence time in the reaction zone and heating rate [33], [47]. In addition, the pressure in the reactor, the composition of the ambient gas or the presence of mineral catalysts can also affect the product yield [33].

2.3.5.1. Temperature

In pyrolysis, the feedstock is heated (at a certain rate) from ambient temperature to a maximum temperature known as the pyrolysis temperature. The pyrolysis temperature is kept constant until the process is completed [33]. At very low temperatures (<300°C), heavy tars are formed. This is because the breakdown of biomass bonds occurs mainly in specific areas of its structure. On the other hand, at very high temperatures (>550°C) numerous types of chemical compounds are formed. This is due to extensive fragmentation of biomass [61].

The pyrolysis process conducted at low temperatures will support higher biochar yield production and the yield of gas will be low. In contrast, the pyrolysis process conducted at high temperatures will support higher production of gas yield. High temperatures will have the effect of reducing the yield of biochar. It can be summarized that as the temperature increases, the yield of biochar decreases and the yield of gas increases [33].

Apaydin-Varol et al. [62] studied the effect of temperature on the maximum yield of bio-oil obtained in the pyrolysis of pistachio shells. The pyrolysis process was carried out in a fixed bed reactor with a heating rate of 7^{o}C/min. It was shown that the bio-oil yield is sensitive to the pyrolysis temperature in the range of 300-700^{o}C. As the final temperature increased to 500-550^{o}C, the bio-oil yield increased, while above 550^{o}C to 700^{o}C a decrease in bio-oil yield was observed. In addition, it was shown that as the pyrolysis temperature increased, the biochar yield decreased, while the gas yield increased. The same relationship of the influence of temperature on the yield and properties of pyrolysis products was observed by Gupta et al. [51], who studied the slow pyrolysis of walnut shells.

2.3.5.2. Residence time

The long residence time of the product in the reactor, with the use of slow heating, increases the yield of biochar. Under such process conditions, volatiles are slowly or gradually removed from the reactor, which promotes the occurrence of a secondary reaction between biochar particles and volatiles, resulting in secondary biochar [33].

In addition, an increase in residence time and temperature promotes cracking of the liquid or tar, which increases the percentage of gas, and therefore reduces the bio-oil yield [63]. To achieve optimum bio-oil yield in pyrolysis, it is recommended that the residence time of the vapour should be maintained in the range of a few seconds to a few minutes [64].

2.3.5.3. Heating rate

The yield and composition of the pyrolysis product are significantly influenced by the heating rate of the biomass particles. Slow heating rates to moderate temperatures (400-600^{o}C) affect a higher yield of biochar. On the other hand, a fast heating rate to the same temperature liquefies more volatile substances and therefore affects a higher yield of liquid (bio-oil) [64].

Somerville et al. [63] investigated the effect of heating rate on biochar yield during radiata pine wood pyrolysis. The researchers showed that lower heating rates positively influence biochar formation reactions at lower temperatures. This is because the temperature range favourable for biochar formation reactions can be maintained longer at lower heating rates. In addition, low heating rates affect the longer residence time of pyrolysis vapours in the reactor, which facilitates the formation of secondary biochar.

2.3.5.4. Size of feed particles

The size of the feedstock particles by influencing the heating rate affects the pyrolysis products. The use of fine biomass particles affects higher liquid (bio-oil) yields. Smaller particles have a larger surface area, which supports interaction with the pyrolysis medium and the formation of volatile products without secondary reactions. In contrast, the use of larger biomass particles facilitates secondary reactions by increasing the yield of biochar [33].

Gupta et al. [51] studied the effect of particle size on the yield and properties of walnut shell pyrolysis products. The researchers showed that as particle size increases, biochar yields increase, and bio-oil and gas yields decrease. In addition, the difficulty of volatiles escaping with increasing particle size may cause them to re-polymerise into more stable char, increasing biochar production.

2.4. Research work on the slow pyrolysis of biowaste

The process of slow pyrolysis of industrial materials such as agricultural residues, forestry materials, energy crops and algal biomass is widely studied. One type of food waste, usually from the food industry, and municipal solid waste (MSW) are also increasingly being studied [42].

Yang et al. [39] studied the possibility of converting municipal solid waste into fuels and energy at high efficiency. For this purpose, the researchers performed a techno-economic analysis of a waste-to-energy plant based on an integrated pyrolysis system and a combined heat and power (CHP) plant. In this system, the pyrolysis temperature was maintained up to 600^{o}C. The feedstock was the organic fraction of municipal waste from local households. The waste was collected in the winter in Leicester, UK. The overall efficiency of the plant's cogeneration was found to be almost 60%, which was defined as the thermal and electrical output compared to the input of the feedstock fuel.

Chhabra et al. [40] investigated the possibility of extracting energy from mixed waste using a pyrolysis process. Municipal solid waste (MSW) was collected in the Mumbai Metropolitan Region and sorted into 10 fractions (including yard waste and food waste). Each fraction was pyrolysed separately. The pyrolytic behaviour of each fraction was shown to be different and, on this basis, the optimum temperature range for pyrolysis of a mixed MSW sample was found to be between 170 and 520^{o}C.

Tokmurzin et al. [65] studied the process of coprolysis of the organic fraction of municipal solid waste mixed with coal in different proportions to obtain biochar. The organic waste samples were collected in the city of Astana, (Kazakhstan) and consisted of food waste, fruit waste and small waste fractions. Carbon samples with high volatility were obtained from the Shubarkol coal deposit in the northern region of Kazakhstan. Tests conducted showed that such a solution could be used to produce biochar, as well as syngas and liquids. The study showed that increasing the pyrolysis temperature increases the gas yield and reduces the biochar content. In addition, low-temperature pyrolysis was shown to be more beneficial for samples of the organic fraction of municipal solid waste.

Czajczyńska et al. [66] stated that a big advantage of pyrolysis is that any material that contains organic carbon can be used as raw material. The paper analyzed what types of waste can be pyrolyzed. Special attention was paid to the fraction of food waste, wood biomass and garden waste, paper waste, plastics waste and municipal solid waste.

The authors showed that the pyrolysis process of selected single types of food waste has been widely studied, e.g. pyrolysis of fruit peels or nut shells. In contrast, they noted limited information on the pyrolysis of mixed household food waste. In addition, they showed that there is a lack of information in the case of pyrolysis of mixed garden waste. According to the authors, this may be because mixed garden waste is mainly processed biologically into compost.

Ronsse et al. [67] tested the effect of different process conditions on the biochar yield in a slow pyrolysis process in a fixed-bed reactor. Pine wood, wheat straw, green waste and dried algae were used as feedstock. It was observed that the yield of biochar decreased with the intensity of the pyrolysis process (i.e. residence time and higher processing temperature).

Kabenge et al. [68] investigated the feasibility of using banana peels for the pyrolysis process to produce banana peel vinegar (BPV), tar and biochar. The study showed that banana peels were suitable for a slow pyrolysis process and the maximum rate of biomass decomposition from banana peels occurred in the temperature range 450-550^{o}C.

Gupta et al. [51] studied the slow pyrolysis of walnut shells in a solid bed. The effects of process parameters such as temperature, particle size, bed height on the yield and properties of pyrolysis products were studied. In addition, to increase the yield of pyrolysis products, a pretreatment of walnut shells was applied, which consisted of the feedstock being treated with phosphoric acid at different concentrations (0.2-0.8M). The pretreatment showed an increased yield of biochar and bio-oil. Due to the properties of the pyrolysis products obtained, it was shown that biochar can be used as a fuel or for wastewater treatment. Bio-oil, on the other hand, can be used as a mixed fuel or as a source of chemicals. The pyrolysis gas, due to the presence of CH_4, H_2 and CO, has good combustion properties.

Walnut shells have also been studied by Senneca et al. [69]. In this work, pyrolysis was carried out in a fixed bed reactor at 600^{o}C in a nitrogen or carbon dioxide atmosphere. The study allowed the kinetics of the reaction to be investigated.

2.5. Applications of biochar

The physical, chemical and mechanical properties of biochar depend on the type of feedstock and the operating conditions of the pyrolysis process [47]. Furthermore, the chemical properties of biochar mainly depend on the percentage content of C, H, N, S and O [52]. The characteristics of biochar affect its potential for use in various applications.

2.5.1. Application of biochar in soil

Depending on the type of soil and biochar used, biochar has different effects on soil properties and microbial populations [70]. From the perspective of agricultural and gardening applications, biochar was tested as a component of chemical fertilizers. In addition, it has been studied how the addition of biochar to soil affects crop productivity by increasing nutrient availability, water retention capacity and soil microbial activity [71]. As the world's population has grown, the demand for food has increased. Therefore, to produce enough food, farmers are increasingly applying chemical fertilizers to the soil, which contributes to a reduction in soil fertility. The use of biochar can be an alternative to chemical fertilizers. Many studies have shown that biochar reduces soil acidity [17] . Due to its high nitrogen (N) and low phosphorus (P) content [70] and the presence of significant amounts of potassium (K) and small amounts of magnesium (Mg), calcium (Ca), copper (Cu), zinc (Zn) and iron (Fe), biochar is suitable for use as a fertilizer. Studies have shown that even in the absence of nitrogen fertilizers, the use of biochar as a soil additive significantly increased crop yields [17].

The application of biochar as a soil additive improves the absorption capacity of fertilizers, affects nutrient absorption properties and reduces nutrient leaching [17], [52]. Biochar improves soil quality because its porous structure improves the penetration of nutrients, water and air. In addition, biochar facilitates the degradation of pesticides and thus increases microbial activity and reduces the spread of contaminants through soil erosion and water washing out [52]. Biochar applied to the soil also has the effect of retaining water in the soil increasing water availability and improving nutrient cycling [17]. It has been studied that biochar applied in excess can also benefit the growth of plants exposed to water stress. Adding biochar to soil changes the chemical properties of the soil, which affects the composition and structure of the microbial community present in the soil. Many studies have shown a positive effect of biochar on the diversity and activity of microorganisms that promote plant growth [52], [70].

In most cases, the application of biochar to the soil results in improved soil quality and increased crop productivity. However, by improperly applying biochar, soil quality can be degraded, and crop productivity reduced [53]. For instance, the application of biochar derived from the residue of O. sativa L. had a negative impact on earthworm populations, that is, a decrease in abundance and biomass, and an increase in genotoxicity and mortality. Other examples of inappropriate application of biochar have been shown to increase N_2O emissions, reduce crop yields, decrease phosphorus content in plant leaves, or reduce the dry weight of plant roots [70]. In addition, it has been shown that the application of biochar to heavy clay soils can cause waterlogging and damage to acidophilic organisms. Biochar can also contain a significant amount of ash containing salts, causing soil salinization [53].

Haider et al. [70] concluded that it is important to use a specific type of biochar for a specific type of soil. Moreover, just because a particular biochar is effective on one type of soil does not necessarily mean that it will be equally effective on another type of soil.

2.5.2. Application of biochar in water treatment

Biochar can be applied to remove heavy metals, toxic elements and pollutants from water and wastewater [17]. Studies have shown that the adsorption of contaminants from water using biochar depends on the form of the biochar and the physicochemical properties of the contaminants. Removal of organic and inorganic contaminants, as well as antibiotics and other antimicrobial drugs has been the most studied. In addition, it has been shown that heavy metals such as Zn^{2+}, Pb^{2+}, As^{5+} and Cd^{2+} can be removed from water and wastewater using biochar [53]. When biochar is used to treat water and wastewater Wang et al. [72] stated that its recycling should be considered.

2.5.3. Application of biochar in carbon sequestration

The process of removing CO_2 from the atmosphere (either artificially or naturally) and storing it in soil for an extended period in liquid or solid form is known as soil carbon sequestration [70]. Biomass is usually considered a carbon-neutral material. It is assumed that in the process of burning biomass, the balance of CO_2 emissions is zero because the amount of CO_2 is emitted into the atmosphere as much as the plants intake through photosynthesis. Biochar produced from biowaste and added to the soil is considered a long-term sink for atmospheric carbon dioxide. Applied in this way, biochar increases carbon fixation and reduces emissions of gases, including CH_4, N_2O and CO_2 [17].

Converting organic matter into biochar that has high stability minimizes CO_2 emissions from the soil by reducing the rate of decomposition. Although direct CO_2 emissions occur during pyrolysis, producing biochar and placing it in the soil is a promising method for permanently storing carbon in the soil. The carbon content of biochar may reach 600 to 800 g/kg, which results in 2.20 to 2.94 tons of sequestered CO_2 per ton of biochar. Biochar can stay in the soil for decades after being introduced, effectively storing carbon for long-term sequestration [70]. Researchers have demonstrated that as the depth at which biochar is deposited increases, the rate of carbon accumulation in the soil also increases [17].

2.5.4. Application of biochar to reduce greenhouse gas emissions

Greenhouse gas emissions increase global warming potential thereby negatively affecting climate change. The application of biochar to soil reduces greenhouse gas emissions such as carbon dioxide (CO_2), methane (CH_4), nitric oxide (NO) and nitrous oxide (N_2O) [17], [52].

Crop cultivation method and soil moisture affect NO emissions from soil. Because of its high surface area, biochar limits nitrogen to tiny pores that denitrifying bacteria cannot access. In addition, the large surface area of the biochar increases water retention in the soil. Therefore, when the pores of biochar are 73-78% filled with water, the NO emissions of wet soils are reduced by 90%.

On the other hand, studies have shown that if water fills more than 83% of the biochar pores, there will be increased NO emissions from the soil [70]. The application of biochar to soil also reduces N_2O emissions from soil. This may be related to increased soil aeration, which increases the oxygen content of the soil and thus prevents the occurrence of soil denitrification, which occurs under oxygen-limited conditions [52].

The main sources of CH_4 emissions to the atmosphere are industrial emissions, natural gas exploitation and rice soils. According to several studies, adding biochar to rice paddy soil decreased the formation of CH_4. In addition, adding biochar to soil can reduce CH_4 emissions from soil to the atmosphere by reducing the macroporosity of saturated soil hydraulic conductivity. On the other hand, there are studies based on which it has been shown that adding biochar to soil increases CH_4 emissions. Therefore, it is important to select the right biochar for the type of soil [70].

The application of biochar to soil can induce mineralization of soil organic carbon causing an increase in CO_2 emissions. On the other hand, CO_2 emissions can be reduced when adsorption of CO_2 molecules occurs on the biochar surface. In addition, biochar in soil affects the activity and diversity of soil microorganisms that metabolize CO_2 [52].

2.5.5. Application of biochar as a construction material

Hu et al. [71] highlighted the use of biochar as a cementitious admixture for concrete and mortar. The application of biochar as an additive in cementitious building materials is an alternative to cement, sand and other energy-intensive admixtures used in concrete production. The use of a biochar additive can improve the strength and ductility of mortar. It can also increase the durability of the composite by reducing capillary water absorption and water penetration in the biochar-mortar mixture. Studies have shown that higher compressive strength of cement mortar is observed for smaller biochar particles with meso- and micropores. The mechanical performance and durability of concrete with biochar and mortar are influenced by the particle size of the biochar, its porosity, elemental content and the dose of biochar used (relative to the total mortar) [71].

3. Materials and experimental methods

3.1. Preparation of biowaste samples

The biomass residues used in this work were three different types of biowaste collected in the Silesia region of Poland. The biowaste was collected from different types of residential buildings and at different seasons of the year.

3.1.1. Kitchen biowaste

The first type was kitchen biowaste, which was collected in the summer in blocks of flats. Kitchen biowaste is organic waste that results from the preparation of meals by a single household living in a flat. This waste was collected from several different households and then mixed to obtain a representative sample for the study.

The main components of this biowaste are vegetable and fruit waste (such as their inedible parts, peelings, seeds, etc.), bread and bakery products, pasta, rice, groats, meat, milk and dairy products, ready meals that have not been eaten, eggshells, coffee grounds, tea leaves, nut shells. Kitchen biowaste is shown in Figure 2.

3.1.2. Spring garden biowaste

The second type of biomass residue tested was garden biowaste collected from single-family houses in spring. This waste was collected from several different households and then mixed to obtain a representative sample for the study. The main component of this biowaste is grass, as gardening work is carried out during the spring period, mainly cutting grass and planting flowers and other plants. On the other hand, there may also have been partial amounts of kitchen waste among this biowaste. This is because, in single-family housing buildings, kitchen and garden biowaste are collected in one container. Spring garden biowaste is shown in Figure 3.

3.1.3. Autumn garden biowaste

The third type of biomass residue tested was garden biowaste collected from single-family houses in autumn. This waste was collected from several different households and then mixed to obtain a representative sample for the study. The main components of this biowaste are leaves and small twigs, as cleaning work is carried out in the garden during the autumn period, mainly raking leaves (among which there are also small twigs). In addition, there may also be other withered plants and cut grass. As with spring garden biowaste, there may also have been partial amounts of kitchen waste among this biowaste. This is because, in single-family housing buildings, kitchen and garden biowaste are collected in one container. Autumn garden biowaste is shown in Figure 4.

3.1.4. Drying and grinding of biowaste samples

The biowaste samples after collection (on a wet basis) were used to determine the total moisture content. After the determination of the total moisture content, the prepared samples were completely dried in a laboratory dryer. Drying was carried out at 105^{o}C for 24 h. After drying, the biowaste samples were ground in an IKA-WERKE M20 mill (Figure 1), which is used for dry grinding hard and friable substances. The dried and ground samples were placed in sealed transparent containers and were used for further analyses, which are described in the following work. Figure 2 to Figure 4 show samples of kitchen, spring garden and autumn garden biowaste before drying, after drying and after grinding.

Figure 1. IKA-WERKE M20 mill used to grind the biowaste samples.

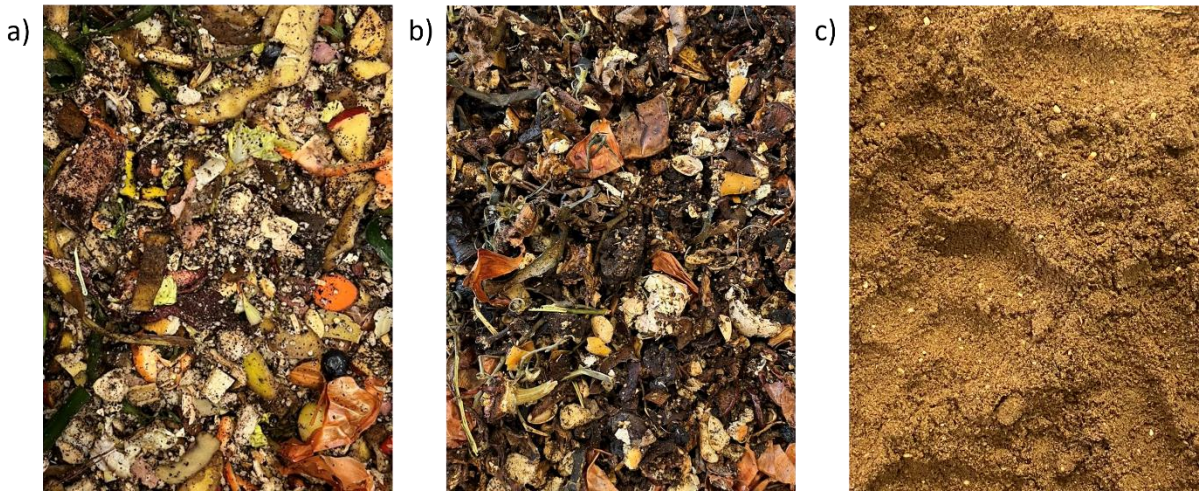

Figure 2. Kitchen biowaste: a) before drying, b) after drying, c) after grinding.

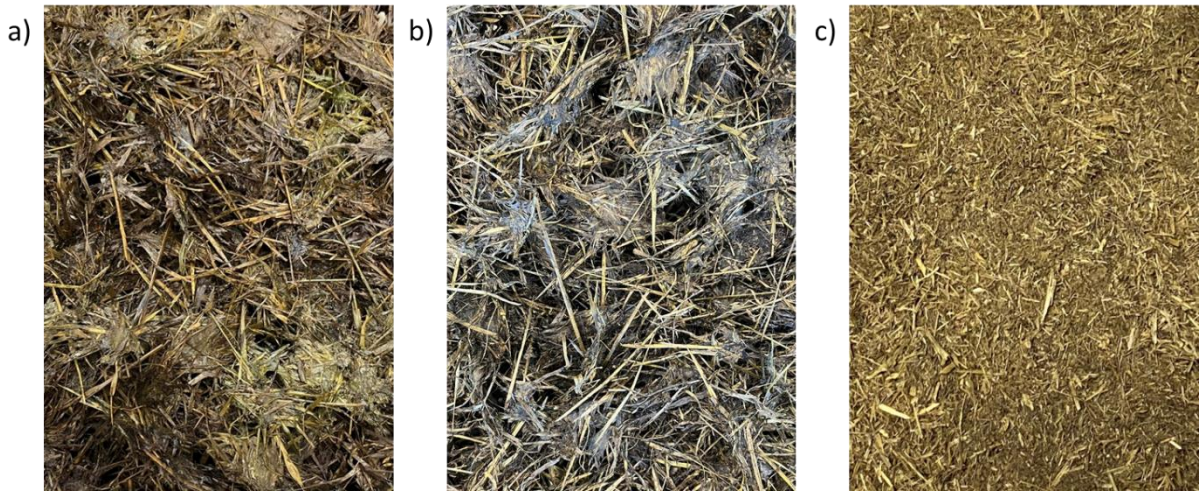

Figure 3. Spring garden biowaste: a) before drying, b) after drying, c) after grinding.

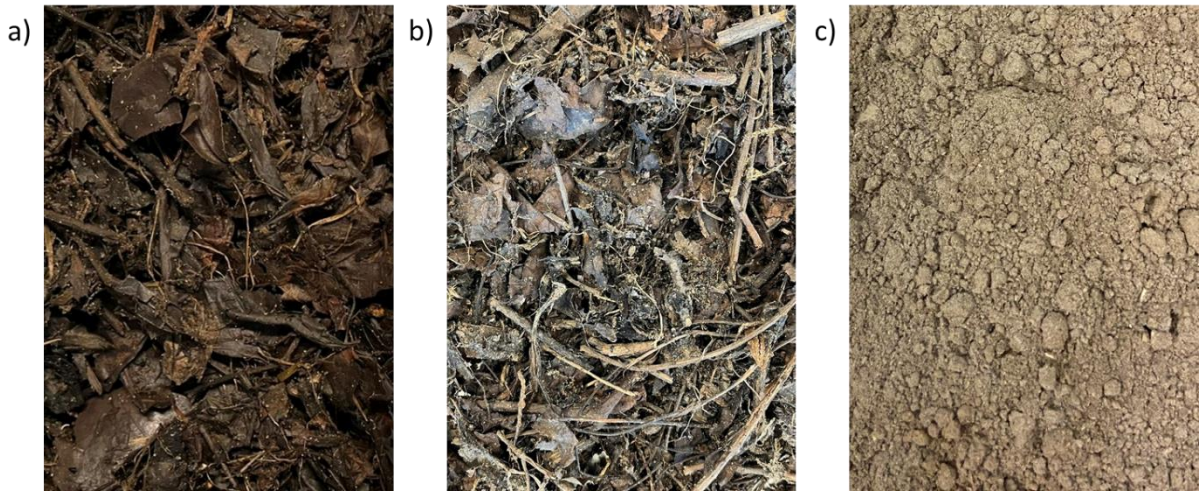

Figure 4. Autumn garden biowaste: a) before drying, b) after drying, c) after grinding.

3.2. Characterization of the biowaste samples

The properties of biowaste and the concentrations of elements that are present in it vary depending on its origin and type [33]. The analysis of biowaste properties influences its use for energy. Proximate analysis, ultimate analysis and heating values of biowaste can provide a clear understanding of its thermochemical conversion characteristics [30] and will help in the selection of an appropriate biowaste thermal utilization system design [33].

3.2.1. Proximate analysis

The proximate analysis includes the determination of the moisture, volatile matter, fixed carbon and ash content of the biowaste. Wet biowaste samples were used to determine the total moisture content. Whereas the other determinations were carried out on dry samples. Each determination was performed in three parallel measurements and the results were presented as an average. If the differences between the determinations were too large, an additional measurement was performed.

3.2.1.1. Total moisture content

The aim of the experiment was to determine the total moisture content of biowaste samples.

The determination of the total moisture content of biowaste samples was carried out in accordance with the standard PN-EN ISO 18134-1:2023-02 [73]. The method consists of drying a biowaste sample at 105°C. The total moisture content of the biowaste can be determined by weight analysis of the test sample.

Measurement procedure

First, a weighing dish was weighed. A sample of fresh biowaste with a mass of 2-5 g was weighed into the dish and distributed evenly over the whole surface of the dish. The dish with the sample was placed in a dryer (the temperature was set to 105^{o}C) and dried for 30 minutes. The dish with the sample was then removed from the dryer, cooled to ambient temperature and weighed. The next step was to place the dish with the sample back in the drier and dry at 105^{o}C for 15 minutes. After this time, the dish with the sample was removed from the dryer, cooled to ambient temperature, and weighed. Drying should be repeated until a constant weight is obtained, meaning that two consecutive measurements do not differ by more than 0.001 g.

Calculation of the results

To calculate the total moisture content (MC) on a wet weight basis, the formula was used [34], [73]:

$$\mathrm{MC} = \frac{\mathrm{m}_1 - \mathrm{m}_2}{\mathrm{m}_1} \cdot 100\ [\%] \qquad (1)$$

where:

m_1 – mass of the sample before drying, g

m_2 – mass of the sample after drying, g

3.2.1.2. Volatile matter content

The aim of the experiment was to determine the volatile matter content of biowaste samples.

The determination of the volatile matter content of the test samples was conducted in accordance with the standard PN-EN ISO 18123:2016-01 [74]. The method consists in burning a biowaste sample at 850°C under anaerobic conditions for 3 minutes. The volatile content of the biowaste can be determined by weight analysis of the test sample.

Measurement procedure

First, the crucible with lid was weighed. Next, 1.0 g of the sample was weighed into the crucible and covered with the lid (Figure 5). The prepared crucible was placed in a furnace heated to 850°C and burned for 7 minutes after closing the furnace (3-4 minutes are needed for the furnace to reach 850°C). The crucible was then removed from the furnace, cooled, and transferred to a desiccator for 10 minutes. The crucible with the sample was weighed again.

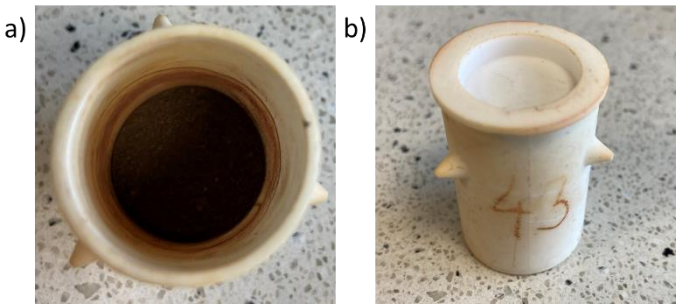

Figure 5. Determination of the volatile matter content: a) sample in the crucible, b) crucible with sample and closed lid

Calculation of the results

To calculate the content of volatile matter (VM) on a dry weight basis, the formula was used [34], [74]:

$$VM = \frac{m_1 - m_2}{m_1} \cdot 100\ [\%] \qquad (2)$$

where:

m_1 – mass of the sample before degassing, g

m_2 – mass of the sample after degassing, g

3.2.1.3. Ash content

The aim of the experiment was to determine the ash content in biowaste samples.

The determination of ash content in biowaste samples was carried out in accordance with standard PN-Z-15008-03 [75], which allows for the determination of the combustible and noncombustible components in the test sample. The number of noncombustible components corresponds to the ash content. The method involves the calcination of a biowaste sample to a constant mass at a temperature of 815 ± 10°C. The content of combustible and noncombustible components (ash) in biowaste can be determined by weight analysis of the test sample.

Measurement procedure

The crucible was weighed first. Then 1.0-2.0 g of the sample was weighed into the crucible. The prepared sample was placed in an electric furnace and calcinated for 20 minutes at 815 ± 10°C. After this time, the test sample was carefully removed from the oven, cooled, and transferred to a desiccator for about 10 minutes. After cooling, the crucible with the sample was weighed. All steps were repeated until the results did not differ by 0.001 g.

Calculation of the results

To calculate the content of combustible compounds (CC) on a dry weight basis, the formula was used [34], [75]:

$$\mathrm{CC} = \frac{\mathrm{m}_1 - \mathrm{m}_2}{\mathrm{m}_1} \cdot 100\ [\%] \tag{3}$$

where:

$\mathrm{m}_1 -$ mass of the sample before calcination, g

$\mathrm{m}_2 -$ mass of the sample after calcination, g

To calculate the ash content (A) on a dry weight basis, the formula was used [34], [75]:

$$\mathrm{A} = 100 - \mathrm{CC}\ [\%] \tag{4}$$

3.2.1.4. Fixed carbon

Fixed carbon is the material remaining after determining the moisture content, volatile matter and ash content [37]. Fixed carbon represents the solid carbon in the biowaste that remains in the char after devolatilization [30], [33].

To calculate the fixed carbon content (FC) on a wet weight basis, the formula was used [30], [33]:

$$\mathrm{FC} = 100 - (MC + VM + A)\ [\%] \tag{5}$$

where:

$\mathrm{MC} -$ total moisture content, % (wet basis)

$\mathrm{VM} -$ volatile matter content, % (wet basis)

$\mathrm{A} -$ ash content, % (wet basis)

To calculate the fixed carbon content (FC) on a dry weight basis, the formula was used:

$$\mathrm{FC} = 100 - (VM + A)\ [\%] \tag{6}$$

where:

$\mathrm{VM} -$ volatile matter content, % (dry basis)

$\mathrm{A} -$ ash content, % (dry basis)

3.2.2. Ultimate analysis

The ultimate analysis includes the determination of the elemental content of biowaste, that is, carbon, hydrogen, oxygen, nitrogen, and sulphur, as well as other elements such as chlorine. All determinations were carried out on dry samples. Each determination was performed in three parallel measurements and the results were presented as an average. If the differences between the determinations were too large, an additional measurement was performed.

3.2.2.1. Carbon and hydrogen content

The aim of the experiment was to determine the carbon and hydrogen content of a biowaste sample.

The determination of carbon and hydrogen content of the test samples was conducted in accordance with the standard ISO 609:1996 [76]. The method of determination consists of the combustion of a biowaste sample at 950°C in the presence of oxygen. During combustion, the carbon and hydrogen contained in the sample are oxidised and exothermic reactions lead to the formation of CO_2 and H_2O [35]. Based on the mass of CO_2 and H_2O, the elemental content of hydrogen and carbon can be calculated.

Measurement procedure

The combustion process takes place in a high temperature furnace. The furnace should be heated to 950°C. The oxygen flow through the furnace should be 300 cm^3/min. Absorbers containing magnesium chlorate (III) (or calcium chloride) and sodium asbestos (or sodium calcium), which serve to absorb water and carbon dioxide respectively, were weighed. After weighing, the absorbers were connected to the furnace outlet in the correct order (Figure 6).

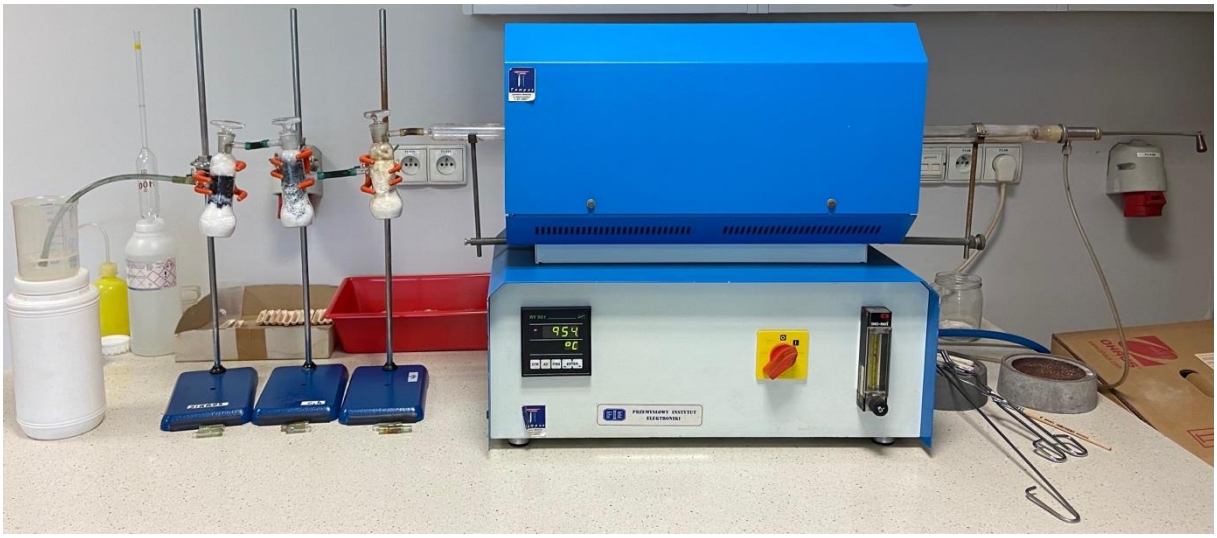

Figure 6. Test stand for the determination of carbon and hydrogen content

To prepare the sample (Figure 7), first a crucible was tared. In the crucible was placed a 0.2 g biowaste sample. Then, a layer of catalyst (aluminum oxide) was applied to the sample, the weight of which should be comparable to that of the biowaste sample.

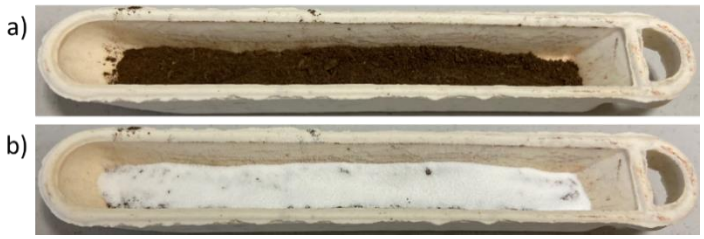

Figure 7. Sample preparation a) crucible with the sample, b) crucible with sample coated with catalyst.

The prepared sample was placed in a glass tube of the furnace heated to 950°C. The sample was slowly and carefully moved toward the outlet of the furnace. During this time, the moment of ignition was observed, after which the sample was moved step by step until it was in the centre of the furnace. After the sample was burned, the crucible was removed from the glass tube of the furnace. The absorbers were then disconnected and allowed to cool for 30 minutes. After this time, the absorbers were weighed.

Calculation of the results

To calculate the content of carbon (C) on a dry weight basis, the formula was used [76]:

$$C = \frac{m_2 - m_1}{m_x} \cdot 0.2729 \cdot 100\ [\%] \tag{7}$$

where:

$m_1 -$ summary mass for absorbers B and C before combustion, g

$m_2 -$ summary mass for absorbers B and C after combustion, g

$m_x -$ mass of the sample, g

$0.2729 - CO_2$ recalculation coefficient

To calculate the hydrogen content (H) on a dry weight basis, the formula is required [76]:

$$H = \frac{A_2 - A_1 - \frac{W_s \cdot m_s}{100}}{m_x} \cdot 0.1119 \cdot 100 - 0.1119 \cdot MC_x\ [\%] \tag{8}$$

where:

$A_1 -$ mass of the absorber A before combustion, g

$A_2 -$ mass of the absorber A after combustion, g

$m_x -$ mass of the sample, g

$m_s -$ mass of the Al_2O_3 used for sample combustion, g

$W_s -$ water content in the Al_2O_3, %

$MC_x -$ moisture content in the sample, %

It was assumed that the water content of Al_2O_3 (W_s) and the moisture content of the sample (MC_x) were equal to zero, which consequently resulted in the formula used to calculate the hydrogen content:

$$H = \frac{A_2 - A_1}{m_x} \cdot 0.1119 \cdot 100\ [\%] \tag{9}$$

3.2.2.2. Total nitrogen content

The aim of the experiment was to determine the total nitrogen content of a biowaste sample.

The determination of the total nitrogen content of the biowaste samples was conducted in accordance with the standard PN-G/-04523 [77]. This method is known as the Kjeldahl method and involves converting nitrogen into ammonium sulphate by heating the organic sample to boiling point with concentrated sulphuric acid with the addition of a catalyst. The ammonia is then distilled from the alkaline medium into a measured volume of standard acid solution. The ammonia content of the distillate is determined by titration.

Measurement procedure

Initially, 0.25-0.30 g of biowaste sample, 1.5 g of catalyst mixture and 10 cm^3 of concentrated sulphuric acid (VI) (H_2SO_4) were weighed into a 300 cm^3 Kjeldahl flask. The Kjeldahl flask was placed in the mineralizer under the extractor, the outlet was closed with a reflux condenser and the flask was heated. Mineralization was carried out until the liquid became clear.

The solution from the flask was transferred quantitatively, using about 25 cm^3 of distilled water, to a flask that is part of the distillation apparatus. Then, a few drops of phenolphthalein solution were added. Successively, a 40% sodium hydroxide (NaOH) solution was added until a purple colour was obtained. Finally, boiling spores (broken porcelain) were added to the flask.

The distillate receiver was then prepared. 25 cm^3 of 0.02 M hydrochloric acid (HCl) was measured into a beaker and a few drops of methyl red were added. The receiver was filled with enough distilled water so that the lower end of the condenser was immersed in the receiver.

In the next step, the distillation flask and distillate receiver were connected to the distillation apparatus, the cooling circuit was turned on and the distillation was carried out (Figure 8).

Figure 8. Test stand for determination of total nitrogen content

When about 150 - 200 cm^3 of the solution was distilled, it was checked with indicator paper, whether ammonia (NH_3) was still emitted. To do this, the indicator paper was placed under the lower end of the cooler. When the indicator paper was colored green, the distillation process should be continued. On the other hand, when its color does not change, the distillation should be finished.

After the distillation process was completed, the receiver was disconnected first, and then the heating mantle was disconnected. In the reverse order, the solution from the receiver would have been drawn through the cooler into the distillation flask. The excess acid was titrated with 0.02M sodium hydroxide (NaOH) solution.

Calculation of the results

To calculate the total nitrogen content (N) on a dry weight basis, the formula was used [34], [77]:

$$N = \frac{0.28 \cdot (b - a) \cdot 100}{m_x} \ [\%] \tag{10}$$

where:

$a -$ volume of 0.02 M NaOH solution used to titrate the excess of HCl, cm^3

$b -$ volume of 0.02 M HCl solution measured into the receiver, cm^3

$m_x -$ mass of the sample, mg

3.2.2.3. Total sulphur content

The aim of the experiment was to determine the total sulphur content of a biowaste sample.

The determination of the total sulphur content of the biowaste samples was conducted in accordance with the standard PN-ISO351/1999 [78]. The method involves combustion of the biowaste sample at 950°C in the presence of oxygen. During combustion, the sulphur contained in the sample is oxidised to sulphur oxides, which are adsorbed in hydrogen peroxide. From the alkalimetric indications of the sulphuric acid, the total sulphur content can be calculated.

Measurement procedure

The combustion process takes place in a high temperature furnace. The furnace should be heated to 950°C. The oxygen flow through the furnace should be 300 cm^3/min. The absorber was filled with 100cm^3 of dihydrogen dioxide solution and connected to the furnace outlet (Figure 9).

Figure 9. Test stand for the determination of total sulphur content

To prepare the sample, the crucible was first tared, and 0.2 g of the biowaste sample was placed in it. After that, a layer of SiO_3 was applied to the sample, the mass of which should be comparable to that of the sample. The prepared sample was placed in a glass tube of the furnace heated to 950°C. The sample was slowly and carefully moved towards the furnace outlet. During this time, the moment of ignition was observed, after which the sample was moved step by step until it was in the centre of the furnace. After the sample had burned, the crucible was removed from the glass tube of the furnace. The absorber was then disconnected, and its content transferred to a glass flask. The flask with the solution was heated to boiling point and boiled for 5-10 minutes. After this time, the content of the flask was cooled to ambient temperature. A few drops of methyl red were added and titrated with 0.05M NaOH solution until the colour changed from pink to yellow. A control test was performed in parallel with the test samples.

Calculation of the results

To calculate the total sulphur content (S) on a dry weight basis, the formula was used [78]:

$$S = \frac{(V_x - V_{cs})}{m_x} \cdot 0.0008 \cdot 100\ [\%] \tag{11}$$

where:

V_x – volume of 0.05M NaOH solution used for sample titration, cm^3

V_{cs} – volume of 0.05M NaOH solution used for control sample titration, cm^3

m_x – mass of the sample, g

0.0008 – mass of sulphur per $1\mathrm{cm}^3$ of 0.05M NaOH, $\frac{\mathrm{g}}{\mathrm{cm}^3}$

3.2.2.4. Chlorine content

The aim of the experiment was to determine the chlorine content of the biowaste samples.

The determination of the chlorine content of the biowaste samples was carried out in accordance with the standard PN-ISO 587:2000 [79]. The method consists of the combustion of a biowaste sample, which is in direct contact with an Eschka mixture, at 675°C in an oxidizing atmosphere. The process is intended to remove the combustible substance and convert the chlorine to alkali chlorides, which are extracted with nitric acid (V) and determined by the Mohr method.

Measurement procedure

At first, the crucible was tared. 0.5 g of Eschka mixture was weighted and covered the bottom of the crucible with it. Then 0.5 g of the sample was weighted and mixed with 2.5 g of the weighted Eschka mixture. The mixture was transferred to the crucible. The contents of the crucible were covered with an additional 1.0 g of Eschka mixture. The prepared sample is shown in Figure 10. The prepared sample was placed in a cold muffle furnace and the temperature was increased to 675°C for 1 hour. This temperature was then maintained for a further two hours. After this time, the crucible was removed and cooled.

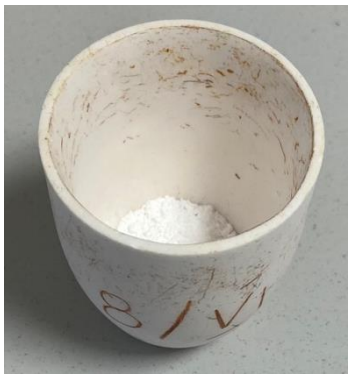

Figure 10. Sample prepared for determination of chlorine content.

The content of the crucible was transferred to a beaker. To completely transfer the content of the crucible, the crucible was washed several times with hot water. The agglomerated ash in the beaker was crushed with the tip of a glass rod. The content of the beaker was then boiled and immediately filtered in a glass funnel lined with a filter (Figure 11). The residue in the beaker and on the filter was washed several times with hot water.

Figure 11. Sample preparation: a) transfer the content of the crucible to the beaker, b) boiling the content of the beaker, c) filtration.

The filtered solution was neutralised by adding concentrated nitric acid (V), an indicator paper was used to check the pH. Then 10 drops of indicator (potassium chromate solution) were added to the solution and titrated with 0.05 mol/dm^3 silver nitrate solution. The first appearance of a brown colour indicated the end of the titration (Figure 12). A control test was performed in parallel with the test samples.

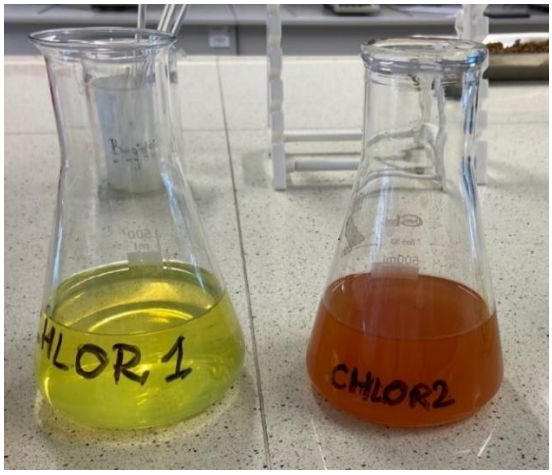

Figure 12. Comparison of solution colours before titration (yellow) and after titration (brown)

Calculation of the results

To calculate the content of chlorine (Cl) on a dry weight basis, the formula was used [79]:

$$Cl = \frac{3.545 \cdot c \cdot (V_2 - V_1)}{m_x} \ [\%] \tag{12}$$

where:

c – concentration of silver nitrate (V) solution, $\frac{\text{mol}}{\text{dm}^3}$

V_1 – volume of the silver nitrate (V) solution used to determine the blank sample, cm^3

V_2 – volume of the silver nitrate (V) solution used to determine the sample, cm^3

m_x – mass of the sample, g

3.2.2.5. Oxygen content

The oxygen content of the biowaste samples was determined by difference. In the expression of the ultimate analysis, the sum of the percentages of moisture, ash, carbon, hydrogen, nitrogen, sulphur and chlorine was subtracted from 100% [37].

To calculate the oxygen content (O) on a wet weight basis, the formula was used [37]:

$$O = 100 - (MC + A + C + H + N + S + Cl) \ [\%] \tag{13}$$

where:

MC – total moisture content, % (wet basis)

A – ash content, % (wet basis)

C – carbon content, % (wet basis)

H – hydrogen content, % (wet basis)

N – total nitrogen content, % (wet basis)

S – total sulphur content, % (wet basis)

Cl – chlorine content, % (wet basis)

To calculate the oxygen content (O) on a dry weight basis, the formula was used:

$$O = 100 - (A + C + H + N + S + Cl) \ [\%] \tag{14}$$

where:

A – ash content, % (dry basis)

C – carbon content, % (dry basis)

H – hydrogen content, % (dry basis)

N – total nitrogen content, % (dry basis)

S – total sulphur content, % (dry basis)

Cl – chlorine content, % (dry basis)

3.2.3. Measurement of other biowaste properties

To further characterize the tested biowaste samples, the higher heating value, lower heating value, total organic matter content, total organic carbon content and pH of the water extract of the biowaste samples were additionally determined. Each determination was performed in three parallel measurements and the results were presented as an average. If the differences between the determinations were too large, an additional measurement was performed.

3.2.3.1. Higher and lower heating value

The aim of the experiment was to determine higher heating value (HHV) and lower heating value (LHV) of biowaste samples.

The determination of the higher heating value (HHV) and lower heating value (LHV) of biowaste samples was carried out in accordance with the standard PN-ISO 1928:2020-05 [80]. The method involves determining the higher heating value (HHV) of a biowaste sample, at a constant volume and reference temperature of 25^{o}C, in a calorimeter bomb calibrated by burning certified benzoic acid. The result obtained is the higher heating value (HHV) of the analyzed sample, at constant volume, including liquid water contained in the combustion products. Based on the higher heating value (HHV), the lower heating value (LHV) is calculated.

Measurement procedure

The crucible was tared and a 1.0 g sample of biowaste was weighed. The prepared sample was placed in the bomb head. Then, a resistance wire was placed in the centre of the sample so that both ends did not touch each other (Figure 13).

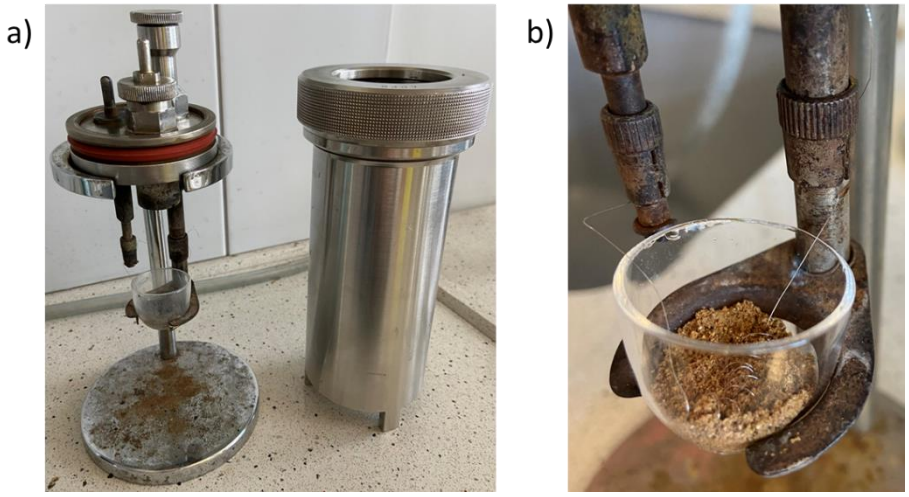

Figure 13. Sample preparation: a) sample placed in the bomb head, b) resistance wire placed in a sample of kitchen biowaste.

The bomb was filled with 10 cm^3 of distilled water and closed. The calorimeter bomb was then filled with oxygen. Before inserting the bomb into the calorimeter, the water level in its lid was checked. Then, the bomb was inserted into the calorimeter (Figure 14) and the measurement began (Figure 15). When the process was finished, it was checked whether the combustion was complete.

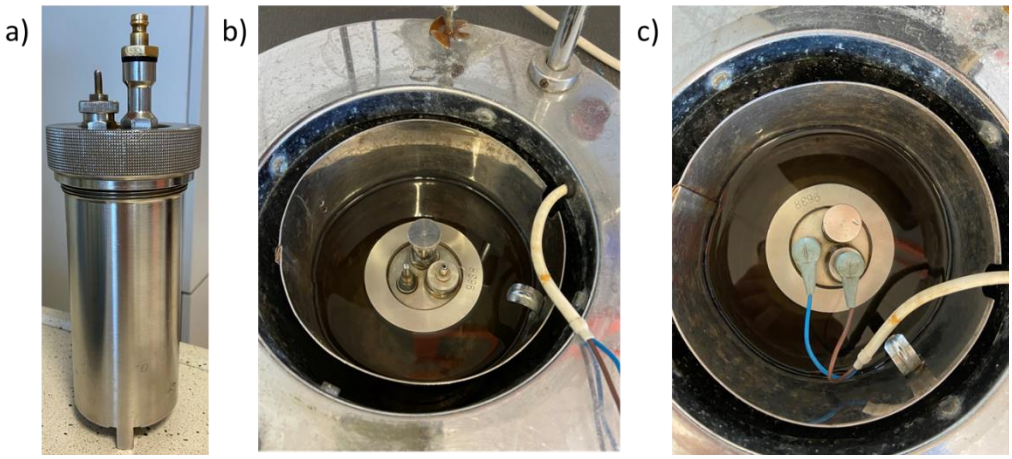

Figure 14. Sample preparation: a) closed calorimetric bomb after filling with oxygen, b) bomb inserted in the calorimeter, c) bomb connected to the calorimeter.

Figure 15. Calorimeter after the start of the measurement

Calculation of the results

To calculate the higher heating value (HHV) on a dry weight basis, the formula was used [38]:

$$HHV = \frac{HHV_x}{m_x} \quad \left[\frac{J}{g}\right] \tag{15}$$

where:

HHV_x – higher heating value obtained for the sample, J

m_x – mass of the sample, g

To calculate the lower heating value (LHV) on a dry weight basis, the formula was used [38]:

$$LHV = HHV - r_n \cdot (mc + 9 \cdot h) \left[\frac{kJ}{kg}\right] \tag{16}$$

where:

HHV – higher heating value, $\frac{\mathrm{kJ}}{\mathrm{kg}}$

r_n – enthalpy of water evaporation in 25°C, $\frac{\mathrm{kJ}}{\mathrm{kg}}$; $\mathrm{r_n} = 2450\,\frac{\mathrm{kJ}}{\mathrm{kg}}$

mc – moisture content of the sample, $\frac{\mathrm{kg H_2O}}{\mathrm{kg\ of\ fuel}}$

h – hydrogen content of the sample, $\frac{\mathrm{kg H_2}}{\mathrm{kg\ fuel}}$

The moisture content of the samples was assumed to be zero ($mc = 0$) because the analysed samples were completely dry.

To calculate the lower heating value (LHV) on a wet weight basis, the formula was used [38]:

$$LHV = (1 - mc) \cdot HHV - r_n \cdot (mc + 9 \cdot h) \left[\frac{kJ}{kg}\right] \quad (17)$$

where:

$HHV -$ higher heating value, $\frac{\mathrm{kJ}}{\mathrm{kg}}$

$r_n -$ enthalpy of water evaporation in 25°C, $\frac{\mathrm{kJ}}{\mathrm{kg}}$; $\mathrm{r_n} = 2450 \frac{\mathrm{kJ}}{\mathrm{kg}}$

$mc -$ moisture content of the sample, $\frac{\mathrm{kg H_2O}}{\mathrm{kg\ of\ fuel}}$

$h -$ hydrogen content of the sample, $\frac{\mathrm{kg H_2}}{\mathrm{kg\ fuel}}$

3.2.3.2. Total organic matter content

The aim of the experiment was to determine the total organic matter content of biowaste samples.

The method involves the combustion of the biowaste sample to a constant mass at 600°C. The total organic content of the biowaste can be determined by weight analysis of the test sample [34]. The mass loss correspond to the content of organic matter in the sample, and the residue after burning the sample is equal to the ash content of the biowaste.

Measurement procedure

First, the crucible was weighed. Then a 1.0 g sample of biowaste was weighed into the crucible. The prepared sample was placed in a muffle furnace at 600°C for 30 minutes. After this time, the test sample was carefully removed from the furnace, cooled and transferred to a desiccator for about 10 minutes. After cooling, the crucible with the sample was weighed. All steps were repeated until the results did not differ by 0.001 g.

Calculation of the results

To calculate the total organic matter content (OS) on a dry weight basis, the formula was used [34]:

$$\mathrm{OS} = \frac{\mathrm{m_1} - \mathrm{m_2}}{\mathrm{m_1}} \cdot 100\ [\%] \quad (18)$$

where:

$\mathrm{m_1} -$ mass of the sample before calcination, g

$\mathrm{m_2} -$ mass of the sample after calcination, g

In addition, the mineral matter content (MS) on a dry weight basis, of the biowaste was calculated according to the formula [34]:

$$\mathrm{MS} = \frac{\mathrm{m_2}}{\mathrm{m_1}} \cdot 100\ [\%] \quad (19)$$

where:

$\mathrm{m_1} -$ mass of the sample before calcination, g

$\mathrm{m_2} -$ mass of the sample after calcination, g

3.2.3.3. Total organic carbon content

The aim of the experiment was to determine the total organic carbon content of the biowaste samples.

The method involves the determination of biochemically easily degradable organic matter (RSO) in biowaste using the dichromate method. To do this, the sample is mixed with a solution of potassium dichromate and a solution of sulfuric acid. Excess dichromate is titrated with Mohr's salt solution in the presence of biphenylamine as an indicator. As soon as the reduction of dichromate is completed, the colour of the solution turns from brownish green to blue. At the end of the titration, the blue colour changes to a distinct green colour. The amount of Mohr salts consumed during the titration allows the determination of the biochemically easily degradable organic matter content (RSO) of the biowaste. Based on the RSO content, the total organic carbon content of the biowaste sample can be calculated [34].

Measurement procedure

First, 0.1 g of biowaste was weighed and poured into a conical flask. 20 cm^3 of 2M potassium dichromate (VI) ($K_2Cr_2O_7$) was added to the flask and mixed thoroughly. While mixing, 20 cm^3 of concentrated sulfuric acid (VI) (H_2SO_4) was added drop by drop. The content of the flask was left for 30 minutes. During this time, the content was mixed from time to time.

The content of the conical flask was transferred quantitatively to a volumetric flask, filled up to the mark with distilled water and mixed thoroughly. Then 25 cm^3 of the solution was transferred to the conical flask using a pipette. 200 cm^3 of distilled water, 2.5 cm^3 of concentrated orthophosphoric (V) acid (H_3PO_4), 4 to 5 drops of biphenylamine and 0.05 g (pinch) of sodium fluoride (NaF) were added. After adding each reagent, the sample was mixed thoroughly. Thus, prepared sample was titrated with Mohr's salt solution (0.5M $FeSO_4(NH_4)_2SO_4$) until the color changed from blue to green. The amount of Mohr salt consumed was read. A control test was performed in parallel with the test samples.

Calculation of the results

Assuming that, the amount of organic carbon represents 0.47 of biochemically degradable organic matter (RSO) and that 1 cm^3 of 2M potassium dichromate (VI) ($K_2Cr_2O_7$) oxidizes 3 mg of C to CO_2, the amount of biodegradable organic matter (RSO) in the tested biowaste was calculated according to the formula [34]:

$$RSO = \frac{(a-b)\cdot c \cdot 2 \cdot 0.003 \cdot 100}{m_x \cdot a \cdot 0.47}\ [\%] \tag{20}$$

where:

$a -$ volume of Mohr's salt used for control sample titration, cm^3

$b -$ volume of Mohr's salt used for sample titration, cm^3

$c -$ volume of the added 2M $K_2Cr_2O_7$ solution, cm^3

$m_x -$ mass of the sample, g

To calculate the total organic carbon content (C_{org}) on a dry weight basis, the formula was used [34]:

$$C_{org} = 0.47 \cdot RSO\ [\%] \tag{21}$$

3.2.3.4. pH

The aim of the experiment was to determine the pH of the water extract from biowaste samples.

The method involves the potentiometric measurement of electromotive force in a system using a glass electrode as the measuring electrode, a water extract of biowaste as the test solution, and a calomel electrode as the reference electrode. The pH can be determined using the measured electromotive force of the system [34].

Measurement procedure

At first, a water extract was prepared from the biowaste samples. For this, a 50 g sample of biowaste was weighed and transferred to a flask containing a measured 500 cm^3 of distilled water. The prepared flask was placed in a laboratory shaker and shaken for 25 minutes. After this time, the solution was left until the heavy particles fell off. The liquid was then decanted by filtering it through a filter paper placed on a glass funnel.

The device used to measure pH was a pH meter. First, a measuring electrode and a temperature sensor were connected to the corresponding slots of the pH meter. Then the measuring electrode and temperature sensor were immersed in the previously prepared biowaste extract so that these elements did not touch the edges or bottom of the beaker. The pH meter was turned on, and after the values stabilized, the result was read. The measurement was repeated three times. After the measurement, the measuring electrode was removed from the test solution and washed with distilled water, and the excess liquid was gently removed with blotting paper.

The average of two determinations that did not differ by more than 0.2, is taken as the determination result.

3.2.4. Surface analysis of biowaste by scanning electron microscopy (SEM)

The aim of the experiment was to record images of the surface of the studied biowaste. Analysis of the morphology of the studied biowaste was performed using a scanning electron microscope (SEM) (JEOL, model JSM-7001F).

The method involves capturing images of the surface of samples at high magnifications through secondary or backscattered electron registration using a scanning electron microscope (SEM). The scanning electron microscope (SEM) is an advanced imaging and analysis tool used to visualize and analyze materials at the nanoscale. It involves generating a focused electron beam, interacting with the sample to produce signals, and producing high-resolution images. SEM is widely used in scientific research to study the surface morphology, composition and microstructure of various materials [81].

3.3. Slow pyrolysis of biowaste

The slow pyrolysis process was carried out on a laboratory batch scale. An electrically heated horizontal tube furnace (HTF) with a water-cooled vessel from the Portuguese company Termolab-fornos Eléctricos Lda. was used (Figure 16).

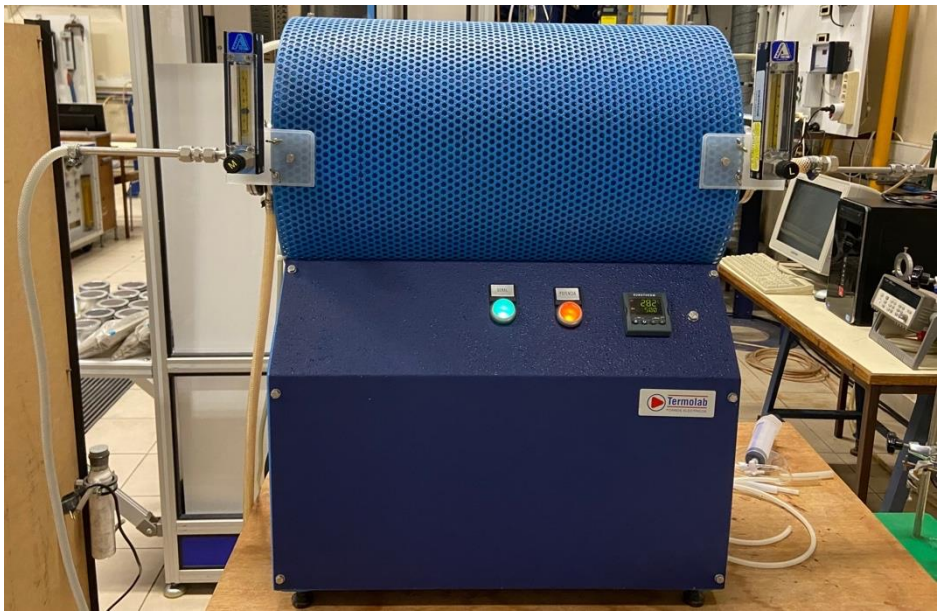

Figure 16. Horizontal tube furnace used for the slow pyrolysis process.

The unit operates at a maximum temperature of 1300ºC. The wall temperature is continuously monitored using an S-type thermocouple. Inside the furnace is a horizontal tube with an internal diameter of 4 cm and a length of 55 cm made of recrystallised alumina. Inside this tube, the atmosphere of the slow pyrolysis process can be controlled. Two ceramic crucibles were placed inside the HTF, each containing a sample of approximately 2.5 g. The slow pyrolysis processes were carried out at 400ºC, 500ºC and 600ºC, with a heating rate of 33ºC/min and an inert atmosphere (nitrogen), with a residence time of 1 h and a nitrogen flow rate of 2 l/min. Figure 17 shows a scheme of a horizontal tube furnace used in the slow pyrolysis process.

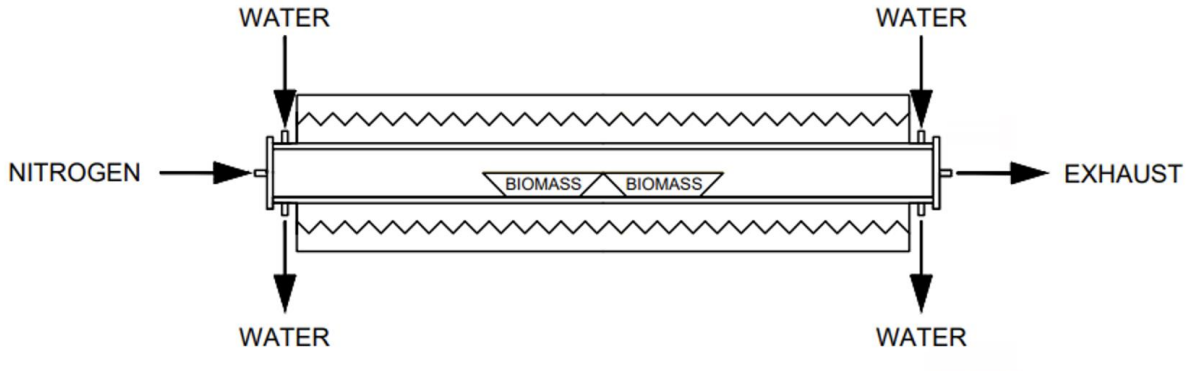

Figure 17. Scheme of horizontal tube furnace used for the slow pyrolysis process.

Measurement procedure

First, the test stand was prepared. The appropriate cooling water flow for the horizontal tube furnace was set. The nitrogen bottle was unscrewed to allow the nitrogen to flow through the HTF. The appropriate heating program for the tube furnace was set. The temperature at which slow pyrolysis was to be carried out was set.

Next, in two ceramic crucibles, samples of the biowaste to be tested were prepared. For this, each crucible was tared and about 2.5 g of biowaste was weighed into each crucible (Figure 18). Such prepared samples were placed in the middle of the horizontal tube of the electric furnace (Figure 19) and the entrance to the furnace tube was closed.

Figure 18. One of two crucibles containing a 2.5 g sample of kitchen biowaste prepared for slow pyrolysis.

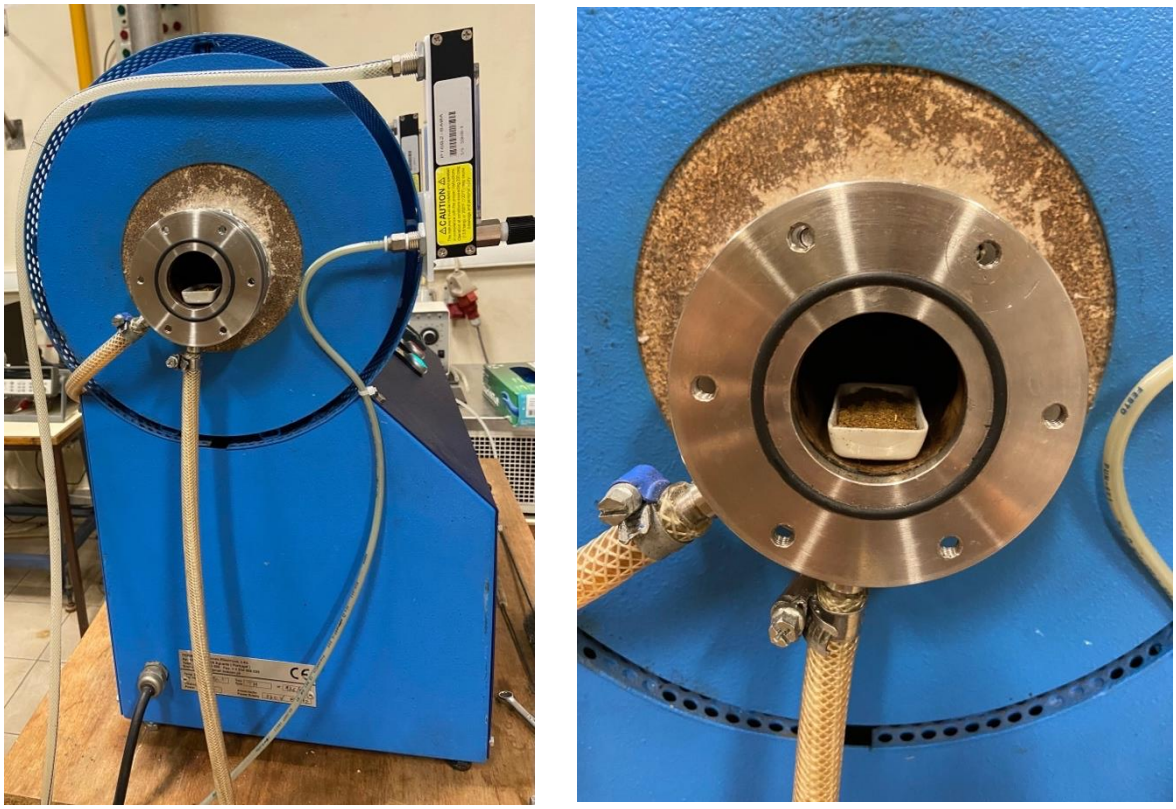

Figure 19. Crucible with sample placed in the horizontal furnace tube (after such placing, the crucible was moved to the center of the HTF).

Then, to make sure that the slow pyrolysis process would be carried out in an inert atmosphere (in the absence of oxygen), the nitrogen flow rate was set to 2 l/min using a manometer (Figure 20) and waited for 5 minutes.

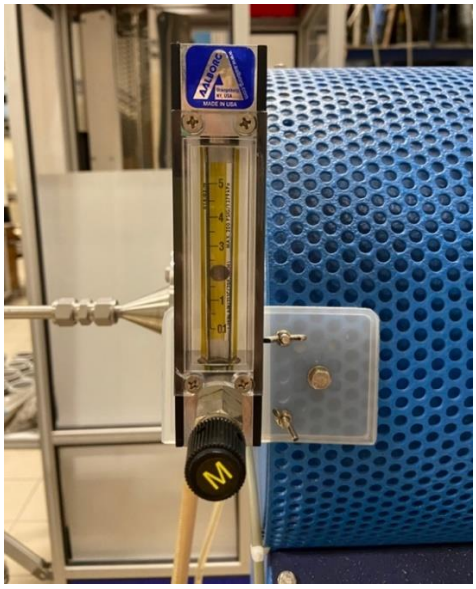

Figure 20. Manometer to control the flow of nitrogen.

After this time, the heating of the horizontal tube furnace was switched on. The heating rate used was 33^{o}C/min. Once the desired temperature was reached, the sample residence time in the furnace was started, which was 1 hour. Throughout the duration of the slow pyrolysis process, the temperature was kept constant by built-in temperature controllers.

After this time, the HTF heating was turned off, the nitrogen flow was reduced to 1l/min and the furnace was allowed to cool naturally to room temperature. The samples were then removed from the HTF (Figure 21), weighed, and placed in sealed transparent containers.

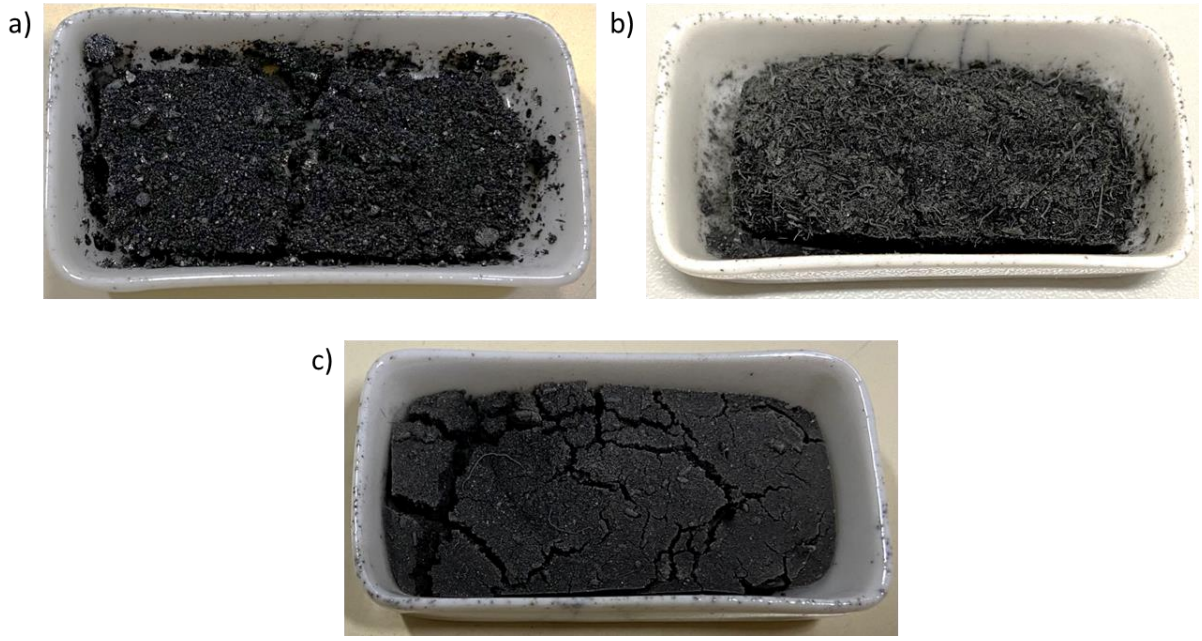

Figure 21. One of two crucibles containing biochar obtained by slow pyrolysis at 600^{o}C from a sample of: a) kitchen biowaste b) spring garden biowaste c) autumn garden biowaste.

Calculation of the results

To calculate the mass yield of biochar (Y_m) in the slow pyrolysis process, the equation was used [82]:

$$Y_m = \frac{m_2}{m_1} \cdot 100\ [\%] \tag{22}$$

where:

$m_1 - \text{mass of the sample before slow pyrolysis, g}$

$m_2 - \text{mass of the sample after slow pyrolysis, g}$

3.4. Characterization of the biochar

To characterize the biochar obtained by slow pyrolysis, proximate analysis, ultimate analysis and determination of higher heating value and lower heating value were performed.

All determinations were made on dry samples. It was assumed that the biochar was completely dried after pyrolysis, so the moisture content was not determined, therefore the results are presented on a dry basis. Each determination was performed in three parallel measurements and the results were presented as an average. If the differences between the determinations were too large, an additional measurement was made.

The proximate analysis includes the determination of the volatile matter, fixed carbon and ash content of the biochar. These determinations were performed according to the procedures described in subchapter 3.2.1 about the determination of the proximate analysis of biowaste.

The ultimate analysis includes the determination of the elemental content of the biochar, that is, carbon, hydrogen, oxygen and nitrogen. These determinations were performed according to the procedures described in subchapter 3.2.2 about the determination of the ultimate analysis of biowaste.

In addition, the higher heating value and the lower heating value were determined. These determinations were made following the procedures described in subchapter 3.2.3.1 about the determination of higher and lower heating values of biowaste.

The surface analysis of the obtained biochar was performed by scanning electron microscopy (SEM), as described in subsection 3.2.4 about the surface analysis of biowaste by scanning electron microscopy (SEM).

4. Results and discussion

4.1. Properties of the biowaste

This chapter presents and discusses the results specifying the properties of the tested biowaste.

4.1.1. Proximate analysis of biowaste

The results of the proximate analysis of the studied biowaste are summarised in Table 2. The results are presented on a dry and wet basis.

Table 2. Proximate analysis of biowaste

biowaste	kitchen	spring garden	autumn garden
proximate analysis (% wt.) (dry basis)			
VM (volatile matter content)	76.55	42.43	43.75
A (ash content)	6.81	17.75	43.83
FC (fixed carbon)*	16.64	39.82	12.43
proximate analysis (% wt.) (wet basis)			
MC (total moisture content)	68.10	81.53	63.51
VM (volatile matter content)	24.42	7.84	15.97
A (ash content)	2.17	3.28	15.99
FC (fixed carbon)*	5.31	7.35	4.53

* by difference

4.1.1.1. Moisture content (MC)

The moisture content of kitchen, spring garden and autumn garden biowaste on a wet basis was 68.10%, 81.53% and 63.51%, respectively. Among the tested biowaste, spring garden biowaste had the highest moisture content and autumn garden biowaste had the lowest.

According to literature data, kitchen biowaste has the highest moisture content. Dubois et al. showed that it can contain up to 80% moisture [32], while Rago et al. showed up to 92.36% [41]. The analysed sample of kitchen biowaste has a lower moisture content (68.10%) compared to the literature data. This difference may be due to the different compositions of the biowaste, e.g. food biowaste that consists of peelings, raw vegetables and fruit will have a higher moisture content than biowaste that consists of partially dried products such as bakery products, eggshells, pasta or rice.

Researchers have shown that garden waste contains 50 - 60% moisture [32], [44], while the organic fraction of municipal solid waste collected in winter contains 42.90% moisture [39].

The moisture content of the analysed sample of spring garden biowaste was as high as 81.53%. This may be because the grass, which is the main component of this biowaste, was mowed after rain and contained more water. Another justification is that this biowaste may include food biowaste with a high moisture content, e.g. vegetable peelings.

The analysed autumn garden biowaste contained 63.51% moisture, which is slightly higher than shown in the literature data. The higher moisture content, as in the case of spring garden biowaste, may be due to the collection of biowaste after rain or the presence of food waste. At the same time, among the analysed samples, autumn garden biowaste has the lowest moisture content. The reason may be that dry leaves and twigs collected in autumn contain less water than mowed grass or fruit and vegetable peelings.

4.1.1.2. Volatile matter content (VM)

The volatile matter content of kitchen, spring garden and autumn garden biowaste on a dry basis was 76.55%, 42.43% and 43.75%, respectively.

According to literature data, garden waste (84.50%) [44], lawn grass (82.60%) [45] and shredded green waste (77.60%) [43] have the highest volatile matter content. Food waste contains about 71.00% [40], [41]. In contrast, mixed biowaste in the form of organic fraction of MSW (51.60%) and yard waste fraction of MSW (52.80%) [40] have the lowest volatile matter content.

Of the samples analysed, kitchen biowaste has the highest volatile matter content (76.55%). This result is slightly higher than the literature data.

The volatile matter content of the analysed spring and autumn garden biowaste is similar (about 43%), while it is almost twice as low as the presented literature values for garden waste (84.50%) [44]. The volatile matter content of spring garden biowaste (which consists mainly of grass) is twice as low as the volatile matter content of lawn grass. The volatile matter content of both studied garden biowaste is more similar to the volatile matter content of the organic fraction of MSW and yard waste. This can be explained by the fact that the tested garden biowaste may be mixed, meaning that it contains kitchen biowaste in addition to garden waste.

Typical biomass materials used for biochar production by pyrolysis, such as wood, almond shells and rice husk, contain 82.00% [18], 79.70% [30] and 67.70% [83] volatile matter, respectively. Of the analysed biowaste, a comparable volatile matter content was obtained for kitchen biowaste, which may suggest that this material is suitable for biochar production.

4.1.1.3. Ash content (A)

The ash content of kitchen, spring garden and autumn garden biowaste on a dry basis was 6.81%, 17.75% and 43.83%, respectively.

According to literature data, the highest ash content is found in the organic fraction of MSW (44.30%) [39] and the yard waste fraction of MSW (39.20%) [40]. Kitchen biowaste contains about 10% ash [40], [41]. In contrast, garden waste has the lowest ash content (1.00%) [43], [44]. Compared to the literature data, the ash content of the analysed kitchen biowaste is lower by 3%. Garden waste, on the other hand, contains significantly more ash than the literature data. Spring garden biowaste contains 17.75% ash while the ash content of lawn grass is 3.85% [45]. The ash content of autumn garden biowaste is as high as 43.83% and is more similar to the ash content of the organic fraction of MSW (44.30%) [39].

Such large differences in the ash content of both garden biowaste samples may indicate its contamination. Garden biowaste is collected from the ground, usually with a rake it is collected in one place and then manually or with a spatula it is put into a container. During the raking of grass or leaves, there is a risk of collecting soil, rocks or other contaminants, which will be the main inorganic component of the raw material [33]. For the garden biowaste analysed, it can be concluded that autumn biowaste was more contaminated than spring biowaste.

Typical biomass materials used for biochar production by pyrolysis, such as wood, almond shells and rice husk, contain 1.00% [18], 2.30% [30] and 16.22% [83] ash content, respectively. Of the analysed biowaste, comparable ash content was obtained for kitchen and spring garden biowaste, which may suggest that these materials are suitable for biochar production.

4.1.1.4. Fixed carbon content (FC)

The fixed carbon content in kitchen, spring garden and autumn garden biowaste on a dry basis was 16.64%, 39.82% and 12.43%, respectively.

According to literature data, the highest fixed carbon content is in food biowaste and reaches 18.50% [40], [41]. Garden biowaste contains about 15.00% fixed carbon [43], [44]. In contrast, the organic fraction of MSW (4.10%) [39] and the yard waste fraction of MSW (8.00%) [40] have the lowest fixed carbon content.

The fixed carbon content in the analysed kitchen biowaste and autumn garden biowaste is similar to literature values. In contrast, the fixed carbon content of spring garden biowaste is twice as high as the fixed carbon content of kitchen biowaste and is significantly higher than the values presented by other researchers.

Typical biomass materials used for biochar production by pyrolysis, such as wood, almond shells and rice husk, contain 17.00% [18], 4.90% [30] and 16.08% [83] fixed carbon, respectively. Of the analysed biowaste, comparable fixed carbon content was obtained for kitchen and autumn garden biowaste, which may suggest that these materials are suitable for biochar production.

4.1.2. Ultimate analysis of biowaste

The results of the ultimate analysis of the studied biowaste are summarised in Table 3. The results are presented on a dry and wet basis.

Table 3. Ultimate analysis of biowaste

biowaste	kitchen	spring garden	autumn garden
ultimate analysis (% wt.) (dry basis)			
C (carbon content)	43.36	31.94	29.99
H (hydrogen content)	7.03	4.53	4.02
N (nitrogen content)	3.12	2.84	1.19
S (sulphur content)	0.10	0.07	0.03
O (oxygen content)*	38.87	42.82	20.92
Cl (chlorine content)	0.71	0.05	0.01
ultimate analysis (% wt.) (wet basis)			
C (carbon content)	13.83	5.90	10.95
H (hydrogen content)	2.24	0.84	1.47
N (nitrogen content)	1.00	0.53	0.44
S (sulphur content)	0.03	0.01	0.01
O (oxygen content)*	12.40	7.91	7.64
Cl (chlorine content)	0.23	0.01	0.00
H/C atomic ratio	1.93	1.69	1.60
O/C atomic ratio	0.67	1.01	0.52

* by difference

4.1.2.1. Carbon content (C)

The carbon content of kitchen biowaste on a dry basis (43.36%) is comparable to literature data according to which this biowaste contains 46.10% [40] or 41.70% [41] carbon.

The carbon content of both spring and autumn garden biowaste tested is similar to each other at 31.94% and 29.99%, respectively, while it is much lower than reported in the literature. The carbon content in garden biowaste can be as high as 50.12% [44], while in grass it ranges from 42.85% [45] to 45.57% [35].

Typical biomass materials used for biochar production by pyrolysis, such as wood, almond shells and rice husk, contain 51.60% [18], 54.70% [30] and 41.78% [83] carbon content, respectively. Of the biowaste analysed, the most similar carbon content was obtained for kitchen biowaste, which may suggest that this material is suitable for biochar production.

4.1.2.2. Hydrogen content (H)

The hydrogen content of kitchen, spring garden and autumn garden biowaste on a dry basis was 7.03%, 4.53% and 4.02%, respectively.

According to literature data, both kitchen and garden biowaste contain between 5.66% and 7.47% hydrogen [40], [41], [43], [45]. In contrast, biowaste fractions of MSW have the lowest hydrogen content, with 3.31% for the yard waste fraction [40] and 4.70% for the organic fraction [39].

The hydrogen content of the tested kitchen biowaste is within the upper range reported by other researchers. In contrast, the hydrogen content of both garden biowaste studied is lower than reported in the literature for garden waste. However, it is comparable to the hydrogen content obtained for the organic fraction of MSW (4.70%) [39].

Typical biomass materials used for biochar production by pyrolysis, such as wood, almond shells and rice husk, contain 6.30% [18], 7.50% [30] and 5.35% [83] hydrogen content, respectively. Of the biowaste analysed, the most similar hydrogen content was obtained for kitchen biowaste, which may suggest that this material is suitable for biochar production.

4.1.2.3. Nitrogen content (N)

The tested kitchen biowaste on a dry basis contained 3.12% nitrogen, which is comparable to the nitrogen content of the canteen food biowaste of 3.49% [41]. In contrast, this is three times higher than the nitrogen content of the MSW food waste fraction, which contains 1.02% nitrogen [40].

The nitrogen content of the dry spring garden and autumn garden biowaste was 2.84% and 1.19%. Both studied garden biowaste contain significantly more nitrogen than garden waste studied by other researchers, which contains between 0.14% [44] and 0.20% [43] of this component. The nitrogen content of the spring garden biowaste studied is 2.84% which is similar to the nitrogen content of lawn grass, equal to 2.68% [45]. At the same time, this value is twice as high as the nitrogen content of grasses, at 1.30% [35]. The nitrogen content of the tested autumn garden biowaste is twice as low as that of the tested spring garden biowaste, at 1.19%. This content is similar to the nitrogen content of the yard waste fraction of MSW, which is 1.15% [40].

Typical biomass materials used for biochar production by pyrolysis, such as wood, almond shells and rice husk, contain 0.00% [18], 0.30% [30] and 0.30% [83] nitrogen content, respectively. Compared to these values, all analysed biowaste had a higher nitrogen content.

4.1.2.4. Oxygen content (O)

The oxygen content of kitchen, spring garden and autumn garden biowaste on a dry basis was 38.87%, 42.82% and 20.92%, respectively.

Comparing the oxygen content of the analysed kitchen biowaste (38.87%) with the oxygen content of the food biowaste studied by Rago et al. (37.09%) [41] and Chhabra et al. (36.55%) [40], it can be concluded that its content is similar.

According to literature data, the oxygen content of garden biowaste ranges from 39.40% [42] to 45.91% [43]. The obtained oxygen content for spring garden biowaste is within the given range. The oxygen content of autumn garden biowaste, on the other hand, is significantly lower than indicated in the literature. It is also lower than the oxygen content of the yard waste fraction of MSW, which is 26.39% [40].

Typical biomass materials used for biochar production by pyrolysis, such as wood, almond shells and rice husk, contain 41.50% [18], 37.40% [30] and 36.31% [83] oxygen content, respectively. Of the analysed biowaste, comparable oxygen content was obtained for kitchen and spring garden biowaste, which may suggest that these materials are suitable for biochar production.

4.1.2.5. Sulphur content (S)

The sulphur content of kitchen, spring garden and autumn garden biowaste on a dry basis was 0.10%, 0.07% and 0.03%, respectively. This is significantly less than the sulphur content of the organic fraction of MSW, which is 0.40% [39]. Furthermore, the sulphur content of the two analysed garden biowastes is similar to the literature values, which for garden biowaste ranges from 0.03% [43] to 0.08% [44].

Typical biomass materials used for biochar production by pyrolysis, such as wood, almond shells and rice husk, contain 0.10% [18], 0.30% [30] and 0.08% [83] sulphur content, respectively. Compared to these values, all analysed biowaste had a similar sulphur content.

4.1.2.6. Chlorine content (Cl)

The chlorine content of kitchen, spring garden and autumn garden biowaste on a dry basis was 0.71%, 0.05% and 0.01%, respectively. From the analysed biowaste, kitchen biowaste has the highest chlorine content. This may be because table salt, namely sodium chloride (NaCl), is added to food, which by weight consists of 60% chloride [84]. Both garden biowaste analysed contain significantly less chlorine than the content shown for grasses, which is 0.74% [35].

4.1.3. Analysis of other properties of biowaste

The results of the other properties of the tested biowaste are summarised in Table 4.

Table 4. Other properties of biowaste

biowaste		kitchen	spring garden	autumn garden
other measurements				
HHV (higher heating value)	MJ/kg (dry basis)	17.24	10.60	11.16
LHV (lower heating value)	MJ/kg (dry basis)	15.69	9.60	10.27
LHV (lower heating value)	MJ/kg (wet basis)	2.28	-1.04	1.63
CC (combustible compounds)	(%wt.) (dry basis)	93.19	82.25	56.17
OS (total organic matter content)	(%wt.) (dry basis)	90.06	81.77	55.32
MS (total mineral substances content)	(%wt.) (dry basis)	9.94	18.23	44.68
C_{org} (total organic carbon content)	(%wt.) (dry basis)	37.47	35.29	23.18
pH	– (wet basis)	5.18	9.20	8.62

4.1.3.1. Higher Heating Value (HHV)

The higher heating value of the analysed kitchen biowaste (on a dry basis) was 17.24 MJ/kg. This is higher than the value of 15.08 MJ/kg obtained for the canteen food waste analysed by Rago et al. [41]. From the analysed biowaste, kitchen biowaste had the highest carbon and hydrogen content. This had a positive effect on the higher heating value, which is the highest for kitchen biowaste. On the other hand, this biowaste contained as much as 38.87% oxygen, which negatively affects the higher heating value.

The higher heating value of the analysed spring and autumn garden biowaste was 10.60 MJ/kg and 11.16 MJ/kg, respectively. These values are significantly lower than the 18.12 MJ/kg obtained for shredded green waste [43]. The higher heating values of the tested garden biowaste are similar to each other because these biowastes had similar carbon and hydrogen contents. However, the oxygen content of the autumn garden biowaste was about half that of the spring biowaste, which influenced the little difference between these values.

The higher heating value of typical biomass materials used to produce biochar by pyrolysis, such as wood and rice husks, is 18.60 MJ/kg [18] and 15.44 MJ/kg [83], respectively. Of the analysed biowaste, kitchen biowaste had a comparable higher heating value.

4.1.3.2. Lower Heating Value (LHV)

The lower heating values of the analysed kitchen, spring garden and autumn garden biowaste on a dry basis were 15.69 MJ/kg, 9.60 MJ/kg and 10.27 MJ/kg, respectively. These values result from the higher heating value but are lower because it does not include the latent heat of water vapour condensation produced during the combustion process [37].

The lower heating values of the analysed kitchen, spring garden and autumn garden biowaste on a wet basis are 2.28 MJ/kg, -1.04 MJ/kg and 1.63 MJ/kg, respectively. These values are so low due to the high moisture content of the tested biowastes. Within the tested biowaste, the spring garden biowaste contained the highest moisture content (81.53 %) which contributed to the negative lower heating value. By comparing the lower heating value on a wet and dry basis for the biowaste tested, it can be seen how important the drying process of biowaste is.

4.1.3.3. Combustible compounds

The combustible compounds content of kitchen, spring garden and autumn garden biowaste on a dry basis was 93.19%, 82.25% and 56.17%, respectively. This means that, compared to the tested biowaste, kitchen biowaste is the easiest to ignite and autumn garden biowaste is the most difficult to ignite.

4.1.3.4. Total organic matter and total organic carbon content

The total organic matter content of kitchen, spring garden and autumn garden biowaste on a dry basis was 90.06%, 81.77% and 55.32%, respectively. This means that kitchen biowaste is the most degradable, while autumn garden biowaste is the least degradable. The total organic matter content of the biowaste will influence how the waste is collected and how it is stored [32]. In addition, the total organic carbon content was determined in the kitchen, spring garden and autumn garden biowaste tested, which was 37.47%, 35.29% and 23.18% on a dry basis, respectively.

4.1.3.5. Total mineral substances content

The total mineral substances content of kitchen, spring garden and autumn garden biowaste on a dry basis was 9.94%, 18.23% and 44.68%, respectively. The spring and autumn garden biowaste has a high content of total mineral substances. Similar to the high ash content of this biowaste, this may indicate contamination of the samples with inorganic materials such as soil or rocks that entered the container during biowaste collection.

4.1.3.6. pH

The pH values of the tested kitchen, spring garden and autumn garden biowaste on a wet basis were 5.18, 9.20 and 8.62, respectively. This means that the kitchen biowaste has an acidic pH, while both garden biowaste has an alkaline pH.

4.1.4. Surface analysis of biowaste by SEM

Figure 22 shows SEM images of the kitchen biowaste studied. The kitchen biowaste is composed of particles with different shapes and sizes which confirms the heterogeneous nature of the biowaste. Some particles have a smooth surface and mark sharp edges while the surface of other particles is rough or irregular and the edges are not marked.

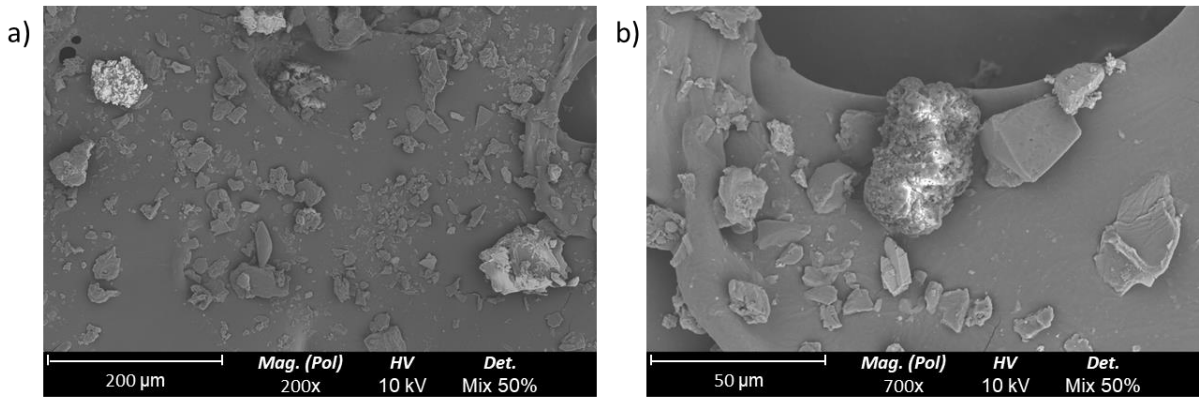

Figure 22. SEM images of the kitchen biowaste, image scale: a) 200 µm, b) 50 µm

SEM images of spring garden biowaste reveal its heterogeneous surface structure. Figure 23 shows particles of different sizes and shapes. There are elongated particles with clearly defined edges, particles with a rough and heterogeneous surface as well as smooth particles with sharp edges. Typical of this biowaste are large, elongated particles that have visible edges which form a porous structure within these particles. This structure is characteristic of plants, including the blade of grass.

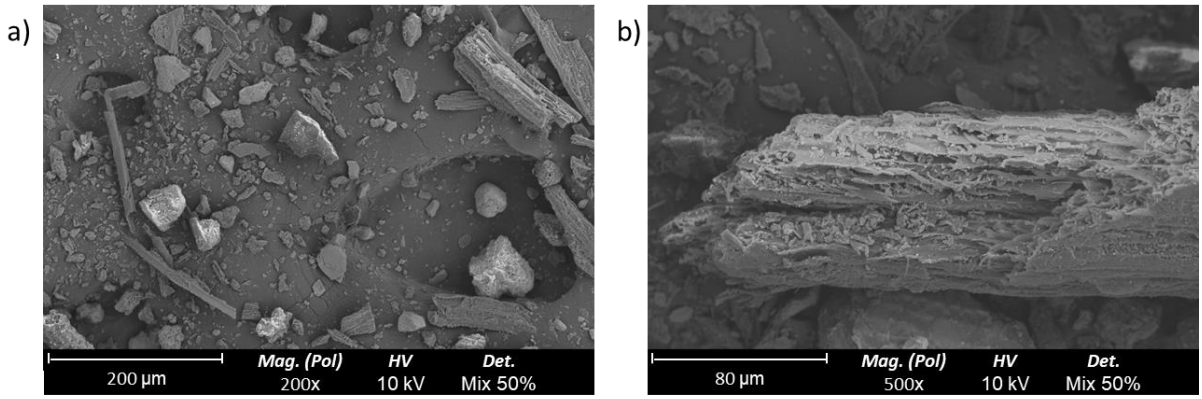

Figure 23. SEM images of the spring garden biowaste, image scale: a) 200 µm, b) 80 µm

Figure 24 shows SEM images of the tested autumn garden biowaste. The biowaste consists of particles of different shapes and sizes, confirming the heterogeneous nature of the biowaste. Characteristic of autumn garden biowaste are relatively small particles with an irregular, rough surface with visible cavities.

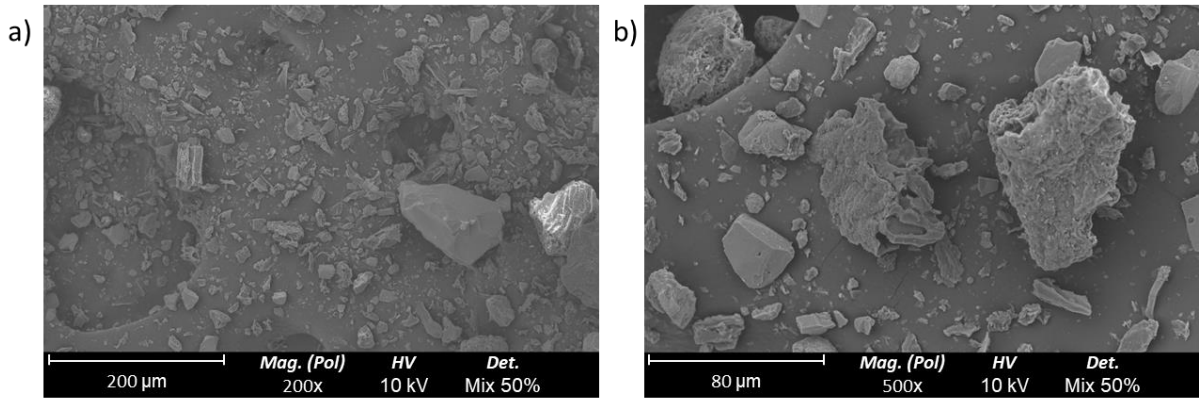

Figure 24. SEM images of the autumn garden biowaste, image scale: a) 200 µm, b) 80 µm

4.1.5. Summary of the properties of biowaste

The high moisture content of the tested biowaste requires pre-drying before slow pyrolysis.

Among the studied biowaste, kitchen biowaste contains the highest volatile matter (76.55%), carbon (43.36%) and hydrogen (7.03%) and the least ash (6.81%), which has a positive impact on biochar production through the slow pyrolysis process. In addition, its HHV value (17.24 MJ/kg) is also the highest. On the other hand, kitchen biowaste, of all tested, contains the highest amount of nitrogen (3.12%), chlorine (0.71%) and sulphur (0.10%) which can negatively affect NO_x, SO_x or HCl emissions. In addition, the chlorine and sulphur content can cause corrosion of the installation.

Summarising the results obtained for kitchen biowaste, it can be concluded that its properties are similar to literature values obtained for food waste. This means that the properties of the analysed kitchen biowaste collected in Poland are similar to those of food biowaste collected from the canteen of the University of Mauritius [41] and to the food waste fraction in MSW studied in the Mumbai Metropolitan Region [40]. The comparable characteristics of food biowaste occurring in the three geographically distant regions support the conclusions reached by Ilakovac et al. [29], who showed that, overall, the composition of food waste generated in households is the same. This means that knowing the amount of household food waste generated, based on the properties of kitchen biowaste, it is possible to estimate its potential and select an appropriate treatment technology.

In addition, it was shown that the proximate analysis, ultimate analysis and HHV results obtained for kitchen biowaste are similar to the results for typical biomasses (wood, almond shells and rice husks) used for biochar production. On this basis, it can be concluded that of the biowaste analysed, kitchen biowaste shows the greatest potential for use as a feedstock for biochar production by slow pyrolysis.

The properties of both spring and autumn garden biowaste differ significantly from the garden waste data of other researchers. Compared to the literature data of other garden wastes, the studied spring garden biowaste is characterised by higher contents of moisture (81.53%), ash (17.75%) and fixed carbon (39.82%) and lower contents of volatile matter (42.43%), carbon (31.94%), hydrogen (4.53%) and chlorine (0.05%). In contrast, the content of oxygen (42.82%), nitrogen (2.84%) and sulphur (0.07%) in spring garden biowaste is similar to literature data for garden waste. In addition, compared to the literature data, the spring garden biowaste has a lower higher heating value (10.60 MJ/kg).

In contrast, autumn garden biowaste has a higher moisture content (63.51%), nitrogen content (1.19%) and a much higher ash content (43.83%) compared to literature data. On the other hand, it has lower volatile matter (43.75%), carbon (29.99%), hydrogen (4.02%), oxygen (20.92%), chlorine (0.01%) and a lower HHV (11.16 MJ/kg). In addition, the fixed carbon (12.43%) and sulphur (0.03%) content is similar to literature data for garden waste.

Compared to the properties of typical biomasses used for biochar production, e.g. wood, almond shells and rice husks, the properties of spring and autumn garden biowaste differ significantly. Because of this, it is not possible to accurately predict their behaviour during the pyrolysis process. In addition, these biowaste have lower contents of key elements for pyrolysis compared to kitchen biowaste, therefore it can be concluded that these biowaste will show less potential as feedstock for slow pyrolysis.

Analysis of the images by scanning electron microscope (SEM) showed that all the biowaste studied was heterogeneous and consisted of particles of different shapes and sizes. At the same time, it is worth noting that kitchen, spring garden and autumn garden biowaste are different from each other and consist of different types of particles.

4.2. Biochar yield from slow pyrolysis process

The mass yield of biochar (Y_m) from the slow pyrolysis of the analysed biowaste is shown in Table 5.

Pyrolysis of kitchen biowaste at 400ºC, 500ºC and 600ºC resulted in yields of biochar by weight on a dry basis of 36.64%, 32.02% and 28.71%, respectively. By analysing these results, it can be concluded that as the pyrolysis temperature increases, the yield of kitchen biochar decreases. This is in accordance with theoretical knowledge, because at low temperatures carbonisation reactions take place, while at higher temperatures devolatilisation reactions take place releasing more volatiles, leading to an increase in bio-oil and gas yields, which were not investigated in this work [33].

Pyrolysis of spring garden biowaste at 400ºC, 500ºC and 600ºC resulted in biochar yields of 66.53%, 58.13% and 60.07% by weight on a dry basis, respectively. From the presented results, it can be concluded that the biochar yield decreases with increasing temperature. However, at 600ºC, the biochar yield is higher than at 500ºC, which is inconsistent with the theoretical information. This difference is about 2% and can be explained by the heterogeneous nature of the biowaste tested.

Pyrolysis of autumn garden biochar at 400ºC, 500ºC and 600ºC resulted in biochar by weight on a dry basis of 66.99%, 63.15% and 60.68%, respectively. The results indicate that as the pyrolysis temperature increases, the yield of autumn garden biochar decreases, which is consistent with theory [33].

Ronsse et al. [67] studied the effect of temperature on the biochar yield during pyrolysis of green waste. The slow pyrolysis process was carried out in an electrically heated vertical reactor and the green waste placed in this reactor was in pellet form. The residence time was 60 minutes and pyrolysis was carried out at temperatures of 300ºC, 450ºC, 600ºC and 750ºC. The biochar yield on a dry basis for these temperatures was 45.30%, 24.46%, 21.13% and 20.52%, respectively [67]. The biochar yield obtained by Ronsse et al. [67] is lower than the biochar yield obtained for both garden biowaste analysed. These differences may be due to differences in the properties of the biowaste and differences in the conduct of the pyrolysis process.

Comparing all the biowaste analysed, the highest biochar yields at each pyrolysis temperature were obtained for autumn garden biowaste, while the lowest biochar yields were obtained for kitchen biowaste. However, it should be noted that the analysed autumn garden biowaste contained as much as 43.85% ash, the spring garden biowaste 17.75% and the kitchen biowaste 6.81%, which also affects the biochar yield on a dry basis, because the ash contained in the biowaste will also be present in the obtained biochar. The biochar yield makes it possible to assess how much of the biowaste will be converted into biochar. However, in addition to yield analysis, the properties of the biochar need to be analysed for a complete evaluation of the obtained biochar.

Table 5. Yield and properties of biochar obtained from slow pyrolysis of biowaste.

biochar	kitchen			spring garden			autumn garden		
	400°C	500°C	600°C	400°C	500°C	600°C	400°C	500°C	600°C
Y_m (mass yield of biochar), % wt. (dry basis)	36.64	32.02	28.71	66.53	58.13	60.07	66.99	63.15	60.68
proximate analysis (% wt.) (dry basis)									
VM (volatile matter content)	20.49	14.88	11.14	12.59	11.65	5.89	15.42	12.10	5.76
A (ash content)	18.57	21.81	21.09	64.69	65.38	72.57	61.71	64.38	71.32
FC (fixed carbon) *	60.94	63.31	67.77	22.73	22.96	21.54	22.87	23.52	22.93
ultimate analysis (% wt.) (dry basis)									
C (carbon content)	58.02	54.81	55.55	25.34	26.60	21.00	27.84	27.45	25.62
H (hydrogen content)	4.00	3.02	2.67	2.41	1.71	1.41	2.80	2.54	1.47
N (nitrogen content)	3.64	3.46	3.01	1.44	1.52	1.05	1.15	1.00	1.02
O (oxygen content) **	15.77	16.90	17.68	6.12	4.79	3.97	6.50	4.63	0.57
H/C atomic ratio	0.82	0.66	0.57	1.13	0.76	0.80	1.20	1.10	0.68
O/C atomic ratio	0.20	0.23	0.24	0.18	0.14	0.14	0.18	0.13	0.02
other measurements (dry basis)									
HHV (higher heating value), MJ/kg	22.68	20.84	21.90	9.04	8.95	7.51	9.96	9.02	8.40
LHV (lower heating value), MJ/kg	21.80	20.17	21.31	8.51	8.58	7.20	9.35	8.46	8.07
CC (combustible compounds), (% wt.)	81.43	78.19	78.91	35.31	34.62	27.43	38.29	35.62	28.68

* by difference

** by difference (without considering the sulphur and chlorine content)

4.3. Properties of the biochar

This chapter presents and discusses results determining the properties of biochar obtained by pyrolysis of biowaste at 400°C, 500°C and 600°C.

4.3.1. Proximate analysis of biochar

The results of the proximate analysis of the obtained biochar are summarised in Table 5. The results are presented on a dry basis.

4.3.1.1. Volatile matter content (VM)

Analysing the data in Table 5, as the pyrolysis temperature increases, the volatile matter content of all biochar decreases. This correlation is consistent with theory because volatile matter is released during the pyrolysis process, and as the pyrolysis temperature increases, this process is more intense [33].

Kitchen biochar obtained at a pyrolysis temperature of 400°C exhibited the highest volatile matter content (20.49%). On the other hand, the spring garden and autumn garden biochar obtained at a pyrolysis temperature of 600°C exhibited the lowest volatile matter content (less than 6%). This value is lower than the 7.62% volatile matter content obtained by Ronsse et al. for biochar which is the product of pyrolysis of green waste at 600°C [67].

Comparing the content of volatile matter in biochar with its content in biowaste before pyrolysis, it can be concluded that there was a significant decomposition of these substances during pyrolysis. The content of volatile matter in kitchen biowaste was 76.55%, while the content of volatile matter in kitchen biochar was 20.49%, 14.88% and 11.14% for temperatures of 400°C, 500°C and 600°C, respectively. The volatile matter content in spring garden biowaste was 42.43%, while in spring garden biochar it was 12.59%, 11.65 and 5.89% for temperatures of 400°C, 500°C and 600°C, respectively. The volatile matter content of the autumn garden biowaste was 43.75%, while the volatile matter content of the biochar obtained from this biowaste was 15.42%, 12.10 and 5.76% for temperatures of 400°C, 500°C and 600°C, respectively.

4.3.1.2. Ash content (A)

Analysing the data in Table 5, as the pyrolysis temperature increases, the ash content of all biochar increases. This relationship is consistent with theory because organic matter is thermally decomposed, leading to ash remaining in the biochar [33]. Therefore, the ash content of the resulting biochar was higher than the ash content of kitchen biowaste (6.81%), spring garden biowaste (17.75%) and autumn garden biowaste (43.83%) before pyrolysis.

The ash content of kitchen biochar obtained at 400°C, 500°C and 600°C was 18.57%, 21.81% and 21.09%, respectively. The ash content of garden spring biochar was 64.69%, 65.38 and 72.57% for pyrolysis temperatures of 400°C, 500°C and 600°C. The ash content of autumn garden biochar with increasing pyrolysis temperature was 61.71%, 64.38% and 71.32%. From the analysed biochar, kitchen biochar obtained at a pyrolysis temperature of 400°C had the lowest ash content (18.57%). In contrast, spring garden biochar obtained at a pyrolysis temperature of 600°C had the highest ash content (72.57%).

Overall, all biochar obtained from pyrolysis of garden biowaste had a high ash content, ranging from 61.71% to 72.57%. These values are significantly higher than those shown by Ronsse et al. In their work, the ash content of the biochar also increased with pyrolysis temperature, while the highest ash content (13.40%) was of biochar from green waste obtained at 600°C [67].

4.3.1.3. Fixed carbon content (FC)

The fixed carbon content was highest in kitchen biochar and increased with the temperature at which pyrolysis is carried out. Kitchen biochar obtained at 400°C, 500°C and 600°C contained 60.94%, 63.31% and 67.77% fixed carbon, respectively. These values are significantly higher than the fixed carbon content of kitchen biowaste before pyrolysis, which was 16.64%. This relationship is in line with theoretical knowledge according to which the pyrolysis process removes volatile matter and the remaining material is richer in fixed carbon [33].

For both biochar obtained from garden biowaste when pyrolysis is carried out at the same temperature, the fixed carbon content is similar. For the spring garden biochar, the highest fixed carbon content is contained in the one obtained at 500°C (22.96%), followed by 400°C (22.73%) and the lowest content was obtained at 600°C (21.54%). For autumn biochar, the highest fixed carbon content was obtained for a pyrolysis temperature of 500°C (23.52%), followed by 600°C (22.93%) and the lowest for 400°C (22.87%). When comparing the fixed carbon content of garden biowaste before pyrolysis to that of biochar, the fixed carbon content increased for autumn garden biowaste, while it decreased for spring garden biowaste.

4.3.2. Ultimate analysis of biochar

The results of the ultimate analysis of the obtained biochar are summarised in Table 5. The results are presented on a dry basis.

4.3.2.1. Carbon content (C)

Of the analysed biochar, the carbon content was highest in kitchen biochar, reaching 58.02%, 54.81% and 55.55% for pyrolysis temperatures of 400°C, 500°C and 600°C, respectively. This is significantly higher than the carbon content of kitchen biowaste before pyrolysis, which was 43.36%. This relationship is consistent with the theory according to which slow pyrolysis results in a carbon-rich material (biochar) [33].

In the case of spring garden biochar, the carbon content was 25.34%, 26.60% and 21.00% for pyrolysis temperatures of 400°C, 500°C and 600°C, respectively. In contrast, for autumn garden biochar, the contents were 27.84%, 27.45% and 25.62%. All these values are significantly lower than the 78.98% carbon content of green waste biochar obtained at a pyrolysis temperature of 600°C by Ronsse et al. [67]. In all garden biochar analysed, the carbon content was lower than it was in the biowaste before pyrolysis (for spring garden biowaste it was 31.94% and for autumn garden biowaste 29.99%).

4.3.2.2. Hydrogen content (H)

Analysing the data in Table 5, as the pyrolysis temperature increases, the hydrogen content of all biochar decreases. For pyrolysis temperatures of 400°C, 500°C and 600°C, kitchen biochar contained 4.00%, 3.02% and 2.67% hydrogen, spring garden biochar 2.41%, 1.71% and 1.41%, while autumn garden biochar contained 2.80%, 2.54% and 1.47%, respectively. These relationships are consistent with theory, as during pyrolysis part of the hydrogen is released as volatiles [35]. On the other hand, as the temperature increases, the pyrolysis process is more intense and therefore a greater proportion of hydrogen can be released. This also explains why all these values are lower than the hydrogen content of kitchen (7.03%), spring garden (4.53%) and autumn garden (4.02%) biowaste before the pyrolysis process.

4.3.2.3. Nitrogen content (N)

Of the analysed biochar, the kitchen biochar had the highest nitrogen content and was 3.64%, 3.46% and 3.01% for pyrolysis temperatures of 400°C, 500°C and 600°C, respectively. The initial nitrogen content of the kitchen biowaste was 3.12%. This means that the content increased at pyrolysis temperatures of 400°C and 500°C and decreased at 600°C.

For the same pyrolysis temperatures, the nitrogen content of the spring garden biochar was 1.44%, 1.52% and 1.05% and for the autumn garden biochar 1.15%, 1.00% and 1.02%, respectively. The initial values of the nitrogen content of the spring garden biowaste (2.84%) and autumn garden biowaste (1.19%) were higher than the nitrogen content of the biochar obtained from these biowastes.

4.3.2.4. Oxygen content (O)

The oxygen content of kitchen biochar increased with pyrolysis temperature and was 15.77%, 16.90% and 17.68%, respectively. In contrast, the oxygen content of both types of garden biochar decreased with increasing pyrolysis temperature. For pyrolysis temperatures of 400°C, 500°C and 600°C, the oxygen content of spring garden biochar was 6.12%, 4.79% and 3.97%, respectively, while for autumn garden biochar it was 6.50%, 4.63% and 0.57%.

Before the slow pyrolysis process, the oxygen content of the kitchen biowaste (38.87%), spring garden biowaste (42.82%) and autumn garden biowaste (20.92%) were significantly higher than the oxygen content of the biochar obtained from these biowastes. According to theory, this should be the case because oxygen-containing volatile compounds, e.g. water or carbon dioxide, are released during the pyrolysis process [33].

4.3.3. Analysis of other properties of biochar

4.3.3.1. Higher heating value (HHV)

The higher heating values for kitchen biochar obtained at 400°C, 500°C and 600°C were 22.68 MJ/kg, 20.84 MJ/kg and 21.90 MJ/kg, respectively. These values are higher than the higher heating value of kitchen biowaste, which was 17.24 MJ/kg. This is because the biochar obtained contains a significantly higher carbon content and lower oxygen content than kitchen biowaste, which has a positive effect on the HHV of biochar [35].

In the case of garden biochar, the higher heating values decreases with increasing pyrolysis temperature. The higher heating value of spring garden biochar obtained at 400°C, 500°C and 600°C were 9.04 MJ/kg, 8.95 MJ/kg and 7.20 MJ/kg, respectively, while for autumn garden biochar were 9.96 MJ/kg, 9.02 MJ/kg and 8.40 MJ/kg. The higher heating values of garden biochar were lower than those of spring garden biowaste (10.60 MJ/kg) and autumn garden biowaste (11.16 MJ/kg) from which it was produced. The reason for this may be the lower carbon content of biochar compared to biowaste.

4.3.3.2. Lower heating value (LHV)

The lower heating values for kitchen biochar obtained at 400°C, 500°C and 600°C were 21.80 MJ/kg, 20.17 MJ/kg and 21.31 MJ/kg, respectively. These values are higher than the lower heating value of kitchen biochar, which was 15.69 MJ/kg.

The lower heating values of spring garden biochar obtained at 400°C, 500°C and 600°C were 8.51 MJ/kg, 8.58 MJ/kg and 7.20 MJ/kg, respectively, while the values for autumn garden biochar were 9.35 MJ/kg, 8.46 MJ/kg and 8.07 MJ/kg. The lower heating values of garden biochar are lower than the spring garden biowaste (9.60 MJ/kg) and autumn garden biowaste (10.27 MJ/kg) from which it was produced.

4.3.3.3. Combustible compounds

Kitchen biochar has the highest combustible compound content. For pyrolysis temperatures of 400°C, 500°C and 600°C, it was 81.43%, 78.19% and 78.91%, respectively. For both types of garden biochar, the content of combustible compounds decreases with increasing pyrolysis temperature. Spring garden biochar contained 35.31%, 34.62% and 27.43% combustible compounds for pyrolysis temperatures of 400°C, 500°C and 600°C, respectively. Whereas, for the same temperatures, the autumn garden biochar contained 38.29%, 35.62% and 28.68% combustible compounds. All of the biochar analysed contains a lower content of combustible compounds than the biowaste from which the biochar was generated. Kitchen biowaste contained 93.19% combustible compounds, spring garden biowaste 82.25% and autumn garden biowaste 56.17%.

4.3.4. Surface analysis of biochar by SEM

Figure 25 shows SEM images of kitchen biochar obtained by slow pyrolysis at 400°C, 500°C and 600°C. It is noticeable, that as the pyrolysis temperature increases, the pores of the biochar gradually enlarge by merging the particles into larger and larger agglomerates. Compared to the SEM image of kitchen biowaste (Figure 22), during pyrolysis, the particles joined together to form aggregates of larger biochar particles.

The biochar obtained at 400°C was characterised by large particles with clearly visible pores. The surface of this biochar is rough with well-defined edges of the pore cavities. In addition, at a higher approximation it was observed, that small rough structures were present in the large pore cavities of the biochar, which also had tiny pores. At 500°C, the biochar was also characterised by large particles with clearly defined pores. In contrast, interesting structures with an elongated form resembling needle-shaped protrusions were observed on the surface of this biochar.

By analysing the image of the biochar obtained at 600°C, it can be concluded that the elongated structures produced on the surface of the biochar obtained at 500°C were intended to facilitate the assembly of biochar particles into larger aggregates. In addition, both large and numerous small pores were observed on the surface of this biochar.

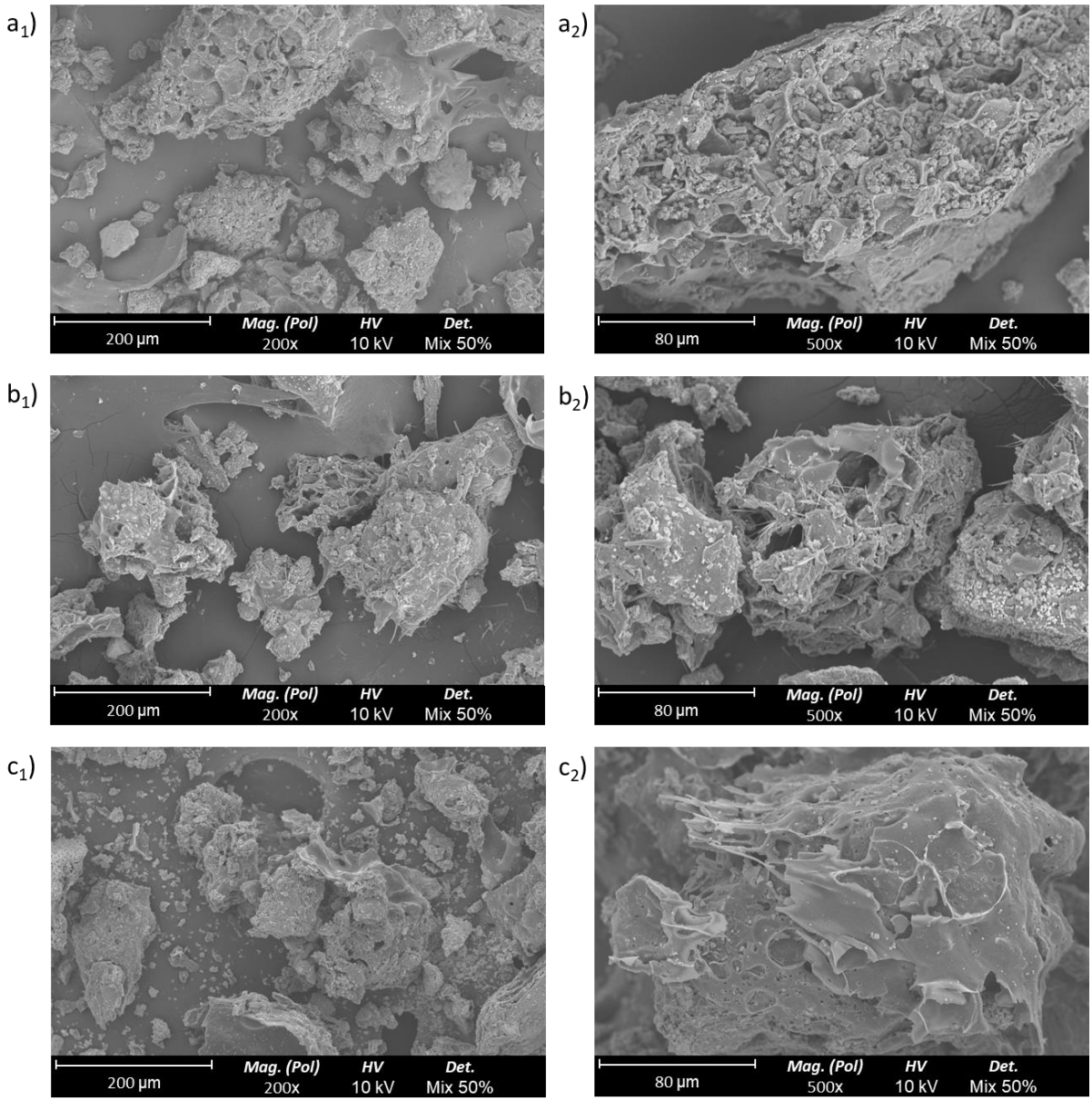

Figure 25. SEM images of the kitchen biochar obtained at pyrolysis temperature: a) 400°C, b) 500°C, c) 600°C. Indexes 1 and 2 indicate that the image scale is 200 µm and 80 µm, respectively.

Figure 26 shows SEM images of spring garden biochar obtained by slow pyrolysis at 400°C, 500°C and 600°C. By analysing these images, the porous particles present in the biochar are similar to the elongated particles originally found in garden spring biowaste (Figure 23).

At 400°C, the spring garden biochar consisted of many small particles. Some of them are elongated with visible grooves, and some of the irregular particles show small pores. Larger particles with a smooth surface and clear edges were also present in the biochar.

The biochar obtained at 500°C consisted of large, elongated particles that had longitudinal grooves and a porous structure within these particles. In addition, smaller rough particles can be observed on the surface of these particles, which probably merged during the slow pyrolysis process. Other, smaller particles also have even smaller particles on their surface, making their surface rough, pores and nonuniform edges visible. In the biochar obtained at 600°C, two types of particles of similar size can be distinguished. One type is particles with a smooth surface with clear, sharp edges and the other type is particles with a rough, nonuniform surface with longitudinal grooves.

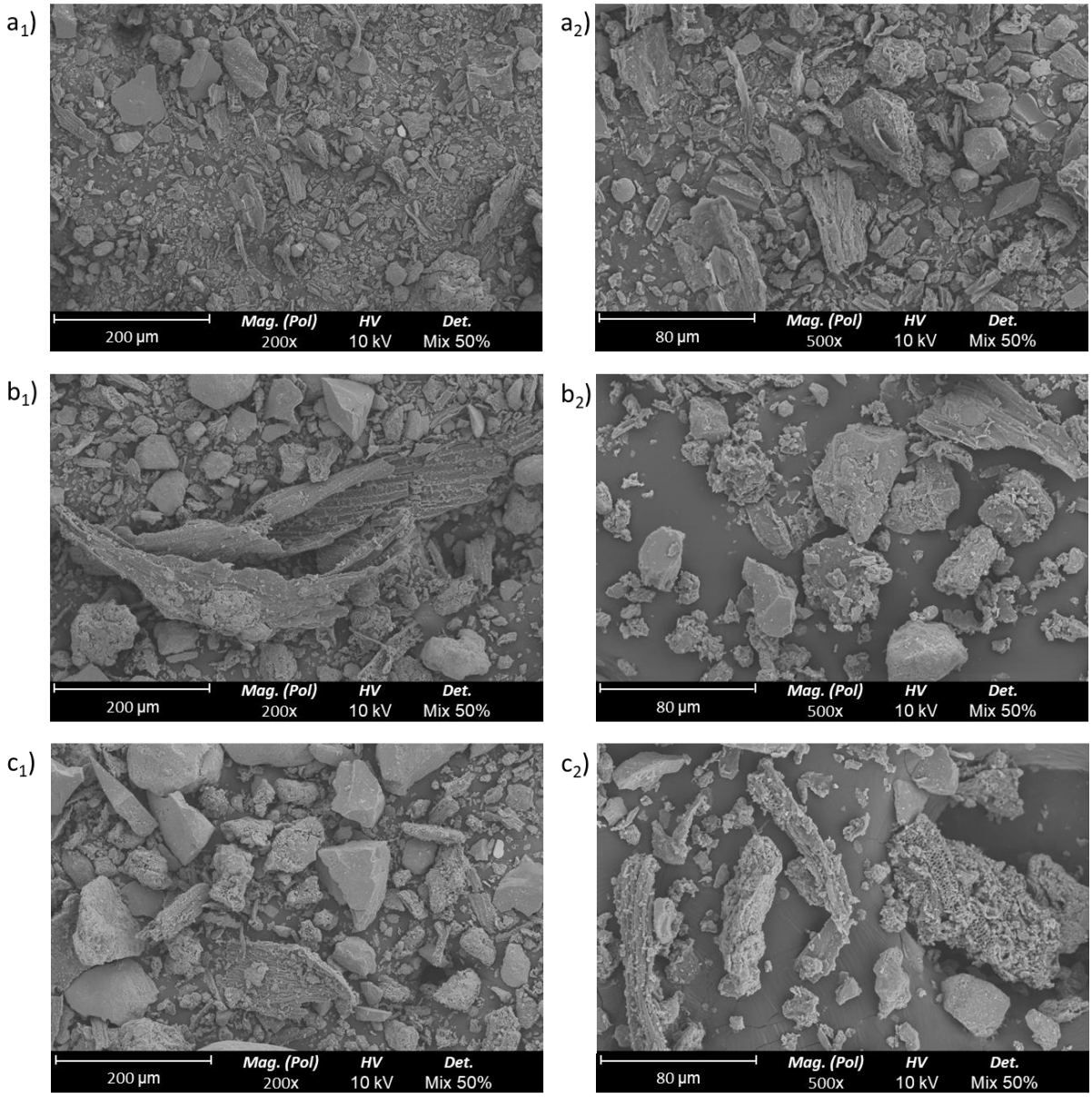

Figure 26. SEM images of the spring garden biochar obtained at pyrolysis temperature: a) 400°C, b) 500°C, c) 600°C. Indexes 1 and 2 indicate that the image scale is 200 µm and 80 µm, respectively.

Figure 27 shows SEM images of autumn garden biochars obtained by slow pyrolysis at 400°C, 500°C and 600°C. By analysing these images, it can be seen that as the pyrolysis temperature increases, the number of porous particles present in the biochar increases.

Compared to the SEM image of the autumn garden biowaste (Figure 24), it can be concluded that the biochar particles are more porous.

The biochar obtained at 400°C consists of single long and thin structures with visible longitudinal grooves, many particles in different sizes with a porous surface structure and particles with a smooth surface with visible sharp edges. Compared to the biochar obtained at 400°C, the biochar obtained at 500°C had larger porous particles, which were probably formed by agglomeration of smaller particles during slow pyrolysis. In addition, large particles with a smooth structure and sharp edges are also present in this biochar. The biochar obtained at 600°C shows many particles with smooth surfaces and sharp edges. However, this biochar also contains structures with longitudinal edges similar to those contained in the spring biochar obtained at 500°C (Figure 26), except that in this case each longitudinal groove is punctuated by dense horizontal edges creating a more porous structure.

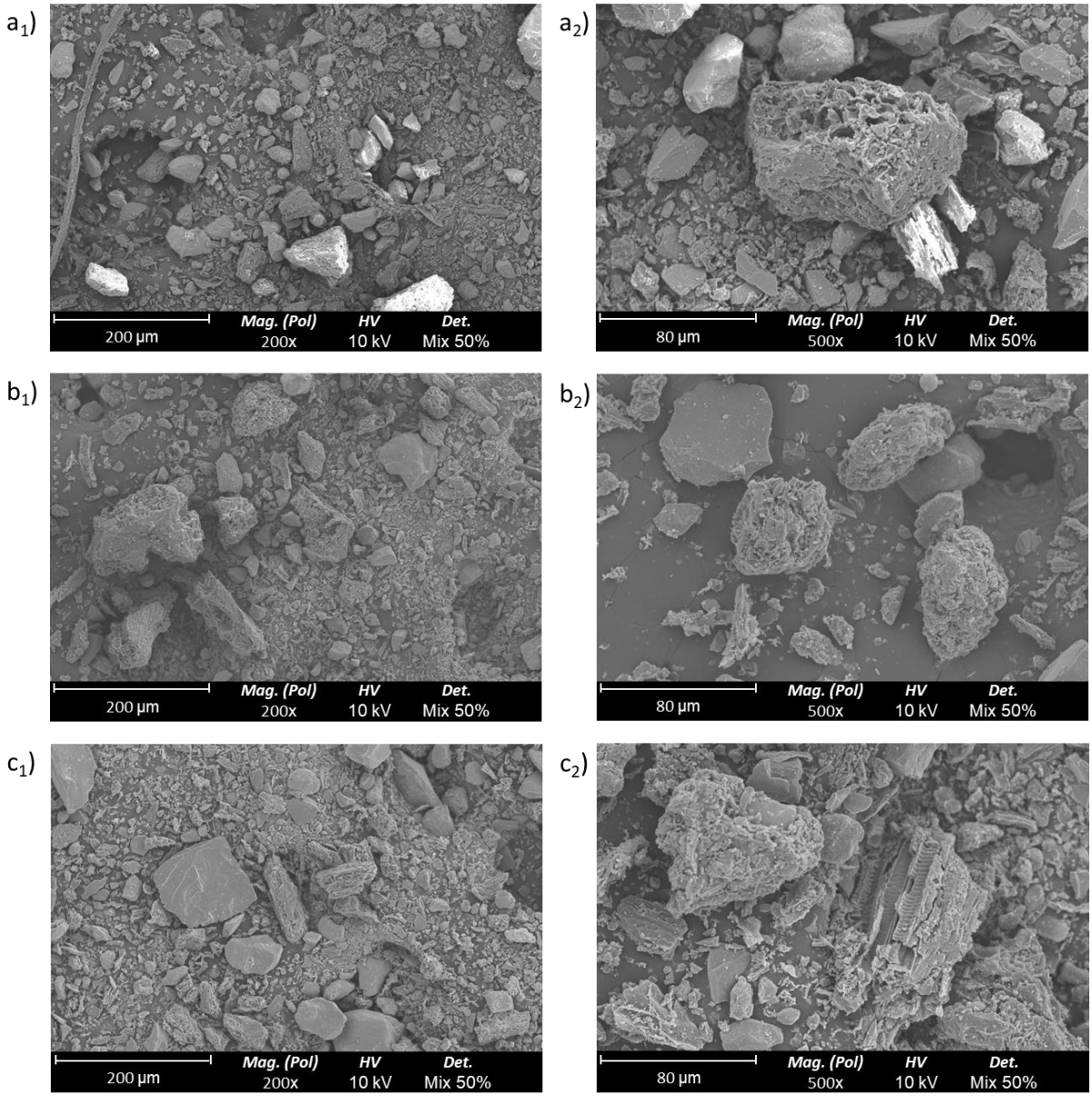

Figure 27. SEM images of the autumn garden biochar obtained at pyrolysis temperature: a) 400°C, b) 500°C, c) 600°C. Indexes 1 and 2 indicate that the image scale is 200 µm and 80 µm, respectively.

4.3.5. Summary of the properties of biochar

Of all the biochar analysed, kitchen biochar obtained at a pyrolysis temperature of 400°C showed the highest content of volatile matter (20.49%), carbon (58.02%), hydrogen (4.00%) and the highest HHV (22.68 MJ/kg). Furthermore, this biochar showed the lowest ash content (18.57%). These properties indicate that this biochar can be used as a fuel. On the other hand, the high nitrogen content (3.64%), which may cause increased NO_x emissions, may have a negative impact. In addition, the high content of combustible compounds (81.43%) may have a negative impact on the storage of such biochar, as there will be a risk of uncontrolled ignition. The yield of this biochar was 36.64% and was the highest obtained for a kitchen biochar. Furthermore, this yield was higher than the typical yield of biochar from a slow pyrolysis process, which according to the literature is 35% [30]. Biochar with such properties could be used as carbon sequestration or soil improvement through enhanced water and nutrient retention.

Compared to kitchen biowaste before pyrolysis, kitchen biochar obtained at any pyrolysis temperature has a higher carbon content, fixed carbon and a higher HHV, which means that kitchen biowaste is a suitable feedstock to produce biochar by slow pyrolysis.

The properties of the obtained spring garden and autumn garden biochar were similar for the respective pyrolysis temperatures, whereas significantly different from those of the kitchen biochar.

The yield of both garden biochar, like that of kitchen biochar, decreased with increasing pyrolysis temperature, while it was almost twice as high as that of kitchen biochar. In addition, the garden biochar contained more than three times as much ash as the kitchen biochar. This high ash content resulted in a lower volatile matter, carbon and hydrogen content than in the kitchen biochar. This also had an impact on HHV, which was at least twice as low compared to kitchen biochar. Furthermore, the biochar contained less carbon and had a lower HHV compared to the spring and autumn garden biowaste before pyrolysis. As biochar should be carbon-rich and have a calorific value in the range of 20-36 MJ/kg [47], this means that the studied garden biowaste is not a suitable feedstock for biochar production by slow pyrolysis. On the other hand, knowing the composition of the ash contained in this biochar, it is possible to use it as a soil amendment to improve soil fertility. In contrast, it is possible that the studied garden biowaste was contaminated (with soil, rocks, etc.) during collection and this could have a negative impact on the properties of the obtained biochar. On the other hand, it is not known whether such contamination can be completely avoided as the garden biowaste is raked and collected directly from the ground.

Image analysis by scanning electron microscope (SEM) showed that all the tested biochars, as well as the biowaste from which it was formed, was heterogeneous and composed of particles of different shapes and sizes. As the pyrolysis temperature increases, the particles of the kitchen biochar become larger and more porous. Irrespective of the pyrolysis temperature, the particles of spring garden biochar were similar to each other and to the elongated porous structures present in the biowaste before pyrolysis. As the pyrolysis temperature increased, the particles of the autumn garden biochar were increasingly porous. At the same time, it is worth noting that the porous structure of both garden biochar was similar while it differed from the porous structure of kitchen biochar.

5. Conclusions

The constant increase in the amount of waste generated by society is creating an urgent need to develop new and better methods for its treatment. The focus of this study was on household biowaste, which is currently considered one of the key waste streams according to the European waste policy. Furthermore, the treatment method considered for biowaste was slow pyrolysis, which leads to the production of biochar.

The study investigated the properties of three types of biowaste collected in Poland, being kitchen biowaste collected in summer in apartment blocks, spring garden biowaste collected from single-family houses in spring and autumn garden biowaste collected from single-family houses in autumn. According to the guidelines for separate collection of biowaste in Poland, in single-family houses kitchen and garden biowaste are collected in one container.

Analysis of the SEM images confirmed the heterogeneous nature of all the biowaste studied. In addition, the kitchen, spring garden and autumn garden biowaste differ from each other and consist of different types of particles with different shapes and sizes.

The analysis of proximate, ultimate and HHV showed that the properties of the tested kitchen biowaste are comparable to those of food waste tested by other researchers in different regions of the world. This means that although kitchen biowaste is a heterogeneous raw material and shows differences in composition, its properties are similar. This is an important observation based on which it can be concluded that the choice of a particular method for treating kitchen biowaste can be effectively applied worldwide. Furthermore, the study shows that the properties of kitchen biowaste are similar to those of typical biomasses (i.e. wood, almond shells and rice husks) used to produce biochar by slow pyrolysis. This means that kitchen biowaste shows potential for use as feedstock for this process.

Analysis of the properties of both spring garden biowaste and autumn garden biowaste showed significant differences from both literature data of other garden wastes and from the properties of typical biomass feedstocks (i.e. wood, almond shells and rice husks) used to produce biochar in the slow pyrolysis process. In addition, it was shown that garden biowaste may have been contaminated (soil, rocks) during collection, which affected the high ash content of spring (17.75%) and autumn (43.83%) biowaste. This in turn affected all the properties of the biowaste.

All the biowaste tested had a high moisture content (between 63.51% and 81.53%), which means that the biowaste needs to be dried before the slow pyrolysis process.

The next stage of the work was to determine the potential for biochar production from the studied biowaste using slow pyrolysis technology. This process was carried out in an electrically heated Horizontal Tube Furnace (HTF) in a nitrogen atmosphere at temperatures of 400^{o}C, 500^{o}C and 600^{o}C. The maximum mass yield of biochar for kitchen, spring garden and autumn garden biowaste was 36.64%, 66.53% and 66.99%, respectively. For all the biowaste tested, it was shown that the biochar yield decreased with increasing pyrolysis temperature.

For a complete assessment of the feasibility of using biowaste to produce biochar by slow pyrolysis, this study also investigated the properties of the obtained biochar.

Kitchen biochar compared to kitchen biowaste before pyrolysis had a higher carbon content, fixed carbon and higher HHV. This means that kitchen biowaste is a suitable feedstock for biochar production by slow pyrolysis. In addition, SEM image analysis showed that with increasing temperature, the particles of kitchen biochar become larger and more porous. Biochar with such properties could be used for carbon sequestration or soil improvement through enhanced water and nutrient retention.

In contrast, both types of garden biochar contained less carbon and had lower HHV than the garden biowaste from which they were produced. This means that, despite the high biochar yield from the spring and autumn garden biowaste, the biochar showed poorer properties than the biowaste before pyrolysis. In addition, garden biochar contained more than three times as much ash as kitchen biochar. On the other hand, this biochar could be used as a soil amendment to improve soil fertility due to its high ash content, but this would require an analysis of the composition of this ash.

Analysis of the SEM images of the spring garden biochar showed that regardless of the pyrolysis temperature, the biochar particles are similar to each other, and the porous structures present in the biochar are similar to the longitudinal porous structures present in the biowaste before pyrolysis. However, in the case of the autumn garden biochar, higher particle porosity was observed with increasing pyrolysis temperature. Meanwhile, compared to kitchen biochar, these particles were smaller.

To summarise, thermochemical methods for treating biowaste are still not very well studied, so there is a lot of potential for future research. The present study shows that kitchen and garden biowaste, have different properties and should therefore be collected separately.

Of the biowaste studied, kitchen biowaste was shown to have the highest potential for biochar production through the slow pyrolysis process. Further research on the slow pyrolysis of kitchen biowaste should focus on the optimisation of the process to obtain a better biochar yield. In addition, due to the laboratory scale of the experiment carried out, it would be appropriate to carry out the same experiment on a pilot or semi-industrial scale. Furthermore, an economic analysis of the slow pyrolysis process of kitchen biowaste would be needed, as despite the promising technological results, it may not be economically feasible to carry out this project, e.g. due to the need to use drying of the biowaste before pyrolysis. In addition, the specific application possibilities of biochar obtained from kitchen biowaste would need to be explored.

On the other hand, in the case of garden biowaste, it should be investigated whether there is a chance to avoid contamination of this biowaste. Furthermore, due to the high yield and high ash content of biochar, the properties of the ash should be investigated, as there is a chance that the ash may contain nutrients that have a positive effect on plant growth but may also have a negative effect on soil properties depending on the type of soil to which it is applied.

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