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ANAEROBIC DIGESTION OF BREWER'S SPENT GRAIN WITH BIOCHAR – BIOGAS PRODUCTION KINETICS AND PROCESS EFFICIENCY

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ABSTRACT

Biochars made from brewer's spent grain were added to the anaerobic digestion of brewer's spent grain to enhance the methane fermentation process and improve biogas production. In research, the effect of biochars made at 300, 450, and 600°C and doses of 1-8% added to anaerobic digestion was tested. The biochemical biogas potential tests in mesophilic conditions were performed. The tests took 28 days, the biogas yield for each reactor varied from 500-650 ml×g_{VS}^{-1}, and around 60% substrate degradation was obtained. For each test, the kinetics parameters using the first-order model were determined. The constant biogas production rate (k), and the biogas production rate (r) varied from 0.05-0.08 d^{-1}, and 42-60 ml×(g_{VS}×d)$^{-1}$ respectively. Though the differences in biogas production turned out to be statistically insignificant ($p<0.05$) due to the high disappearance in obtained data and conflicting effects, the response surface area analysis showed that biochar made at 450°C at the share of 1-4% could be used to maximize biogas production. Nevertheless, supplementation with biochar needs to be done carefully since in many cases, a reduction in biogas production was observed.

1. INTRODUCTION

Beer is one of the most globally consumed alcoholic beverages and it is one of the most popular drinks after water, tea, milk, and coffee. Over the two decades, beer production and consumption have steadily increased from 1.3 billion hL to almost 2 billion hL. In 2020, beer consumption was around 1.9 billion hL (Conway, 2022b), and the overall bear market was worth around 743.8 billion USD (Beer market report, 2022). Beer production is evenly spread between three regions of the world. Asia, Americas, and Europe are responsible for 0.55 billion hL, 0.61 billion hL, and 0.50 billion hL of beer production, respectively (Conway, 2021). Although the biggest beer manufacturers are China (0.34 billion hL), the United States (0.21 billion hL), Brazil (0.15 billion hL) (Conway, 2022c), the European Union (EU) countries produce 0.32 billion hL of beer. The biggest manufacturer in the EU is Germany and Poland with 0.087 and 0.039 billion hL produced in 2020, respectively (Conway, 2022a).

Though beer is a popular beverage, its production has a negative effect on the environment. The brewing industry is considered one of the largest industrial users of water. In the beer production process, water is used for technological processes like washing, cleaning sterilizing, and beer production itself. It is estimated that modern breweries consume from 4 to 7 L of water per 1 L of produced beer (Olajire, 2020). Besides water, the brewing process required a lot of energy. According to the Brewers Association, to produce 1 L of beer, electrical energy from 0.10 to 0.19 kWh_{el} and thermal energy from 0.32 to 0.37 kWh_t are needed (Cheri et al., 2014). The specific values of consumed water and energy depend on the used technology and the size of the brewery. The larger the size, the lower the specific resource consumption. Besides resource consumption, beer production leads to waste production and greenhouse gas emissions (Olajire, 2020). It is estimated that beer production has a global warming potential (GPW) of 0.40-1.47 $kg_{CO2eq.}$×L_{beer}^{-1} (Amienyo & Azapagic, 2016) and together with other alcoholic beverages accounts for 0.7% of global greenhouse gas (GHG) emissions when the complete product lifecycle is considered (R. Shin & Searcy, 2018). The beer production process consists of several steps during which various waste and by-products are

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generated. With each liter of beer, around 7 liters of wastewater is created. Also by-products like malt barley rootlets (MBR ~ 0.03-0.05 kg×kg_{malt}^{-1}), brewer's spent grain (BSG ~ 0.14-0.19 kg×L_{beer}^{-1}), spent hops/hot trub (HT ~ 0.002-0.004 kg×L_{beer}^{-1}), and brewer's spent yeast (BSY ~ 0.02-0.04 kg×L_{beer}^{-1}) are produced (Cimini & Moresi, 2021). Spent grains, hops, and yeast are high-energy materials that have the potential for vast applications in biotechnology for microalgae production, biofuel production, extraction of proteins, polyphenolic and antioxidative substances, and the food industry (Karlović et al., 2020). Nevertheless, most of the potential applications are at the beginning of the research and it is unknown if they are economically feasible for all brewery wastes. Mainly, the high moisture content and perishable nature of by-products prevent their safe usage in the human food chain and other applications (Cimini & Moresi, 2021). As a result, in most cases, brewing by-products are used as animal feedstock, are spread on the field, or are incinerated (Karlović et al., 2020).

Even though some applications are not economically feasible yet, they may turn out to be feasible in the future. Due to the huge amount of beer produced annually worldwide, by-products are available in large quantities throughout the year and their proper and smart utilization may reduce the negative effects of beer production. Taking into account that worldwide around 1.9 billion hL of beer is produced annually (Conway, 2022b), and with each litter of beer around 0.14-0.19 kg of wet spent grain is produced (Cimini & Moresi, 2021), the world spent grain potential is around 26.6-36.1 million Mg of which 7.0-9.5 million Mg in the EU.

One of the potential applications and economically feasible processes that can be applied to BSG is methane fermentation (a.k.a anaerobic digestion). Anaerobic digestion (AD) is a process that allows converting a huge quantity of wet and biodegradable biomass into biogas and digested in a relatively short time. Biogas is a flammable gas that can provide heat and electricity to the brewing process as a replacement for natural gas or coal while digestate can be used as a fertilizer. Using digestate reduces the need for fuel consumption related to synthetic fertilizers production. As a result of AD, beer production can become more environmentally friendly and provide additional income to the owner of the brewery plant (Li et al., 2011; Miller et al., 2021). The biochemical methane potential tests (BMP) show that spent grains are characterized by a methane yield (MY) of 305 m^3_{CH4}×Mg_{VS}^{-1}. Assuming that BSG's total solids and volatile solids are 15% and 95% respectively, the MY of fresh BSG is 43.4 m^3_{CH4}×Mg_{wetBSG}^{-1} (Oliveira et al., 2018). The methane yield of BSG is comparable to other biomasses and wastes that are applied to AD worldwide. Most manures have an MY of 157-438 m^3_{CH4}×Mg_{VS}^{-1}. The MY of lignocellulosic biomass varies from 160 to 212 m^3_{CH4}×Mg_{VS}^{-1}, and the MY of organic municipal solid waste varies from 143 to 516 m^3_{CH4}×Mg_{VS}^{-1}. The MY depends on biomass compositions (the content of carbohydrates, proteins, and lipids) and AD process conditions (process time, temperature, and used technology) (Nwokolo et al., 2020).

BSG is characterized by high protein and fiber content (hemicellulose, cellulose, and lignin). By dry weight, protein constitutes 15.3-24.7%, hemicellulose 19.2-29.6%, cellulose 16.8-25.3%, lignin 11.9-27.8%, and ashes 0.12-0.46% (Ikram et al., 2017). Though BSG is high-energy content material (high heating value of 21 MJ×kg^{-1}) (Arranz et al., 2021), its lignocellulosic nature hinders the anaerobic digestion and does not allow for fully utilized energy potential. It is mainly due to the slow rate of lignocellulose degradation under AD conditions and the fact that biogas production can be inhibited by phenolic intermediates (such as p-cresol) produced during lignocellulose degradation (Bougrier et al., 2018). The AD of BSG as a mono-substrate is troublesome, even at a low organic loading rate (OLR ~1–2 g_{VS}×dm^{-3}×d^{-1}). Usually, mono-fermentation of BSG collapses after ~2-4 months (Bougrier et al., 2018; Sežun et al., 2011). Nevertheless, proper supplementation with trace elements solves this problem and the process can be performed efficiently and stably (Bougrier et al., 2018).

A lot of methods for pretreatment of lignocellulose biomass before AD was proposed and tested, i.e., mechanical, thermal-pressure, chemical, and biological treatments. These methods are used to change the physical properties and chemical composition of the biomass making it more available for the AD microorganism. For physical properties change counts decrease in particle size, increase in pore volume, and specific surface area available for microorganisms (Stachowiak-Wencek et al., 2021). Pretreatment which affects the chemical structures of biomass promotes the effective enzymatic conversion of carbohydrate polymers into monomeric sugars. For example, chemical treatment with base results in breaks in lignin structure and breaking bonds between lignin and other carbohydrates in biomass. Also, alkali treatment reduces the degree of cellulose polymerization and crystallinity, making them more available for microorganisms (Zborowska et al., 2022).

Another method recently studied extensively to enhance AD is biochar supplementation. Biochar (BC) is a carbonaceous material made during the pyrolysis of biomass. Biochar due to its specific properties can promote the AD process and improve its stability. BC supplementation works at many levels and stages of AD. It is stated that BC has adsorption and immobilization ability of ammonia, heavy metals, and toxins. Besides, AD microorganisms can attach to the highly porous surface of BC which promotes an increase in microorganism populations. In the case of organic overloading, BC can absorb generated metabolites improving process stability. The stability of the process is also improved by BC buffering ability, which comes from the presence of functional groups (–OH, –COOH, $–NH_2$), alkali metals ions (Na^+, K^+), and alkaline-earth metals ions ($Ca2^+$, Mg^{2+}) (W. Zhao et al., 2021). BC is also considered a conductive material promoting direct interspecies electron transfer (DIET) between syntrophic bacteria and methanogens. As a result enhances the syntrophic conversion of organic substances to methane, increasing process stability and decreasing the lag phase (Chen et al., 2022). Nevertheless, the effect of biochar supplementation depends on biochar properties, amounts of added BC, and AD characteristics. Due to the abundance of possible AD substrates and BCs properties, there is a need for more research on

biochar addition to the AD process to find the right biochar properties and their amounts (Syguła et al., 2022). Biochar properties significantly depend on the substrate used in the pyrolysis process and pyrolysis conditions (temperature, residence time, heating rate, etc.). In general, the higher temperature of the pyrolysis the better quality of biochar is obtained. Nevertheless, in some cases, with increasing temperature, important properties deteriorate. Moreover, the higher the pyrolysis temperature and time the higher the cost of BC production (Morales et al., 2015).

Taking into account that BSG is abundant material that can be processed in AD, and BC can improve the AD process, in this study, the effect of the addition of different biochars made from substrates of AD was tested. According to our knowledge, there is no other research except Dudek et al., 2019, where BC made at 300°C from BSG was added to the AD process. The idea of using the substrate for BC production came from the fact that such BC can be produced in a biogas plant using residual heat from the CHP unit. The temperature of exhaust gases from a gas turbine differs from 400 to 600°C (OGL, 2021), while residual heat consists of around 70% of all heat produced in a biogas plant (Sobol et al., 2021). In the case of significant improvement of the AD process efficiency by BC such combined processes could be beneficial to the environment and economy.

2. MATERIALS AND METHODS

Firstly, materials used in the study were collected and prepared for analysis. After preparation, materials were subjected to analyses to reveal their characteristics. Then, the biochemical biogas potential test (BBPT) was performed with different biochars added to the process. Next, AD data were used to determine process kinetics. Finally, statistical analyses were performed to find the effect of BC supplementation on biogas production, kinetics, and process efficiency.

2.1 Materials

In the study, liquid digestate, the brewer's spent grain, and biochars were used (Figure S1 a-c). The digestate (D) used as inoculum in batch tests was collected from a 1 MW_{el} commercial biogas plant (Bio-Wat Sp. Z o. o., Świdnica, Poland). The biogas plant was fed mainly with maize silage and other unspecified seasonal agricultural substrates. The digestate was collected from a post-fermentation chamber and placed in a plastic canister with a total volume of ~100 dm^3. The same day, digestate was taken to the laboratory where it was strained through a tetra cloth diaper to remove large solids particles and other solid contaminations. As a result, two digestate fractions were obtained, solid and liquid respectively. The solid digestate was ejected, while liquid digestate was stored in plastic containers in a laboratory incubator (POL-EKO-APARATURA, model ST 3 COMF, Wodzisław Śląski, Poland) at 4°C.

The main substrate used in the batch tests was brewer's spent grains (BSG). BSG was obtained from a laboratory-scale beer production installation (Wroclaw University of Environmental and Life Sciences, Wrocław, Poland) as a residual after the beer production process. The beer was made from a mashed pilsner malt Viking Malt (Strzegom), produced from malting barley. After the beer production process, the BSG was dried at 80°C to dry mass in a laboratory dryer (WAMED, model KBC-65W, Warsaw, Poland). A standard drying temperature for biomass (105°C) was not used to prevent a possible occurrence of Maillard's reactions. The dry BSG was stored at -31°C in a laboratory freezer (Electrolux, model EC5231AOW, Jászberény, Hungary).

Biochars (BC) were made from brewery-spent grains. According to the previous methodology, biochars were produced at temperatures 300, 450, and 600°C respectively (Świechowski et al., 2020). In short, biochars were made using a laboratory muffle furnace (SNOL, model 8.1/1100, Utena, Lithuania). Around 300 g of dry BSG was placed in the glass tray and placed into the furnace chamber (Figure S1 d). Afterward, the chamber was filled with CO_2 inert gas, and the furnace was turned on. The CO_2 was supplied into the chamber during the whole pyrolysis process to keep an inert atmosphere. The heating rate of 50°C·min^{-1} was used to heat the reactor from room temperature (~20°C) to the setpoint temperature. The material was pyrolyzed at setpoint temperature for 60 minutes. After carbonization, the furnace was turned off and left to cool. Thus, produced biochars were stored in plastic bags at room temperature.

2.2 Methods

2.2.1 Materials analyses

Basic and elemental analyses were performed on the study's materials, including the liquid digestate, the spent grain from the brewery, the biochar, and the process residues from the biochemical biogas potential test (BBPT). The basic analysis included total solids (TS) and volatile solids (VS), while the elemental analysis include carbon (C), hydrogen, (H), nitrogen (N), sulfur (S), and oxygen (O). Also, pH and electrical conductivity were measured (EC).

BSG and biochars were additionally subjected to proximate analysis, specific surface area (SSA) determination analysis, FTIR analysis, cation exchange capacity (CEC) determination analysis, and volatile organic compounds (VOC) analysis. The proximate analysis consists of moisture content (MC), volatile matter (VM), fixed carbon (FC), ash content (AC), and high heating value (HHV). Alongside SSA, total pore volume <50 nm (V_t), and average pore size <50 nm (L) were analyzed. Used equipment and methods were summarized in the Supplementary content, Table S1.

2.2.2 Biochemical biogas potential test

Biochemical biogas potential tests (BBPT) were performed using the OxiTop® Control AN measuring system (Oxitop Control AN6, Weilheim, Germany) and laboratory incubator (POL-EKO-APARATURA, ST 3 COMF, Wodzisław Śląski, Poland), Figure S1 e,f. The OxiTop system consists of glass bottles (reactor chamber), head adapters, pressure measuring heads, and a reading pilot. The reactor has a total volume of 1 dm^3 and is ended with three stubs. The side stubs are for biogas collection/pressure release while

the middle stub is for pressure measuring head. The head is connected to a reactor by an adapter. The principle of using BPPT is to measure the pressure increase caused by produced biogas and its recalculation to the volume of produced biogas in standard conditions.

BBPT was performed in 3 setups that were duplicated. One setup analyzed the effect of one biochar (BC300, BC450, BC600). During each setup, 10 reactors were used. Always 1 reactor contained inoculum, 1 reactor contained inoculum and BSG and 8 reactors contained inoculum, BSG, and biochars in shares ranging from 1 to 8% by TS of the BSG. The substrate-to-inoculum ratio (SIR) was kept around 0.80-0.86 by VS (0.48-0.52 by TS, ~0.10 by wet mass). Each reactor was filled with 160 g of liquid digestate (inoculum) and around 3.4 g of dry BSG mixed with BC. The mass of specific materials placed into the reactors and the reactors' main parameters were summarized in Table S2.

2.2.3 Biogas production, kinetics, and process efficiency determination

The results of the BBPT were subjected to kinetics parameters determination by estimation to the first-order kinetic model, Equations (1) and (2). The model provides information about the constant reaction rate (k), the estimated maximum biogas production potential (emBBP), methane production rate (r), and cumulative biogas production (BBP) after a given time (t). The kinetics determination was performed using Statistica 13.0 software (TIBCO Software Inc., Palo Alto, CA, USA).

$$BBP = emBBP \times (1 - e^{(-k \times t)}) \quad (1)$$

$$r = k \times emBBP \quad (2)$$

where:

- BBP is the cumulative biogas production after a given time t, ml×g_{VS}^{-1};
- emBBP is the estimated value of experimental maximum biogas production, ml×g_{VS}^{-1};
- e is the mathematical constant (a.k.a. Euler's number) equal to ~2.718, -;
- k is constant biogas production rate, d^{-1};
- t is process time, d;
- r is biogas production rate, ml×(g_{VS}×d)$^{-1}$.

To determine process efficiency (degree of substrate conversion into biogas), theoretical biochemical biogas potential (TBBP) production was calculated according to Equation (3) which is Boyle's modification of the Buswell and Mueller stoichiometric formula.

$$C_aH_bO_cN_dS_e + \left(a - \frac{b}{4} - \frac{c}{2} + \frac{3d}{4} + \frac{e}{2}\right) H_2O \rightarrow \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8} - \frac{e}{4}\right) CH_4 + \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4} + \frac{3d}{8} + \frac{e}{4}\right) CO_2 + dNH_3 + eH_2S \quad (3)$$

where:

- $C_aH_bO_cN_dS_e$ is the elemental composition of the substrate, C – carbon, H – hydrogen, O – oxygen, N –nitrogen, S – sulphury, and a, b, c, d, e stands for molar % share of specific elements contained in the volatile solids of the substrate.
- H_2O is the water needed for substrate decomposition, mol;
- CH_4 is the methane, mol;
- CO_2 is the carbon dioxide, mol;
- NH_3 is the ammonia, mol;
- H_2S is the hydrogen sulfide, mol.

The description of how to calculate TBBP using Equation (3) is presented elsewhere (Świechowski et al., 2022). Afterward, substrate conversion into biogas (BD) was calculated using data from the BBPT experiment and TBBP according to Equation (4).

$$BD = \frac{EBMP}{TBMP} \; x \; 100 \quad (4)$$

where:

- BD is the substrate biodegradation (degree of substrate converted into biogas), %;
- EBMP is the experimental biochemical biogas potential, ml×g_{VS}^{-1};
- TBMP is the theoretical biochemical biogas potential, ml×g_{VS}^{-1}.

Next, to determine quantitatively the effect of biochar added on process efficiency, the biogas production effect (BPe) was calculated according to Equation (5). BPe provides information on how much percent biogas production increased/decreased after biochar was added in comparison to control without biochar added.

$$BPe = \frac{Biogas_{with\ BC} - Biogas_{without\ B}}{Biogas_{without\ B}} \; x \; 100 \quad (5)$$

where:

- BPe is the biogas production effect, %;
- $Biogas_{with\ BC}$ is the biogas produced from a substrate without biochar added, ml;
- $Biogas_{without\ BC}$ is the biogas produced from a substrate with biochar added, ml.

2.2.4 Statistical analyses of the BC effect on the AD

Due to a large number of BBMP measurements, its typical presentation in the form of a line diagram with standard deviations is unreadable. For the better visualize obtained data and the effect of biochar added on process kinetics and efficiency, the regressions using the response surface area model were performed. To study the effect of biochar dose, and temperature of its production on process kinetics and efficiency it was assumed that the independent variables are biochar share, and temperature of biochar production while the dependent variables are emBBP, r, k, BD, and BPe. The regression analysis was performed using Statistica 13.0 software (TIBCO Software Inc., Palo Alto, CA, USA).

To check if between obtained results are statistically significant differences, ANOVA with post hoc Tukey test at the level of α = 0.05 was performed using Statistica 13.0 software (TIBCO Software Inc., Palo Alto, CA, USA).

3. RESULTS AND DISCUSSION

3.1 Materials analyses

In Table 1 and Table 2, the properties of the materials used in the study are presented. The moisture content of fresh BSG was 79.6% and dry mass consist of 20.4%. BSG was characterized by high organic matter content since the

volatile solids were 96.2%, and ash content was only 3.8%. The main elements in BSG were carbon 48.6%, and oxygen 35.0%. The overall energy potential of BSG was 20.76 MJ×kg^{-1} (Table 1).

The obtained biochars made from BSG had also a high amount of organic matter, the VS was in the range of 94.4-85.8%, and its value decreased with the increasing temperature of the pyrolysis. Though a similar amount of VS in comparison to BSG was observed, most of the organic matter was in the form of fixed carbon. The FC in biochar was between 42.8-70%, while BSG had only 14.5% of FC (Table 1). More so, this is also visible in the carbon content (C) which relative amount increased in each biochar from 48.6% in unprocessed BSG to 77.7% in the BC600. With increasing pyrolysis temperature, also a decrease in H, N, S, and O was observed. The change is very significant, especially in the case of oxygen which decreased from 35% for BSG to 1% for BC600 (Table 1). The basic properties of studied BSG and produced BC (Table 1) are similar to those from the literature. The BSG is characterized by the VM of 77-80.3%, the FC of 16.1-19.3%, the AC of 2.1-6.2%, the C of 48.8-49.2%, the H of 6.5-6.8%, the N of 3.9-4.4%, the O of 36-36.8% and HHV of 18.6-21.7 MJ×kg^{-1}. (Balogun et al., 2017; Sanna et al., 2011; Sieradzka et al., 2022). Also, the properties of BCs and trends in changes in their properties are similar to other studies. Only oxygen content in BC450 and BC600 is much lower than in the work of (Sanna et al., 2011) where biochars produced at 460-540°C were characterized by oxygen content of 31.7-24.5%. Nevertheless, such differences may be due to different methods of pyrolysis.

For BSG, determination of specific surface area (SSA), total pore volume <50 nm (V_t), average pore size <50 nm (L), and cation exchange capacity failed. It was due to the physical characteristic of the BSG. The pore size and its amount were too small to be measured and the procedure for CEC determination in biochars turned out to be not suitable for BSG. BSG's pH was 6.4 and its electrical conductivity was 718 µS×cm^{-1}. For comparison, biochar used in the study had similar pH (5.92-7.85), but it had much lower electrical conductivity (214-332 µS×cm^{-1}) (Table 2) which is surprising since biochar is considered the material that supposes to increase conductivity and electron transfer in the anaerobic digestion process and enhance DIET mechanism (Z. Zhao et al., 2020). With increasing pyrolysis temperature, the SSA of biochars increased significantly from 0.5 m^2×g^{-1} to 292 m^2×g^{-1} for BS300 and BS600 respectively. A similar trend was observed for total pore volume which increased from 0.001 to 0.137 cm^3×g^{-1} for the same biochars. Though SSA and V_t increased with pyrolysis temperature, the average pore size slightly decrease from 4.6 nm to 1.9 nm. At the same time, cation exchange capacity increased from 8.7 cmol(+)×kg^{-1} to 31.8 cmol(+)×kg^{-1} (Table 2). Produced BCs properties slightly differ from the work of (Xi et al., 2014) which produced BC from BSG at temperatures from 300°C to 700°C and a processing time of 2-4 h. Biochars made at 300, 400, 500, and 600°C were characterized by pH of 10.3-11.5, CEC of 18.5-22.3 cmol(+)×kg$^{-1,}$ and SSA of 5.86-10.6 m^2×g^{-1} (Xi et al., 2014). This shows that the initial substrate used for pyrolysis and pyrolysis procedures affects significantly biochar properties. The most important parameter that affects BC properties is quality and type of substrate, process temperature, and pyrolysis type (Morales et al., 2015). Nevertheless, the most commonly used biochar for AD is BC made of wood or agricultural residues at the temperature of 300-800°C, and as a result, their properties differ significantly (W. Zhao et al., 2021). In general, the most desirable BC for AD is the one that has the potential to adsorption of ammonia, heavy metals, and excess VFAs (volatile fatty acids), and immobilize toxic substances (e.g. antibiotics) (Ngo et al., 2022). The adsorption and immobilization ability come from the specific surface area, porosity, and functional groups placed on the biochar surface. It is worth noting that too strong an absorption ability or a too large dose of BC may inhibit AD microorganisms as well (Ambaye et al., 2021). Another important BC feature is alkaline pH and the ability to increase reactor stability due to buffer capacity enhancement. It is possible due to the presence of alkaline functional groups and metal ions (Fidel et al., 2017).

TABLE 1: The basic characteristic of BSG and BCs.

Material	TS** (%)	VS (%)	MC** (%)	VM* (%)	FC* (%)	AC* (%)	C* (%)	H* (%)	N* (%)	S* (%)	O* (%)	HHV (MJ×kg^{-1})
BSG	20.4±0.3	96.2±0.0	79.6±0.3	82.4±0.3	14.5±0.4	3.1±0.2	48.6±0.1	7.0±0.0	4.4±0.2	2.0±0.2	35.0±0.3	20.76
BC 300	97.1±0.7	94.4±0.1	2.9±0.7	52.8±0.7	42.8±0.9	4.5±0.4	60.0±0.3	5.3±0.0	4.8±0.2	1.6±0.2	23.9±0.3	26.00
BC 450	99±1.2	89.3±3.0	1.0±1.2	21.9±1.2	68.9±1.2	9.2±0.3	69.6±4.1	3.8±0.2	5.0±1.0	1.1±0.0	11.3±3.7	26.18
BC 600	96±0.4	85.8±0.2	4.0±0.4	17.3±0.4	70.0±0.2	12.8±0.3	77.7±0.5	2.8±0.0	4.7±0.3	1.0±0.1	1.0±0.9	24.75

**as dry base, **as received base*

TABLE 2: Additional characteristics of BSG and BCs.

Material	SSA (m^2×g^{-1})	V_t (cm^3×g^{-1})	L (nm)	CEC (cmol(+)×kg^{-1})	pH	EC (µS×cm^{-1})
BSG	0	0	0	-	6.4	718
BC300	0.5	0.001	4.6	8.7	5.92	214
BC450	3.3	0.004	4.4	14.2	6.03	223
BC600	292	0.137	1.9	31.8	7.85	332

To check, if volatile organic compounds contained in biochar may affect methane fermentation, VOCs determination in BSG and BCs was performed. VOCs are a very vast group of organic compounds and some of them are toxic. The work in the field of biochar shows that during the thermal conversion of organic materials (torrefaction, pyrolysis, etc.) numerous (VOCs) are formed. Due to the porous structure of biochar and the condensation of residual vapors that take place at the last step of pyrolysis (cooling), VOCs stay on the biochar surface, and biochar itself may become a source of VOCs pollutants (Łyczko et al., 2021). Therefore in this study, we wanted to check if VOCs contained in biochars that were applied to the AD process could affect biogas production.

The shortlist of most abundant VOCs (compound share >5%) found in studied materials is presented in Table 3, while a full list of all detected VOCs is presented in the Supplementary content, (Table S3). It turns out that there were no VOCs in the BC450 and BC600.

This is probably due to high pyrolysis temperature and long residence time which result in total organic compounds decomposition (Białowiec et al., 2018). The pyrolysis of BSG at 300°C resulted in a change in the chemical composition of volatile organic compounds and their number. The unprocessed BSG had 37 VOCs compounds, while BC300 had 44 (Table S3). The main VOCs in BSG were 1-Pentanol, 4-methyl- 20.89%, Ethyl amylketone 18.86% and Cyclobutane, 1,2-bis(1-methylethenyl)-, trans- 8.79%, while main VOCs contained in BC300 were Cyclobutane, 1,2-bis(1-methylethenyl)-, trans- 24.95%, Pentanal, 3-methyl- 14.74% and Thuja-2,4(10)-diene 10.35% (Table 3). It is worth noting that the relative amount of Cyclobutane, 1,2-bis(1-methylethenyl)-, trans- increased from 8.79% in BSG to 24.95% in BC300.

Due to the lack of VOCs in BC450 and BC600, it may be concluded that VOCs in biochars produced at higher temperatures than 450°C do not affect anaerobic digestion, and other mechanisms need to be investigated.

The FTIR spectroscopy was performed to determine functional groups present on BSG and BCs surfaces. The spectra with the largest peaks are shown in Figure 1.

The BSG spectra show the largest peaks at 3298, 2924, 2856, 1743, 1632, 1536, 1150, 1075, and 1123 cm^{-1}. Due to BSG being lignocellulose materials, most of the peaks are considered to come from the main polymers which are hemicellulose, cellulose, and lignin (Nasir et al., 2021). A signal at 3298 cm^{-1} is attributed to O-H and N-H bonds that come from hydroxyl, amine, and amide groups. While hydroxyl groups are common in lignocellulosic biomass, the presence of amine and amide groups results from the high content of protein contained in BSG (Hejna et al., 2021). The peaks at the band region of 3000-2800 cm^{-1} show C–H stretching related to the presence of hemicellulose and cellulose, while peaks at the band region of 1700-1600 cm^{-1} shows the presence of amide I and amide II or the aromatic hydrocarbons of lignin (Naibaho et al., 2021). The peak at the band region of 1550-1500 is probably related to N-O stretching resulting from the presence of some nitro compound (IR Spectrum Table&Chart, 2022). The peaks at the band range of 1100-1000 cm^{-1} indicate stretching of C–O–C that comes from the presence of functional groups of aliphatic ethers (Naibaho et al., 2021). Most of the peaks found on the BSG were not observed on the BCs or were less intense. For example, no peaks in the range of 1600-3300 cm^{-1} were found for BC450 and BC600, though smaller peaks for BC300 in the range of 2800-3300 cm^{-1} can be observed. Also in the range of 1000-1530 cm^{-1}, almost all peaks visible on BSG are not present at BCs (Figure 1). Nevertheless, in the case of BC450 and BC600, some peaks that were not present on BSG can be found at 877 and 742 cm^{-1}. These changes in spectra indicate structural changes in BCs composition occurred during the pyrolysis. Flattening of absorbance at the range of 1000-1530 cm^{-1} shows a decrease in the C-H stretching bands in the biochars which are related to aliphatic compounds (Borel et al., 2020).

3.2 Biogas production, kinetics, and process efficiency

In Figures S1-S3 (Supplementary content), mean values from the biochemical biogas potential test (BBPT) are presented. It can be seen that biogas production from BSG, after 28 days varied from 500 $ml \times g_{VS}^{-1}$ to 650 $ml \times g_{VS}^{-1}$, while theoretical biochemical biogas potential (TBBP) production calculated according to Equation (3) is 1020 $ml \times g_{VS}^{-1}$. It means that on average, BSG was converted 56% into biogas while 44% of BSG was not utilized. Due to numerous results presented in Figures S1-S3, the response surface model was used to show the main effects of biochar addition. The results of the regression analysis are presented in Figure 2.

Results show the effect of biochar dose (from 1% to 8%) and biochar production temperature (from 300°C to 600°C) on the biogas production effect (Figure 2a) and substrate biodegradation (Figure 2b). Due to the complex

TABLE 3: Shortlist of most abundant volatile organic compounds contained in materials.

BSG		BC300	
Compound name	**%**	**Compound name**	**%**
1-Pentanol, 4-methyl-	20.89	Cyclobutane, 1,2-bis(1-methylethenyl)-, trans-	24.95
Ethyl amylketone	18.86	Pentanal, 3-methyl-	14.74
Cyclobutane, 1,2-bis(1-methylethenyl)-, trans-	8.79	Thuja-2,4(10)-diene	10.35
2,3-Butanediol	8.78	Naphthalene, 1,2,3,4,4a,8a-hexahydro-	6.86
Butanoic acid	6.32	Benzoyl isothiocyanate	5.32
Hepten-3-ol	5.77	Furan <2-butyl->	5.03

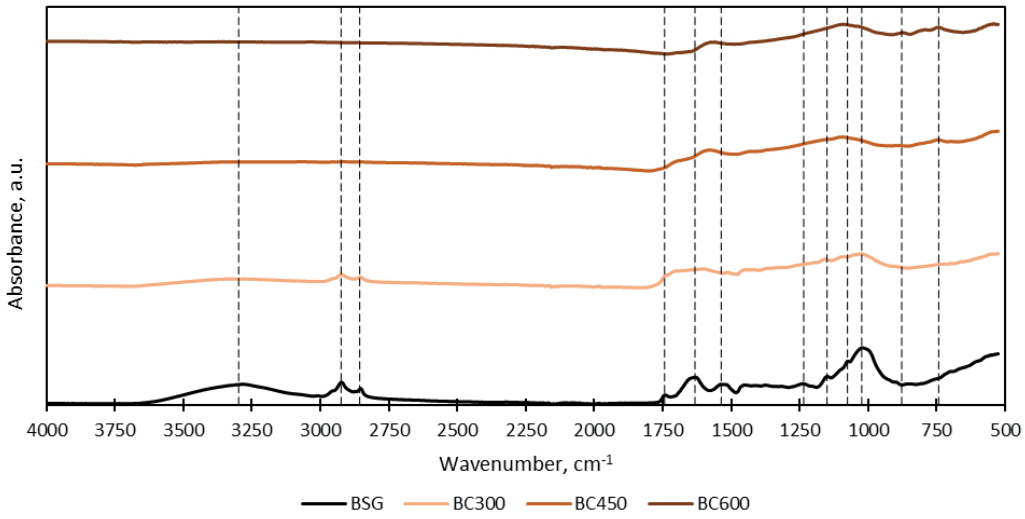

FIGURE 1: FTIR spectra of BSG and its biochars.

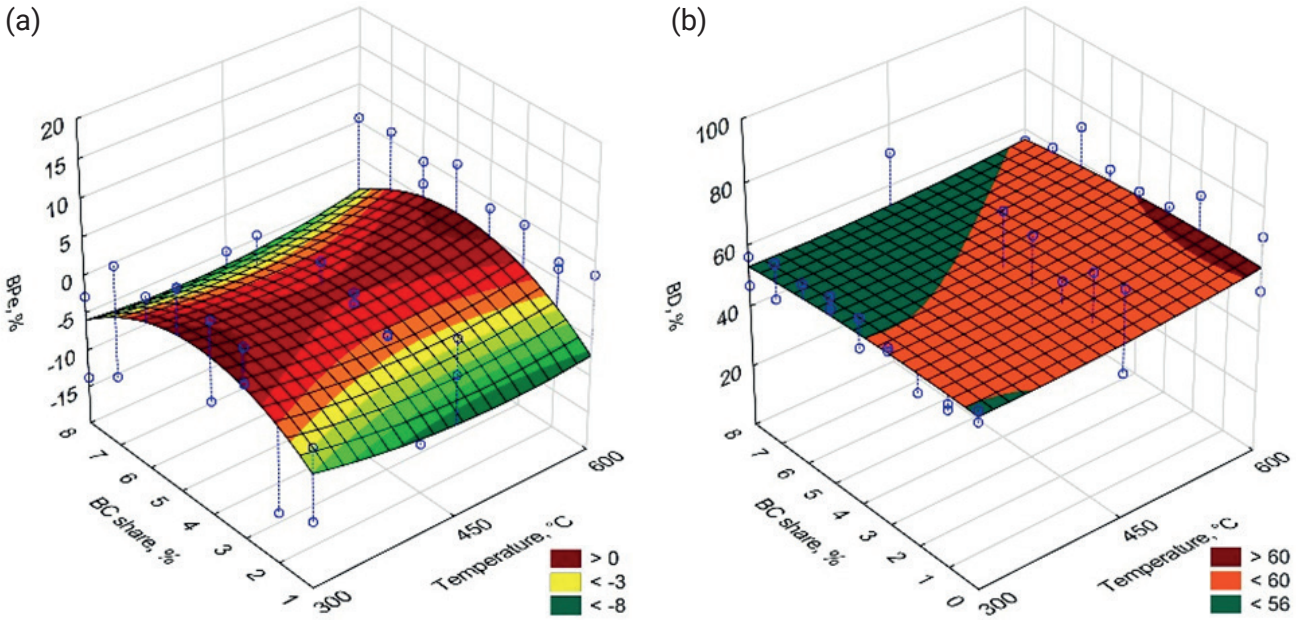

FIGURE 2: a) biogas production effect (BPe), b) substrate biodegradation (BD).

nature of biochar and the biochar mechanisms affecting anaerobic digestion, a large discrepancy in measurements can be observed (blue circles). It can be observed that biochar share, regardless of biochar production temperature (and thus its properties) affects BPe. For BC shares above 6% and lower than 3%, the response surface takes negative values of the BPe though some measurements (blue circles) are far from negative values (Figure 2a). For BD values, the response surface area shows the highest values (>60%) for biochar made at 600°C and BC dose up to 3% though some measurements for 450°C (BC share 1-4%) are much over >60%. (Figure 2b).

The effects of biochar share and biochar production temperature on biogas production kinetics are presented in Figure 3. The estimated value of experimental maximum biogas production (emBBP), the constant biogas production rate (k), and the biogas production rate (r) varied from ~620-820 ml×g_{VS}^{-1}, ~0.05-0.08 d^{-1}, and ~42-60 ml×(g-$_{VS}$×d)$^{-1}$, respectively (Figure 3).

Data shows that the emBBP reaches the highest value for BC produced at 450°C and its share of 2-6%, while lower and higher BC doses and other temperatures result in an emBBP decrease (Figure 3a). At the same time, the k shows a different trend, and the highest k value is obtained at a BC share of 0-3% and a temperature of 600°C (Figure 3b). It seems that k has the opposite trend in comparison to the emBBP, the higher emBBP, the lower the k is. On the other hand, the biogas production rate that results from the multiplication of emBBP and k shows that r has the highest value at a BC dose of 0-3% (Figure 3c).

The effect of biochar addition to the AD process is visible. BC supplementation, on one hand, increases maxi-

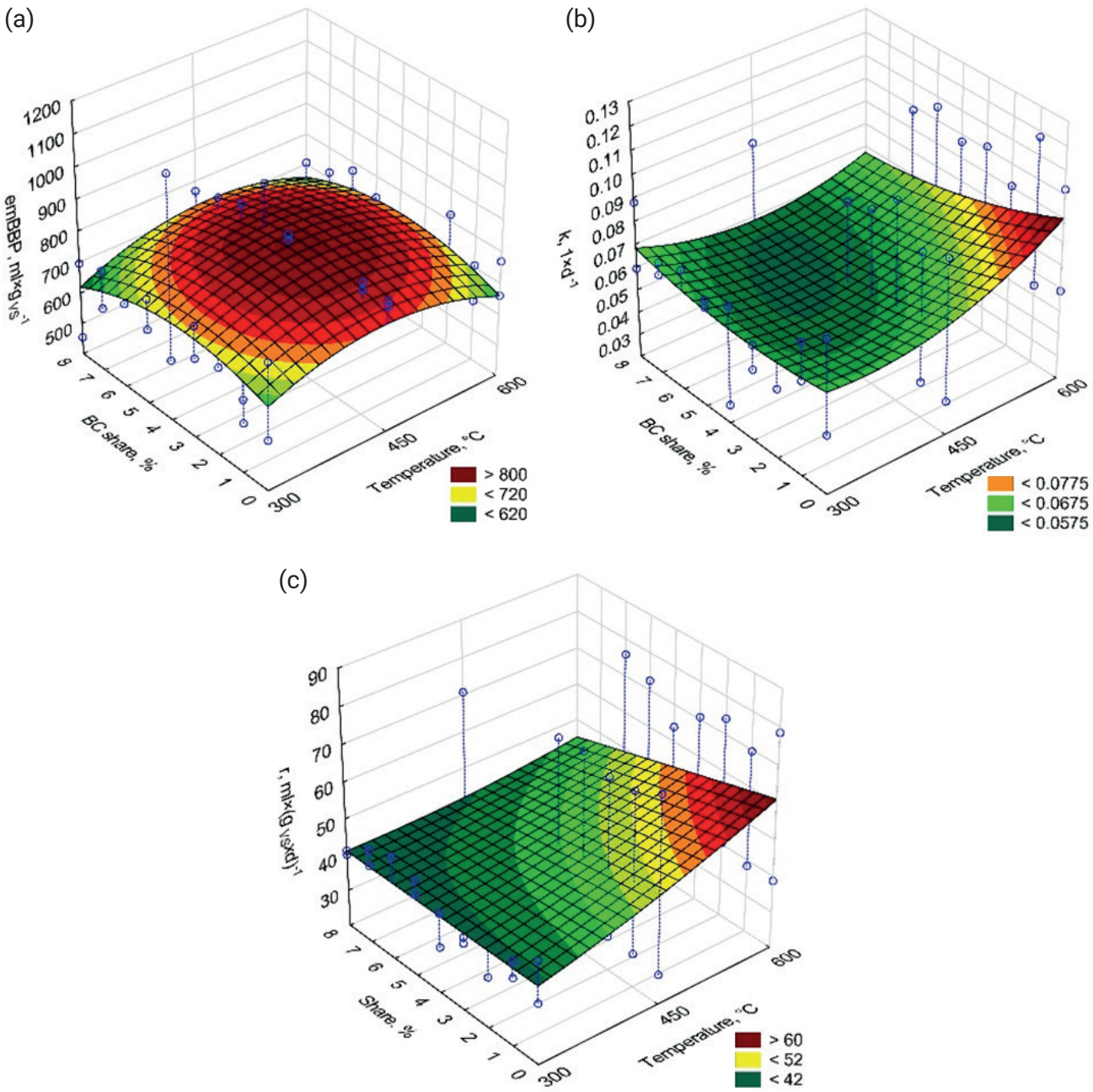

FIGURE 3: Biogas production kinetics, a) the estimated value of experimental maximum biogas production (emBBP), b) constant biogas production rate, c) biogas production rate.

mum biogas production (emBBP) and on the second-hand results in a constant biogas production rate decrease (k). It means that somehow BC increases the amounts of biogas that can be produced from the substrate, and at the same time decrease the speed of its production. Moreover, the biogas production rate (r) that combines emBBP and k is shown to increase with increasing BC production temperature and to decrease with increasing BC share. Though the response surface area shows that the greatest positive effect of BC addition can be obtained for BC600 at the share of 1-3%, all differences in the results turned out to be statistically insignificant ($p<0.05$). The lack of statistical significance may question obtained results and the sense of adding BC made from a substrate to methane fermentation of BSG. Nevertheless, the lack of statistically significant differences comes from the large discrepancy in the measurements and the fact that there are probably other factors that should be taken into account in future research.

To sum up, the theoretical biogas production potential of studied BSG was 1020 ml×g$_{VS}^{-1}$ and during 4 weeks of BSG methane fermentation, around 60% (500-650 ml×g$_{VS}^{-1}$) of this value was obtained in batch reactors. The addition of BC made from the substrate affects the amount of obtained biogas (BPe), substrate conversion (BD), and kinetics parameters of biogas production (emBBP, k, r) sometimes leading to a decrease and sometimes to an in-

crease in its value. Though biochar addition does not make a statistically significant difference ($p<0.05$), to maximize biogas production from BSG, BC450 at the share of 1-4% can be used (Figures 2a and 3a), and to maximize biogas production rate BC600 at the share of 1-3% (Figure 3b-c). Unfortunately, due to the high dispersion of the obtained BBPT results and its complexity, it was not possible to assign specific biochar features that lead to an increase/decrease in biogas production during the anaerobic digestion of BSG.

The average methane concentration in biogas produced during AD of BSG is around 60% (Čater et al., 2015; Poulsen et al., 2017). Since the biogas production in this research varied from 500 to 650 $ml \times g_{VS}^{-1}$ (Figure S2-S4), it can be assumed that around 300-390 $ml_{CH4} \times g_{VS}^{-1}$ were produced. These results are similar to other studies. According to Oliveira et al., 2018, raw spent grain has a biomethane potential of 271-387 $ml_{CH4} \times g_{VS}^{-1}$. Gomes et al., 2021 studied the effect of BSG loading (8.3-19.7 $g \times L^{-1}$) and the AD temperature (31-59°C) on biomethane production. In a batch test at SIR of 0.5, after 21 days obtained methane yield of 81-290 $ml_{CH4} \times g_{VS}^{-1}$, Interestingly for the AD at 35°C and BSG concentration of 10 $g \times L^{-1}$ obtained the highest biomethane yield. This show that biogas and biomethane yields are sensitive to initial AD conditions, substrate quality, and hydraulic retention time (HRT). In theory, maximal biomethane yield is obtained when the organic loading rate (ORL) is low and hydraulic retention time (HRT) is long. (Gunes et al., 2019). In the case of batch reactors, such conditions are mainly obtained by the proper substrate-to-inoculum ratio (SIR ~ 0.5 by VS), and process time of around 30 days. Though a shorter time can be applied if biogas/biomethane production over three following days is lower than 1% of the already cumulated biogas/methane (Filer et al., 2019). Due to the biogas yield being similar to data obtained in other studies, it can be assumed that BBPT tests were performed correctly.

Though there is a lot of research about the supplementation of carbonaceous materials to the AD process, according to our knowledge only two studies analyzed the effect of the BC addition to the AD of BSG. Dudek et al., 2019 studied the effect of biochar addition made from BSG at 300°C and doses ranged from 1% to 50% share by TS of BSG, while Mainardis et al., 2019 studied the effect of biochar made from red spruce woodchips at a temperature of 650°C at a dose of 0.2 $g_{BC} \times g_{VS}^{-1}$ of BSG. In the case of Dudek et al., 2019, the AD process took 21 days, and the biogas yield differed from 61.3 to 122.0 $ml \times g_{VS}^{-1}$. The highest increase in biogas production was observed at 5% BC share where the highest value of 122 $ml \times g_{VS}^{-1}$ was obtained. In comparison to the control (92.3 $ml \times g_{VS}^{-1}$) it was an increase of 32%. On the other hand, BC doses over 20% by TS of BSG lead to a decrease in biogas yield and suggest that an overdose of BC may inhibit the AD process (Dudek et al., 2019). In the case of Mainardis et al., 2019 two types of BSG were tested, BSG1 and BSG2 respectively. The process took around 19 days and methane yield in control samples differed from 300 $ml_{CH4} \times g_{VS}^{-1}$ for the BSG2 that acidified the process after 7 days, up to the 360 $ml_{CH4} \times g_{VS}^{-1}$ for the BSG1 that worked normally by 19 days. Interestingly biochar addition help to overcome acidification for BSG2 increasing methane yield by +26.6% up to 388 $ml_{CH4} \times g_{VS}^{-1}$, while for BSG1 a reduction to 342 $ml_{CH4} \times g_{VS}^{-1}$ was noted (Mainardis et al., 2019).

Contradictory results can be also found for other substrates and BC types. In the work of (D. C. Shin et al., 2022), used five food-waste to produced biochars with the following quantities (0.1, 0.5, 1.0, 3.0, 5.0% by volume, (v/v%)) were added to the AD of sewage sludge processed at 40°C. The BC was made at 500°C and a retention time of 10 min and showed biogas and biomethane production increase with increasing dose. For the 5% variant, the biogas production during the 60-day process was improved by almost 20%, while methane concentration increased from 50.6% to 55.8% (D. C. Shin et al., 2022). On the other hand (Wambugu et al., 2019) performed batch AD of food waste with BC made of brewery residues and waste wood at doses of 0.7, 1.3, 2.0, 2.7, 3.3, 5.0, and 8.0 $g_{BC} \times L^{-1}$. The AD was performed at 30°C and lasted 6 days after the process stopped due to acidification. Moreover, the addition of biochars lowered the amount of biogas produced by the control with only food waste. Interestingly wood waste biochar at a dose of 8 $g_{BC} \times L^{-1}$ used in a continuous up-flow anaerobic sludge blanket reactor (UASB) results in significant biogas production enhancement and increased chemical oxygen demand removal efficiency (Wambugu et al., 2019). The biochar addition does not only show complex effects on biogas production but also on the characteristics of the microorganisms. In the work of (Zhang et al., 2019), nine biochars made from three different materials at 400, 500, and 600°C were added to the AD of sewage sludge at a dose of 8 $g_{BC} \times L^{-1}$ and chosen biochars were tested at doses 6.2, 15.9, 26.1, and 34.2 $g_{BC} \times L^{-1}$. In most cases, the BC supplementation enhanced AD process stability by increasing buffering capacity, releasing volatile fatty acid accumulation, and alleviating ammonia inhibition. Still, excessive BC supplementation turned out to be inhibitory. Interestingly BC addition increased the abundance of acetoclastic methanogens that convert acetate (CH_3COOH) to methane and carbon dioxide, while reducing the abundance of hydrogenotrophic methanogens that produce methane from hydrogen and CO_2 (Zhang et al., 2019). That is opposite to the findings of (S. Wang et al., 2022), that added straw biochar (600°C for 20 min) at 7.1 $g_{BC} \times L^{-1}$ to the AD of cow dung. (S. Wang et al., 2022) also obtained methane production enhancement after biochar addition but this effect was due to an increase of hydrogenotrophic methanogens abundance, while acetoclastic methanogens such as Methanosaeta decreased massively (S. Wang et al., 2022). On the contrary results of (Masebinu et al., 2021) showed that for a well-working AD system without any severe disturbances, biochar does not improve methane production nor decrease it and microbial community composition is not altered.

Such conflicting effects also applied to the data obtained in this study show that in some specific cases, biochar may help to improve the process while in others can inhibit it. The reason for that may be the initial properties of the used inoculum, substrate, biochar, and AD conditions. Proper initial conditions in the AD process allow avoid of

volatile fatty acid accumulation and provide enough time for microorganisms to convert almost all available organic matter (Filer et al., 2019). Too high of organic input cause a drop in the pH that may affect the activity of some AD microorganisms. AD consists of 4 stages, hydrolysis, acidogenesis, acetogenesis, and methanogenesis. In each stage, other groups of microorganisms play a vital role. These groups are respectively hydrolytic, fermentative (acidogenic), syntrophic (acetogenic), and methanogenic microorganisms. In terms of optimal pH, there are two groups. Acid-producing bacteria (acidogenic) with optimal pH of 5.5-6.5, and methane-producing bacteria (methanogens) with optimal pH of 6.6-7.5. The acid-producing bacteria are less sensitive to lower pH values. Therefore the high pH drop related to the depletion of buffer capacity caused by the overloading of the reactor can inhibit methanogens activity and result in process failure (Khanal, 2008). There are pieces of evidence that biochar can enhance the buffer capacity (Shi et al., 2017) and allows for the mitigation of acidification in the AD process (D. Wang et al., 2017). In the research of Wang et al., 2017, the addition of 5% of BC by weight of the total loading to an overloaded AD reactor (50 $g_{TS} \times kg^{-1}$) was studied. The results showed that without biochar, the process was not able to start while BC addition mitigated acidification and kept biogas production going.

It seems that in the case of the performed research, the lack of significant biogas production improvement by supplementation of BC300, BC450, and BC600 could be related to the fact that, the AD process was performed in optimal conditions. And therefore, biochar buffering properties weren't used. Moreover, the observed decrease in some cases after biochar supplementation may come from the fact that biochar has strong adsorption and immobilization ability. Probably as a result of a lack of inhibitors like a too-high concentration of ammonia or VFAs, biochar adsorbs other microelements that could be necessary for microorganisms.

4. CONCLUSIONS

In this research, anaerobic digestion of BSG with BCs addition was performed. The theoretical biogas potential of tested BSG was 1020 $ml \times g_{VS}^{-1}$. The biogas yield after 28 days varied from 500-650 $ml \times g_{VS}^{-1}$ and around 60% substrate degradation was obtained. The kinetics parameters (emBBP, k, r) varied from ~620-820 $ml \times g_{VS}^{-1}$, ~0.05-0.08 d^{-1}, and ~42-60 $ml \times (g_{VS} \times d)^{-1}$, respectively. The addition of biochars showed complex and sometimes conflicting effects. As a result, no specific dependencies between the properties of biochar related to the temperature of its production and its dose were found. Though the differences in biogas production turned out to be statistically insignificant ($p<0.05$) due to the high disappearance in obtained data and conflicting effects, the response surface area analysis showed that to maximize biogas production, biochar made at 450°C at the share of 1-4% can be utilized, and to maximize the biogas production rate, the biochar made at 600°C at the share of 1-3% can be used. The comparison results with other works resulted in a hypothesis that the lack of biogas production improvement could be related to the fact that the AD process was performed in optimal conditions. As a result, biochar could not optimize process performance. In addition, a slight decrease in biogas production was probably due to biochar's strong adsorption and immobilization ability that in higher doses immobilized substances required by the AD's microorganisms.

Therefore, more research is required, where various initial conditions (with higher organic loading) and various BC concentrations would be tested. This would make it possible to determine the appropriate quantity of BC for the particular stress level of the reactor. Future research also should focus on the economic aspects of biochar supplementation and different strategies for BC acquisition. In the current study, BC was made from the substrate which due to the fact of being converted into BC could not be used during AD decreasing total methane production. For that reason, BC made from the AD digestate should be considered as a potential source for pyrolysis feedstock. Also, high-energy demand pyrolysis that requires dry feedstock could be replaced with the hydrothermal carbonization process (HTC) performed at lower temperatures (180-300°C). The HTC can produce biochar-like products (hydrochar) from both raw or anaerobically digested material with slightly difference in its properties (Catenacci et al., 2022). Also, HTC does not require a drying step and can be supplied with waste heat from biogas incineration in combined heat and power units.

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