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Communication

The proof-of-the-concept: the addition of biochar-sulfur composite in the methane fermentation process for biogas yield increase

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Abstract: Methane fermentation of organic waste is one way to minimize organic waste, which accounts for 77% of the global municipal waste stream. The use of biowaste treatment technologies helps to improve the energy independence of the regions. Improving the efficiency of the methane fermentation process by using additives from waste may be an attractive alternative to the original technology. The use of biochar as an additive for methane fermentation has been shown to increase the production potential of biogas. The reasons for the improvement in efficiency are complex among others, it is assumed that the specific surface area of biochar may increase the population of anaerobic organisms. Up to date, there are many researches on the effect of biochar additions on methane fermentation, but there is no research on the effect of sulfur-biochar composite. The composite product in the form of a mixture of biochar and molten sulfur is an interesting area of research. In this experiment additions of the sulfur-biochar composite were tested to improve the fermentation process. The composite consisted of 40% biochar and 60% of sulfur and was added to the process. As results the addition of 1% of the composite increased the biogas potential by 4%.

Keywords: sulfur; biogas; biochar, methane fermentation.

1. Introduction

1.1 Methane fermentation with biochar

The application of methane fermentation technologies for energy production can be an excellent alternative to the uncertainties of regional energy policy. Using biological processes to treat organic materials, which account for 77% of the global municipal waste stream, is an opportunity to exploit the energy potential. At that time, a significant proportion of the organic waste is landfilled. EU legislation requires 10% landfill of organic waste by 2035 [1]. During methane fermentation, organic material is decomposed under anaerobic conditions by anaerobic microorganisms at 37 °C or 55 °C [2].

Anaerobic digestion (AD) technology is a widely used method of waste treatment. Current research focuses on increasing the efficiency of biogas production while respecting the principles of the circular economy. One example is the use of biochar from organic waste in thermal torrefaction and pyrolysis under anaerobic conditions [3,4]. Świechowski and all have shown that the addition of biochar can improve methane yield in AD of organic waste by 3.6% [5]. In contrast, Lou showed an improvement in methane production compared to the sample without the addition of biochar. In these tests, glucose was used as a substrate, therefore the efficiency of the process was much higher and amounted to even 86.6% compared to the control sample - without biochar. [6]. Biochar has been found to help improve methane production, but it is not clear what direct effects this has on

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microorganisms. It can be assumed that the high porosity of biochar has a positive effect on the adhesion surfaces and the increased populations of methanogenic organisms. In the fermentation process, biochar has many functions, including maintaining a stable pH, facilitating the direct interspecies transfer of electrons, and promoting the growth of microorganisms. In addition, the sorption properties of biochar contribute to the reduction of CO_2 and H_2S and other potentially toxic byproducts. A significant specific surface area is favorable for the development of colonies of microorganisms [7]. Compounds such as non-organic nitrogen, long-chain fatty acids, and sulfides harm the AD process. However, the new types of biochar and biochar-based composite materials used for enhancement of the AD are developed. The heterogenous structure and properties of composite materials may create a multifunctional niche for the simultaneous development of different groups of microorganisms. Therefore, we propose for the first-time combining the biochar with elemental sulfur, to achieve the synergistic effect of biochar and sulfur properties. The addition of sulfur to the fermentation process seems controversial, however, preparing the material in advance and keeping it in the right conditions may bring benefits.

1.2 Production of sulfur

Emission standards have been introduced because of an increasingly conscious approach to the environment. These standards vary according to the region and the level of development of the country [8]. Fossil fuel combustion continues to account for the largest share of global energy production. The combustion of fossil fuels generates significant emissions of gases such as SO_x . The exhaust gases from the combustion of fossil fuels are desulphurization, resulting in waste sulfur. Sulfur can also be removed before combustion. This method is commonly used for liquid and gaseous fuels. For example, solid fuels such as coal may have a sulfur content of up to 14% in liquid fuels, while gases may have a sulfur content of up to 5.5% [9]. Sulfur can be produced in two main processes: the extraction of sulfur from deposits and the desulphurization of fuels such as petroleum and natural gas. However, the emission standards have made the extraction of sulfur uneconomic as waste sulfur is available in large quantities and at low prices.

1.3 Composite materials

Sulfur in construction is often used as a component to improve the strength properties of products [10]. However, the use of sulfur in commercial construction is not possible due to the low melting point of sulfur. The use of sulfur concrete is possible in the elements of road and sewer infrastructure [11]. It should be noted that the sulfur coating in contact with the liquid does not alter the pH of the liquid at a temperature below 135 °C [12]. In addition, sulfur in composite materials has antiseptic and hydrophobic properties, which makes sense when used in sewerage infrastructure. The common concrete, consisting of water additives and cement, leaves a significant carbon footprint. The production of 1 ton of cement emits up to 650 kg of CO_2. However, when transport, energy, and heat are taken into account for the production and use of cement, emissions can even be as high as 1:1 [13]. Sulfur concrete consists of molten sulfur and aggregate. Compared to concrete, no cement is used, and therefore no water is used. Waste sulfur from the capture of emissions would be an excellent alternative to a closed loop. In addition, crushed sulfur concrete can be reused to produce this product. After single crushing, the sulfur concrete showed better mechanical properties than the original product [14].

1.4 Properties of sulfur

The basic nutrients are carbon, hydrogen, oxygen, nitrogen, phosphorus, and sulfur. Without these elements, there is no life or development of organisms. Sulfur is an element that plays an important role in the photosynthesis process, being the basic nutrient of plants and directly influencing the yield of crops. Sulfur has antiseptic properties, supporting resistance to pathogens [15]. The physical properties of sulfur depend on the allotropic form. The two main allotropes of sulfur are orthorhombic sulfur and monoclinic sulfur. Orthorhombic sulfur at the temperature of 95.5℃ goes into the form of monoclinic sulfur, then at the temperature of 119.3℃, it changes its state from solid to liquid. The viscosity of liquid sulfur increases with temperature, up to 444.6°C, at which the sulfur boils [6,16]. Temperature also affects the sulfur density as well as the thermal conductivity, where the solid-state of aggregate shows better insulating properties. The combination of sulfur and hydrogen forms hydrogen sulfide, while in the combustion process, the sulfur dioxide formed in combination with water forms sulfuric acid [17].

1.5 Aim of the study

Due to the growing interest in the application of biochar to the methane fermentation process, the application of a sulfur-biochar composite (SBC) composite was proposed. Therefore, the SBC was produced, which was applied to the test sample and compared with the control sample. The addition of sulfur to the methane fermentation process may be controversial, but the fermentation process takes place at a temperature lower than the sulfur melting point. As a result of the above, there is no risk of changing the pH of the environment. On the other hand, it is hypothesized the structure of SBC may influence the production of biogas.

2. Materials and Methods

2.1 Materials

2.1.1 Inoculum

As an inoculum for the experiment, the digestate from agricultural biogas plant was used (Bio-Wat Sp. z. o. o., Świdnica, Poland). Biogas plant carried out the AD process in wet and mesophilic conditions. The digestate was collected from a post-fermentation chamber and delivered to the laboratory where it was filtered to remove solid contaminants.

2.1.2 Kitchen waste

Kitchen waste was prepared according to the recipe of Świechowski and all [18]. The waste consisted of vegetables 41.6% (lettuce, potatoes, carrots - each 13.86%), banana peels 29.7%, basic food 22.3% (pasta, rice, bread, each material 7.43%), chicken 0.2%, eggshell 4%, walnut shell 2.2%. Food waste was ground and dried for 24 hours at 105°C. The moisture content of the kitchen waste was 42.5%, and the dry organic matter content was 95.8%.

2.1.3 Biochar compose

The biochar used to produce SBC was made of applewood chips. The process of low-temperature pyrolysis of apple chips was carried out in a muffle furnace (SNOL, 8.1/1100, Utena, Lithuania) at a temperature of 500°C and a processing time of 1 hour. After the process, the biochar was ground to a powder form to obtain the same granulation of the material as the waste sulfur.

2.1.4 Sulfur waste

For biochar sulfur composite production, the waste sulfur from crude oil desulphurization was used (Refinery in Płock, ORLEN Poland Group S.A.). This product was delivered in the form of a crystal weighing 5 kg. The preparation of the material for the tests consisted in crushing the crystal into smaller agglomerates. The material was then ground to a powder in a laboratory mortar.

2.2 Methods

2.2.1 Production SBC

The ground biochar and sulfur were sieved separately through a 1 mm mesh sieve to homogenize the material. Then fractions below <1 mm was mixed. Subsequently, the mixture of biochar and sulfur was put into a silicone mold which was heated for 2 hours at a temperature of 140°C. The weight ratio of both substrates was 60% sulfur and 40% of biochar. After the process, the SBC was removed from the furnace and was ground using laboratory mortar.

2.2.2 Anaerobic digestion

The biogas potential test was performed using the OxiTop measurement system (Oxitop Control AN6, Weilheim, Germany). The system consists of glass bottles - fermentation reactors and manometric heads calibrated to measure the pressure difference due to biogas production. The measurement was read continuously with the OxiTop OC 100 controller (Weilheim, Germany). A side connection was used to drain excess gas from the reactor. The reactors were kept in a climate chamber at 37°C to ensure mesophilic conditions (Pollab, model 140/40, Wilkowice, Poland).

The process was set up for the digestate only, digested with the addition of kitchen waste (substrate) and digested with substrate, and the addition of 1% by weight of SBC. The diagram of the procedure is presented in Figure 1.

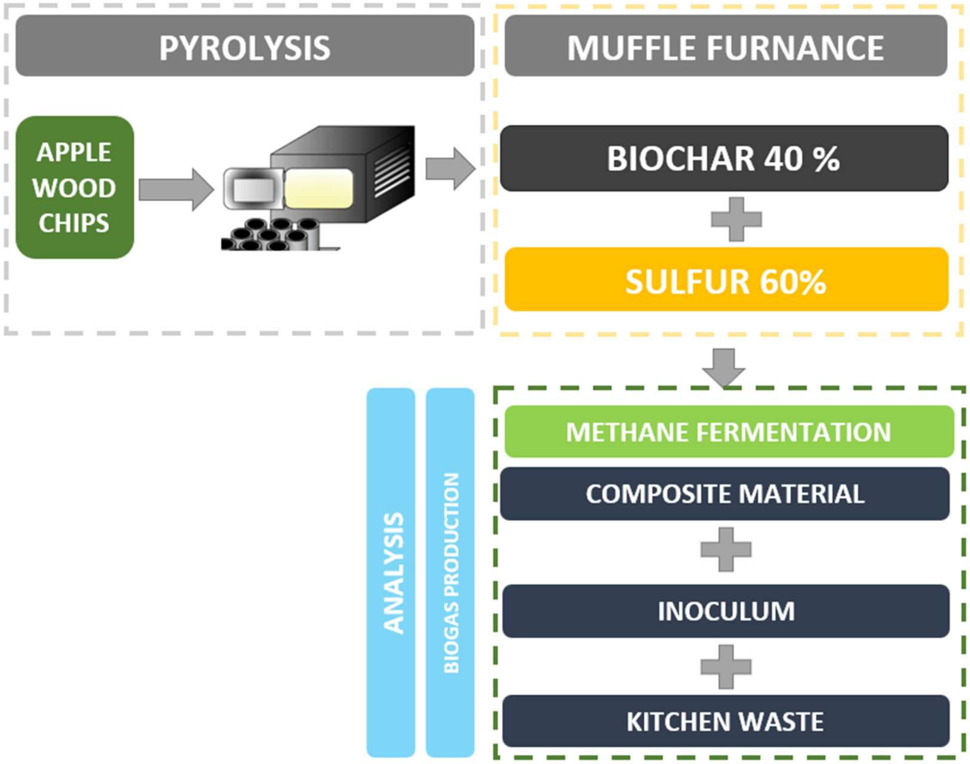

Figure 1. Procedure to produce biogas and SBC mixture to test the potential of biogas production.

The water content in the digestate was 94.91%, in the substrate 42.45%. The dry organic matter content in the digestate was 8.34% and in the substrate 95.80%. The table shows the exact amount of the individual components in the individual reactors. Each mix was set up in duplicate.

Table 1. Masses of individual components in methane fermentation reactors (I - inoculum, IKW – inoculum with kitchen waste, SBC – sulfur-biochar composite).

Reactor ID	Inoculum, g	Kitchen waste, g	SBC, g
I	200.00	-	-
I	200.00	-	-
IKW	200.00	2.500	-
IKW	200.00	2.502	-
IKW + SBC (I)	200.00	2.510	0.2509
IKW+ SBC (II)	200.00	2.509	0.2506

The duration of the AD process was 4 weeks. Data showing the change in pressure over time were downloaded to a computer and then analyzed. Based on the collected data, the free capacity of the reactor, and the number of biogas moles were determined and the production potential was converted into volatile solids (vs). Then, in the Statistica 13 software (StatSoft, Inc., TIBCO Software Inc., Palo Alto, CA, USA), first-order reaction models were evaluated and the biogas production kinetics were calculated. The following formulas were used to calculate the biogas kinetic parameters [2,5]:

$$B_t = B_0 \times (1 - e)^{(-k \cdot t)} \quad (1)$$

where:
B_t – biogas volume over time t, ml × g_{vs}^{-1},
B_0 – maximum production of biogas from the substrate, ml × g_{vs}^{-1},
k – reaction constant rate, d^{-1},
t – process time, days.

$$r = B_0 \times k \quad (2)$$

where:
r – biogas production rate, ml × g_{vs}^{-1} × d^{-1}.

3. Results and Discussion

3.1 Production of SBC

As a result of the thermal process in a muffle furnace of biochar and sulfur mixtures, the SBC material was obtained. As a result of being heated to 140°C, the sulfur turned into a liquid in the formula, and it was a binder in the composite material. The filler was biochar in the amount of 40% of the weight of the material. The process resulted in a solid product, the sulfur was completely dissolved, and no agglomerations of undissolved sulfur were visible. Figure 2 shows the biochar, sulfur, and SBC (60% sulfur and 40% biochar from applewood chips).

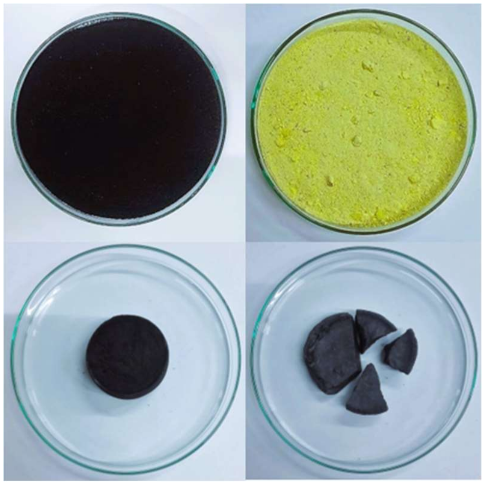

Figure 2. The biochar from applewood chips (left, upper corner); sulfur (right, upper corner), SBC (bottom).

3.2 Anaerobic digestion

The collected data were recalculated and are shown in Figure 3. The graph shows the mean results of three different mixes. Reactors with the digestate alone showed a low potential for biogas production, not exceeding 100 ml × g_{vs}^{-1}. Anaerobic bacteria did not release large amounts of methane due to the lack of organic matter. In the remaining cases, the amount of released biogas reached 657 ml × g_{vs}^{-1} for reactor IKW_SBC (I) and 672 ml × g_{vs}^{-1} for IKW_SBC (II).

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Figure 3 shows that the addition of 1% by weight of SBC with 60% S share increased biogas production compared to digestate used with kitchen waste. Only during the first measurement, the biogas production was higher for reactor IKW(I), with each subsequent entry, the reactors with the addition of SBC showed higher separated amounts of biogas. On the first day, reactors IKW_SBC (I) and IKW_SBC (II) produced 19% more biogas than reactor IKW(I). On days two to four, it was already 6% more, while on each subsequent day of the process, 2-4% more methane was produced. When counting the arithmetic mean for four weeks, it was found that the addition of 1% of the weight of the sulfur-biocarbon composite to the weight of kitchen waste resulted in an increase in biogas production by 4%.

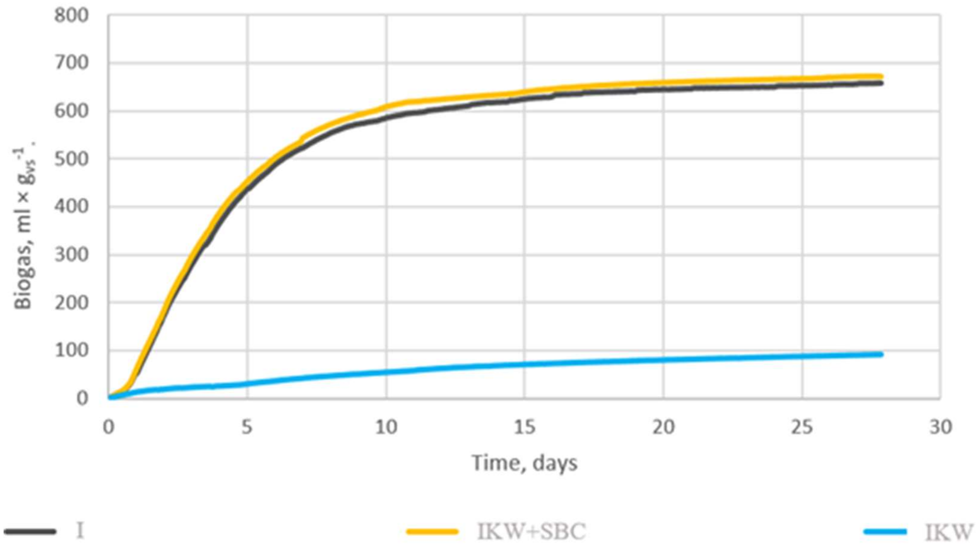

Figure 3. Graph of biogas growth curves over time for the control sample – digestate (I), digestate + substrate (IKW) and for digestate + substrate + SBC (IKW+SBC).

There are many mathematical models used to test the biogas production potential in the AD process. It has not yet been determined which models best reflect the experimental data. The result is an overlapping of many variable factors (type of substrate, chemical reactions taking place or their concentration). Many authors, however, agree with the choice of the first order kinetic model that was used for this test [19].

Table 2. Kinetic parameters of AD

Reactor content	Parameter	Values	Unit
I	k	0.076	d^{-1}
	B_0	102.82	ml × g_{vs}^{-1}
	r	7.81	ml × g_{vs}^{-1} × d^{-1}
	R^2	0.99	-
IKW	k	0.205	d^{-1}
	B_0	658.64	ml × g_{vs}^{-1}
	r	135.02	ml × g_{vs}^{-1} × d^{-1}
	R^2	0.98	-
IKW_SBC	k	0.214	d^{-1}
	B_0	674.60	ml × g_{vs}^{-1}
	r	143.36	ml × g_{vs}^{-1} × d^{-1}
	R^2	0.98	-

The highest values of each kinetic parameter were obtained for the reactor with the addition of SBC. Higher values translate into more biogas production at a faster rate. The highest constant of the biogas production rate (k) had sample IKW_SBC that was 0.214 d^{-1} while reactors without SBBC had k value of 0.205 d^{-1}. The maximum production of biogas from the substrate (B_0) for the IKW and IKW_SBC reactors differed by 1 and 2 ml × g_{vs}^{-1}. The rate of biogas production (r) in reactor IKW_SBC was 6% higher than in reactor IKW. The determination coefficients (R^2) showed a high level of adjustment of the measurements to the model, at the level of >0.98.

5. Conclusions

In the presented tests, the SBC material was produced, consisting of biochar and waste sulfur. The produced SBC material was tested for the addition of methane fermentation. It was shown that the yield of biogas production increased compared to the control samples. The implementation of SBC in the fermentation reactor increased the production by 4% and the maximum methane yield by 18 ml × g_{vs}^{-1}. The fermentation process was optimal, as almost the maximum values were obtained. Waste was used for the research, which does not apply to any economic sector. A significant portion of the stream is recycled, and there is even an idea to dispose of transformed sulfur in the oceans with the awareness that the ecosystem is disturbed [20]. Waste sulfur after transformation into composite shows hydrophobic properties, while other authors have shown that the contact of the material with water does not affect the pH [12] . Demonstrating an increase in biogas production with SBC material opens up opportunities to improve production efficiency. However, the implementation of such procedures should be preceded by detailed research. Quantitative studies have been carried out the next step is to define the qualitative aspects of the implementation of SBC into the reactor.

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