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EFFICIENCY OF THE METHANE FERMENTATION PROCESS OF MACROALGAE BIOMASS ORIGINATING FROM PUCK BAY

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Abstract: The aim of the conducted research was to determine the possibilities of using the biomass of macroalgae obtained from Puck Bay during May–September season in biogas production process. Model respirometry chambers were used to determine the amount of produced biogas and examine its quality composition. Depending on the month in which the algal biomass wasobtained, the experiments were divided into five stages. In each stage, the effectiveness of the biogas production process was tested for the applied loads in model fermentation chambers in the range from 1.0 kg DOM/m^3 · d to 3.0 kg DOM/m^3 · d. During the experiments it was found that the efficiency of biogas production varied from 205 dm^3/kg DOM to 407 dm^3/kg DOM depending on the month of the vegetation season and the applied organic matter load in the chamber. Methane content was very high and ranged from 63% to 74%.

INTRODUCTION

An increase in eutrophication causes a bloom of opportunist, drifting algae along seacoasts worldwide [6]. The level of nutrients flowing to the Baltic Sea has risen since around 1970 andthe nutritive components reaching the Baltic waters increase eutrophication and exert large effects on phytobentos in the coastal areas of the water region [1]. The environmental variability contributes to observed changes in the spatial distribution of algae and invertebrates. Many theories assume that biomass diversity observed in a local environment depends on the number and diversity of species occurring in a wider biogeographic region. It is a well-known general view that the community inhabiting a given region exerts a large influence on this process by, among others, building swimming pools. Similarly, currents transporting stretches of drifting algae are of great importance [6]. Replacement of perennial filamentous algal species by annual species is a common phenomenon alongeutrophized rocky shores. This entails potential consequences for marine biological diversity. An example in the upper part of the northern Baltic littoral is a quantitative decrease in the occurrence of brown algae *Fucusvesiculosus* and an increase in the number of filamentous algae *Pilayellalittotalis* and *Cladophoraglomerata*. Excessive occurrence of filamentous algae may lead to a decrease in the number of perennial macrophytes and bring serious effects for whole ecosystems, especially on shores [8]. In the shallow coastal waters of the Baltic Sea such species as the above-mentioned *Fucus* or *Zostera* and *Chara* must compete with fast-developing filamentous algae, which adapt better to conditions of lower transparency and increased sedimentation [1].

Puck Bay is regarded as the water area of the Baltic most at risk of eutrophication, mainly because of pollutant discharges from the Vistula and the lack of even mixing of the bay waters with open sea waters. The result of excessive eutrophication in the summer seasonis a growth in marine algae, which pollute the surrounding beaches while drifting on the bay waters. The problem of algae on the Tri-city beaches will increase until discharges of excessive quantities of pollutants (mainly nitrogen and phosphorus) to the bay are reduced. An additional source of pollution with algae on the Sopot beach may be their displacement from Puck Bay by means of favourable winds (south-western from May to September) and sea currents (mainly from northern directions). It was estimated that ca. $2.2-4.4 \times 10^2$ ton of dry algal matter could be transported to Sopot beach during 1 hour. In October, strong south-eastern winds may cause the dislocation of these algae deeper inland.

An alternative to the disposal of these materials may be methane fermentation in a biogas plant for energy recovery. This is particularly important because of the limited quantities of other substrates which are a potential source of biomass for a biogas plant. The use of algal biomass will lead toboth an energy gain connected with biogas production and an ecological gain connected with reduction of blooming and related consequences.

The aim of the conducted research was to determine the possibilities of using the biomass of macroalgae obtained from Puck Bay during May–September season in biogas production processes in mesophilic fermentation conditions using respirometric measurements.

The research was orientated towards determining the effectiveness of biogas production depending on the applied technological variant. The conducted analyses concerned the determination of the methane content in gaseous products of anaerobic bacterial metabolism and the effectiveness of biogas production from the introduced plant biomass.

METHODOLOGY OF RESEARCH

The research was carried out in laboratory conditions at the Department of Environmental Protection Engineering of the University of Warmia and Mazury in Olsztyn. The plant material used in the methane fermentation process in the experiment was fresh, mechanically precomminuted biomass of macroalgae obtained from Puck Bay in May–September season. The species composition of the used macroalgal substrate is presented in Table 1.

The inoculum and the model anaerobic reactors used during the experiment came from the fermentation chambers of an agricultural biogas plant in which the fermentation process for pig liquid manure and maize silage is conducted. The characterization of the used anaerobic sediment is presented in Table 2.

Table 1. Characterization of the biomass used in the experiment

Date	Macrophyte components	% share in the sample
May	*Pilayella littoralis* + *Ectocarpus* sp. *Enteromorpha* spp. + *Zostera marina*	90 > 10
June	*Pilayella littoralis* + *Ectocarpus* sp. *Enteromorpha* spp. *Zostera marina*	80 15 5
July	*Pilayella littoralis* + *Ectocarpus* sp. *Enteromorpha* spp. *Ruppia rostellata*	90 > 10
August	*Pilayella littoralis* + *Ectocarpus* sp. *Enteromorpha* spp.	90 > 10
September	*Pilayella littoralis* + *Ectocarpus* sp. *Enteromorpha* spp.	90 > 10

Table 2. Characterization of the anaerobic sediment used in the experiment

Parameter	Unit	min value	max value	mean	standard dev.
pH	-	7.89	8.08	7.98	0.10
Hydration	[%]	96.40	96.80	96.60	0.20
Dry matter	[%]	3.20	3.60	3.40	0.20
Volatile substances	[% DM]	47.32	51.04	49.18	2.63
Ash	[% DM]	48.96	52.68	50.82	1.86
CST	[s]	466	479	472.5	9.2

The experiment was divided into four research series differing in the size of the dry organic matter load for the reactor volume:

Series 1 – 1.0 kg DOM/$m^3 \cdot d$
Series 2 – 2.0 kg DOM/$m^3 \cdot d$
Series 3 – 3.0 kg DOM/$m^3 \cdot d$

In all series, the tested plant biomass used in the experiments was pre-homogenized using an appliance for mechanical destruction of organic substrate structures and then hydrated to the appropriate level with mains water. The hydration degree resulted from the adopted technological guidelines of the experiment.

The research used Oxi-Top Control respirometric unit from WTW, which consisted of reaction chambers tightly connected with measuring/recording equipment. The applied research method determined the activity of anaerobic sediment, the biodegradability of the used organic substrates and the quantity and composition of gaseous metabolism products. The equipment analysed andrecorded changes in partial pressure in the measuring chamber generated by biogas production in anaerobic processes conducted by microorganisms. In each conducted variant of the experiment 100 cm^3 of anaerobic sediment was introduced into the reaction chambers and the planned quantities of prepared organic substrate were then dosed.

A complete measuring unit, consisting of a reaction chamber and a measuring/recording appliance, was placed in a thermostatically-controlled cabinet with hysteresis not exceeding ± 0.5°C. Measurements were carried out at a temperature of 42°C. The measurement time was 20 d andthe pressure values in the reaction chamber were recorded every 15 min. Two days before the end of the measurement, a 30% sodium base (NaOH) was introduced into a special container inside the reaction chamber. This allowed carbon dioxide (CO_2) to be precipitated from the gas phase. The pressure decrease in the reaction chamber corresponded to the carbon dioxide content, while the methane content was responsible for the remaining pressure level. The contents of the reactors were mixed using magnetic stirrers.

The basis for calculations of therespirometrictests is the ideal gas equation:

$$n = \frac{P \cdot V}{R \cdot T} \tag{1}$$

where:
n – number of gas moles [mol],
P – gas pressure [Pa],
V – gas volume [m^3],
R – universal gas constant [8.314 J/mol · K],
T – temperature [K].

Carbon content in the gaseous phase:

$$n_{CO_2} + n_{CH_4} = \frac{P_1 \cdot V_g}{R \cdot T} \times 10^{-4} \tag{2}$$

where:
$n_{CO_2} + n_{CH_4}$ – number of generated moles of carbon dioxide and methane [mol],
P_1 – gas pressure difference in the research vessel at the beginning and at the end of the experiment, caused by oxygen consumption and absorption of the forming CO_2 [hPa],
V – gaseous phase volume in the measuring chamber [ml],
R – gas constant [8.314 J/mol · K],
T – incubation temperature [K],
10^{-4} – conversion factor for Pa to hPa and m^3 to cm^3.

Carbon dioxide content in the gaseous phase:

$$n_{CO_2} = \left(\frac{P_1 \times V_g - P_2 \times (V_g - V_{KOH})}{R \times T} \right) \times 10^{-4} \tag{3}$$

where:

n_{CO} – number of generated moles of carbon dioxide [mol],

P_2 – Gas pressure difference in the appropriate research vessel at the end of the experiment minus the pressure at the beginning of the experiment minus the pressure in the blank test after adding the KOH solution [hPa],

V_{KOH} – volume of the KOH solution [ml].

Methane content in the gaseous phase:

$$n_{CH_4} = n_{CO_2+CH_4} - n_{CO_2} \tag{3}$$

The rate of the biogas production process depending on the type of organic substrate and the applied organic compound load for the chambers was also determined on the basis of the respirometric tests. Pressure measurements inside the chamber carried out by the analyzer at 15-minute intervals assessed the processrate. Constant rates of reactions were determined on the basis of the obtained experimental data by non-linear regression using Statistica 8.0 software. The iterative method was applied, in which the function is replaced in each iterative step with a differential linear in relation to the determined parameters. The coefficient of convergence φ^2 was adopted as the measure of the curve's fit (with determined parameters) to experimental data. This coefficient is the ratio of the sum square of deviations of the values calculated on the basis of the determined function from experimental values to the sum square of deviations of experimental values from the mean value. The convergence improves along with the lowering of the value of the φ^2 coefficient. Such a fit of the model to experimental points was adopted in which the coefficient of convergence did not exceed 0.2.

RESEARCH RESULTS

It was observed that the efficiency of biogas production per kilogram of dry matter introduced into the technological system decreased with a rise in the load of carbon compounds. In the first research series, in which a load of 1.0 kg DOM/$m^3 \cdot d$ was used, it was found that the quantity of produced biogas was from 304 m^3/t DM in August to 327 m^3/t DM in June. The quantity of methane in biogas in this part of the experiment ranged from the level of 63% in September to the value of 66% in May.

In the second series, in which the applied organic matter load was 2.0 kg DOM/$m^3 \cdot d$, the biogas production ranged from the level of 304 m^3/t DM in September to 331 m^3/t DM in June. It was found that, in this research series, the quantity of methane in gaseous metabolism products ranged from 60% in September to 67% in June.

The worst results connected with the quantity of biogas production and its quality composition were found when the applied organic compound load for the chamber was 3.0 kg DOM/$m^3 \cdot d$. The biogas production was recorded at the level of 241 m^3/t DM in May and 276 m^3/t DM in August. The methane content in the gaseous phase ranged from 57% in September to 61% in August.

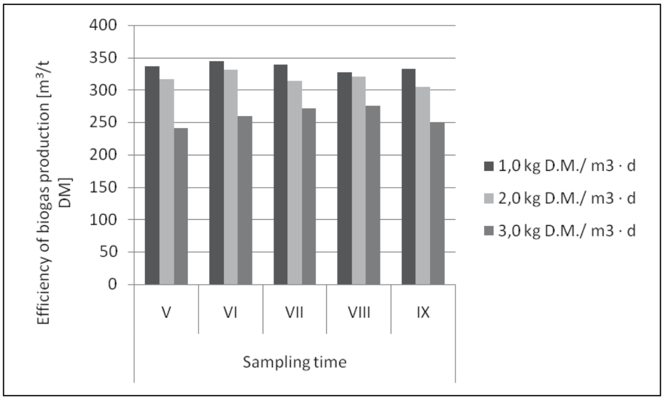

Fig. 1. Efficiency of biogas production depending on the applied load

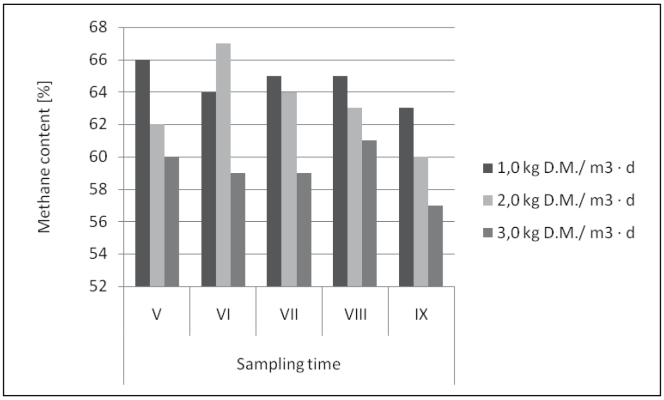

Fig. 2. Methane content in biogas depending on the applied load

DISCUSSION

The concept of using algae as fuel was proposed for the first time by Meier in 1955, this idea was developed in the 1960s by Oswald and Golueke. When the costs of conventional fuels started to rise rapidly around 1970, attention was again drawn to the possibility of using algae as a biofuel [3]. Brennan *et al.* maintained that biogas originating from algae was able to compete with fossil fuels [2].

Poland has a considerable number of large and small biogas plants using plant substrates for biogas production. Although many species of algae, i.e. *Macrocystis*, *Sargassum*, *Laminaria*, *Ulva*, *Cladophora*, have been studied with regard to obtaining biogas, algae are not yet used as substrate in the biogas plants [3]. Considering the results presented by many scientists around the world, algae is a raw material which generates a huge quantity of biomass for the production of high-efficiency biofuels, without competing with food and feedstuffs [13]. Biogas production from algae has several advantages compared with conventional energy crops. Algae are able to double their mass every 24 h, they do not need fresh water for growth and development and they do not require plant protection products. Although they exist in a water environment, they need less water than land plants [17]. The world is facing large energy challenges, therefore it is of the utmost importance to discover new cost-effective technologies, which will be the future of the world power industry [13].

As Kruk-Dowgiałło and Skóra report, the specific composition of algae obtained from the Vistula Lagoon proves the eutrophication of this water body [8, 15]. Filamentous brown algae, which include the species *Pilayellalittoralis* and *Ectocarpussp*., occur in large numbers in the coastal waters of the Baltic, these waters are characterized by considerable fertility and pollution. The mass occurrence of these algae lowers the economic value of the water region, they do not have any economically useful quality and their mass blooms around beaches, making the water region less attractive for tourists [15]. Similar to the above-mentioned species from the brown algae phylum, the increased number of green algae from the genus *Enteromorphademonstratesa* progressive eutrophication process [8]. For this reason, the disposal of these algae would not only create an efficient energy source, but also improve the value of the Vistula Lagoon.

Harun *et al.* conducted research on potential, theoretical methane production from algae, using calculations based on seaweeds. They consisted of 51% protein, 21% carbohydrates and 16% fats. On the basis of the algal composition, they specified four cases of methane production. In the first case, they assumed that all fractions would take part in methane production, in the second, it was obtained from protein and lipids, while the carbohydrates present served to produce ethanol. The third variant consisted in using proteins and sugars, with fats used to obtain biodiesel. In the fourth case, only proteins served to produce methane. It is not surprising that the first case had the highest methane production: 410 m^3/t DM was acquired, daily gas production amounted to 60 dm^3/d, which produced 200 MW/d of electrical energy. The obtained biogas, biodiesel and ethanol were then converted into electrical energy in order to examine which of the obtained biofuels would be the most efficient source of renewable energy. Energy production from the biogas was 14.04 MJ/kg, from the biodiesel 6.6 MJ/kg and from the ethanol only 1.79 MJ/kg.

Considering that the reports described above were only a theoretical model, the results acquired from own research (in the best case around 350 m^3/t DM of biogas) are comparable with those described above. Harun *et al.* also provided the biogas content in methane obtained from algae in the range 55−75%, which also correlates with own resultsof 57−67% [5]. Massgnug *et al.* also conducted research concerning the efficiency of the methane fermentation process for algae. The research aimed at proving that the biogas potential is closely connected with the species of algae which is used for fermentation. They used seven dominant algal species. Thus, for example, the fermentation of green algae – *Chlamydomonasreinhardtii* – provided the highest quantity of biogas 586CH_4/t DM with 66% methane content. The lowest quantity of gas was obtained during biogas tests for *Scenedesmus obliquus*, 287 m^3/t DOM with 62% methane content [11]. Singh and Gu and Parmar *et al.* also recorded the methane efficiency from algae. The best substrate for fermentation seems to be the brown alga *Laminariadigitata* belonging to the order Laminariales – around 500 m^3 CH_4/t DM, followed by an alga from the same class *Macrocystis* 390−410 m^3 CH_4/t DM, Gracilaria sp. 280−400 m^3 CH_4/t DM, *Laminaria* sp. 260−280 m^3 CH_4/t DM and the worst was an alga from the class of green algae *Ulva* sp.

– only 200 m^3 CH_4/t DM [13, 11]. According to Krzemieniewski *et al.*, it is possible to obtain biogas in the methane fermentation process for algae in the quantity of 280 dm^3/kg COD, the methane content according to the authors can even reach 83% [9].

Mussgnug *et al.* compared the results from the fermentation of algae to traditional energy crops. All microalgae studied showed a higher methane content (62–67%) compared with standard maize silage (54%) [11]. Their results were also characterized by a higher methane content. Among traditional energy crops, according to Weiland, around 400 m^3 CH_4/t DM can be obtained from crops such as lucerne and clover, 100 m^3 CH_4/t DM less from ryegrass and Sudan grass [16]. Dinuccio *et al.* recorded the efficiency of biogas production and the methane content in such substrates as maize, grapes, straw, rice and tomato skins. In these cases, the methane content in biogas stabilized to between 50%–60%, less than in the case of the studied algae. Methane production from rice was 416 m^3/t DOM and gas production from straw was 360 m^3/t DOM because of a lower content of cellulose and hemicelluloses [4]. A smaller content of cellulose and hemicelluloses should also be perceived as the cause of the lower quantities of methane obtained from fermentation of algae. Similar conclusions were reached by Brennan and Owende, who claim that a high content of protein fractions in algae influences a low C/N ratio, which is the cause of lower efficiency of methane production from algae compared with land plants. In order to increase methane production, they recommendedthe addition of waste paper in a ratio of 1:1. In this way, they obtained a twofold increase in the quantity of methane production from algae [2]. According to Łebkowska and Załęska-Radziwiłł fraction of protein in the algal biomass may represent from 40 to 60% [10].

CONCLUSIONS

It was found out that the obtained technological effects connected with the quantity of forming biogas and the methane content depended directly on the applied organic compound load for the anaerobic chamber. This is particularly noticeable in the case of biogas production efficiency and with regard to the quantity of the introduced organic matter of the substrate. The highest level of methane production per ton of organic matter introduced into the reactor at the level of 240 m^3CH_4/t DOM was recorded in the range of applied loads from 1.0 kg DOM/$m^3 \cdot d$ to 2.0 kg DOM/$m^3 \cdot d$. Using higher values of this technological parameter directly influenced a reduction of methane production. The percentage of methane in the forming biogas also appeared similar. Values close to 65% were obtained in the first and second series of the conducted experiment. The quantity of methane in biogas fell significantlywith higher loads of dry organic matter used in the chamber.

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REFERENCES

[1] Berglund J., Mattila J., Ronnberg O., Heikkila J., Bonsdorff E.: *Seasonal and inter-annual variation in occurrence and biomass of rooted macrophytes and drift algae in shallow bays Estuarine*, Coastal and Shelf Science, **56**, 1167–1175 (2003).

[2] Brennan L., Owende P.: *Biofuels from microalgae – A review of technologies for production, processing, and extractions of biofuels and co-products*, Renewable and Sustainable Energy Reviews, 14, 557–577 (2010).
[3] Demirbas A.: *Use of algae as biofuel sources*, Energy Conversion and Management, **51**, 2738–2749 (2010).
[4] Dinuccio E., Balsari P., Gioelli F., Menardo S.: *Evaluation of the biogas productivity potential of some Italian agro-industrial biomasses*, Bioresource Technology, **101**, 3780–3783 (2010).
[5] Harun R., Davidson M., Doyle M., Gopiraj R., Danquah M., Forde G.: *Technoeconomic analysis of an integrated microalgae photobioreactor, biodiesel and biogas production facility*, Biomass and bioenergy, **35**, 741−747 (2011).
[6] Kotta J., Paalme T., Püss T., Herkül K., Kotta I.: *Contribution of scale-dependent environmental variability on the biomass patterns of drift algae and associated invertebrates in the Gulf of Riga, northern Baltic Sea*, Journal of Marine Systems, **74**, 116–123 (2008).
[7] Kraufvelin P., Salovius S.: *Animal diversity in Baltic rocky shore macroalgae: can Cladophora glomerata compensate for lost Fucus vesiculosus Estuarine*, Coastal and Shelf Science, **61**, 369–378 (2004).
[8] Kruk-Dowgiałło L., Opioła R.: *Makrofitobentos, Charakterystyka biologiczna*, (w:) *Warunki środowiskowe polskiej strefy południowego Bałtyku w 2000 roku*, IMGW, Materiały Oddziału Morskiego, Gdynia, 160−167 (2001).
[9] Krzemieniewski M., Dębowski M., Zieliński M.: *Glony jako alternatywa dla lądowych roślin energetycznych*, Czysta Energia, **9**, 25−27 (2009).
[10] Łebkowska M., Załęska-Radziwiłł M.: *Usable products from sewage and solid waste*, Archives of Environmental Protection, 37, 15−19 (2011).
[11] Mussgnug J.H., Klassen V., Schlüter A., Kruse O.: *Microalgae as substrates for fermentative biogas production in a combined biorefinery concept*, Journal of Biotechnology, **150**, 51–56 (2010).
[12] Parmar A., Singh N.K., Pandey A., Gnansounou E., Madamwar D.: *Cyanobacteria and microalgae: A positive prospect for biofuels*, Bioresource Technology, **102**, 10163–10172 (2011).
[13] Rawat I., Ranjith Kumar R., Mutanda T., Bux F.: *Dual role of microalgae: Phycoremediation of domestic wastewater and biomass production for sustainable biofuels production*, Applied Energy, **88**, 3411–3424 (2011).
[14] Singh J., Gu S.: *Commercialization potential of microalgae for biofuels production*, Renewable and Sustainable Energy Reviews, **14**, 2596–2610 (2010).
[15] Skóra K.E.: *Dlaczego ochrona przyrody Bałtyku jest nieskuteczna?* [in:] Florek W. (red.): *Słowiński Park Narodowy. 40 lat ochrony unikatowej przyrody i kultury. Smołdzino.*
[16] Weiland P.: *Production and Energetic Use of Biogas from Energy Crops and Wastes in Germany*, Applied Biochemistry and Biotechnology, **109**, 263−274 (2003).
[17] Zamalloa C., Vulsteke E., Albrecht J., Verstraete W.: *The techno-economic potential of renewable energy through the anaerobic digestion of microalgae*, Bioresource Technology, **102**, 1149–1158 (2011).

WYDAJNOŚĆ PROCESU FERMENTACJI METANOWEJ BIOMASY MAKROGLONÓW POCHODZĄCYCH Z ZATOKI PUCKIEJ

Celem prowadzonych badań było określenie możliwości wykorzystania biomasy makroglonów pozyskiwanych z Zatoki Puckiej w okresie od maja do września w procesie wytwarzania biogazu. Do określenia ilości wytwarzanego biogazu oraz zbadania jego składu jakościowego wykorzystano modelowe komory respirometryczne. W zależności od miesiąca, w którym pozyskiwano biomasę glonową eksperymenty podzielono na pięć etapów. W każdym z etapów testowano efektywność procesu biogazowania w zakresie stosowanych obciążeń modelowych komór fermentacyjnych w zakresie od 1,0 kg s.m.o/m^3 · d do 3,0 kg s.m.o./m^3 · d. W trakcie eksperymentów stwierdzono, iż wydajność wytwarzania biogazu kształtowała się w zakresie od 205 dm^3/kg s.m.o. do 407 dm^3/kg s.m.o. w zależności od miesiąca okresu wegetacyjnego oraz stosowanego obciążenia komory ładunkiem substancji organicznej. Zawartość metanu była bardzo wysoka i mieściła się w granicach od 63% do 74%.