

**Mirosław KRZEMIENIEWSKI, Dawid SZWARC, Marcin ZIELIŃSKI,
Karolina KUPCZYK, Magdalena ROKICKA, Marcin DĘBOWSKI**
Uniwersytet Warmińsko-Mazurski w Olsztynie, Olsztyn

THE POSSIBILITY OF USING CARBON DIOXIDE FROM BIOGAS IN THE PRODUCTION OF MICROALGAE BIOMASS

Key words

Microalgae, carbon dioxide, biogas, biosequestration.

Abstract

The use of biogas originating from the methane fermentation process is one of the most promising methods for the production of renewable energy. The study aimed to determine the possibilities of using biogas from anaerobic digestion of dairy wastewater to intensify the production of microalgae biomass. The tested culture was *Chlorella* sp., which originated from the Baltic Algae Culture Collection. The research was conducted in two variants to determine the inhibitory effect of hydrogen sulphide on the growth of microalgae biomass. The results confirmed the possibility of the efficient use of the carbon dioxide contained in the biogas to increase the productivity of *Chlorella* sp. Tests performed in the present research confirmed CO₂ removal of more than 80% in all variants (with raw biogas, desulfurized biogas, and with CO₂).

Introduction

The sustained development of civilisation requires the introduction of new technologies based on ecological methods of energy production. The use of

biogas originating from the methane fermentation process is one of the most promising methods for the production of renewable energy [Piętak, Radkowski, 2011]. Microalgae *Chlorella* sp. is a photoautotrophic organism, which can photosynthesize. This characteristic means that an essential element in the growth of biomass *Chlorella* sp. is access to CO₂. In order to reduce the cost of mass rearing, new and cheaper sources of carbon dioxide are being sought. One of the most promising sources is biogas containing approximately 50% of CO₂ [Chien-Ya et al., 2014].

For the production of biogas in the methane fermentation process, easily accessible substrates are used, which are characterised by a high content of biodegradable substance. It is therefore possible to consider the huge potential of the biomass of microalgae, which may be cultivated for energy production purposes [Dębowski et al., 2013]. Under favourable conditions, numerous algae strains are able to double their mass in 24 hours, or even faster [Lihong, Weigong, 2005]. The process of photosynthesis occurring in algae cells involves the assimilation of simple inorganic compounds, carbon dioxide, water, and biogenic salts, in the presence of luminous energy. This leads to the formation of carbohydrates and oxygen [Brown et al., 2003]. In order to achieve optimum algae growth, it is necessary to provide them with nitrogen and minerals, such as phosphorus, iron, and, in some cases, silicon. In order to define the minimum nutritive requirements, a molecular model of algae was evaluated: $CO_{0.48}H_{1.83}N_{0.11}P_{0.01}$. The carbon content in the dry mass of the algae biomass reaches approx. 50%. On average, synthesis of 1 kg of the algae biomass requires from 2 to 3 kg of CO₂ [Chisti, 2004].

Potentially, the biogas plant installation and the microalgae farm can be connected into one symbiotic system. The presence of carbon dioxide in biogas decreases its calorific value, although it can be used for an improvement in algae cultivation efficiency [Tongprawhan et al., 2014]. The biogas plant effluent delivers biogen necessary for algae cultivation, and the low-temperature waste heat from the burning of biogas provides the proper temperature conditions for its cultivation. The biogas plant supplies the necessary nutrient media, while the algae cultivation is a source of biomass for the fermentation process, and utilises the waste.

The goal of the presented studies was to define the influence of biogas originating from a continuously stirred-tank reactor (CSTR) on the efficiency of microalgae biomass production in a closed photobioreactor. The studies were carried out in three variants, analysing the influence of raw carbon dioxide, raw biogas, and desulfurized biogas.

1. Methodology of the research

The studies were divided into two variants. In the first variant, the algae mixture was fed with raw biogas, while in the second variant, desulfurized biogas was used. Additionally, a control sample was investigated simultaneously, in which the microalgae culture was exposed to pure carbon dioxide. Biogas was added to the photobioreactors once, at the beginning of the breeding cycle. After adding the gas, the photobioreactor was closed hermetically. The biogas used in the experiment was obtained from an anaerobic reactor with a volume of 70 dm³, operating under mesophilic conditions. Model dairy wastewater prepared with sour whey was used as an organic substrate in the fermentation process.

In the second variant, desulfurization of the biogas was carried out using a column with a volume of $V = 1800 \text{ cm}^3$. The desulfurizing column was packed with granulated iron (III) oxide with an average grain size of 0.3 mm. The biogas was pumped through the column at a rate of 1.6 cm³/s. The load of the filtration layer with biogas amounted to 3 dm³/dm³·h. The observed quality of raw biogas at the outflow from the anoxic reactor and after passing through the desulfurizing column is shown in Table 1. In the control test, pure carbon dioxide was used in an amount equivalent to the introduced biogas reactors by varying the pressure of gas introduced. In Variants 1 and 2, 0.451 dm³ of biogas under a pressure of 48 kPa was added to the photobioreactor, while the control contained 0.307 dm³ of carbon dioxide, which generated a pressure of 2.4 kPa.

Table 1. Qualitative composition of raw and desulfurized biogas used in the experiment

Parameter	CH ₄ % v/v	CO ₂ % v/v	O ₂ % v/v	H ₂ S ppm
Carbon dioxide	N/A	99,95	N/A	N/A
Raw biogas	52±2	48±2	0±0.4	1000±100
Desulfurized biogas	52±2	48±2	0±0.4	0

The experiment was carried out under laboratory conditions at a temperature of 22±1°C. The separate test station consisted of a closed photobioreactor, a magnetic stirrer, external light source, and two gas-sampling connectors (Fig. 1). The photobioreactor consisted of a closed glass container with a working capacity of 1.1 dm³ equipped with two connectors, by which it was possible to measure the qualitative composition of the working gas in the culture medium, and all photobioreactors were illuminated with fluorescent lamps with an intensity of 5000 lux.

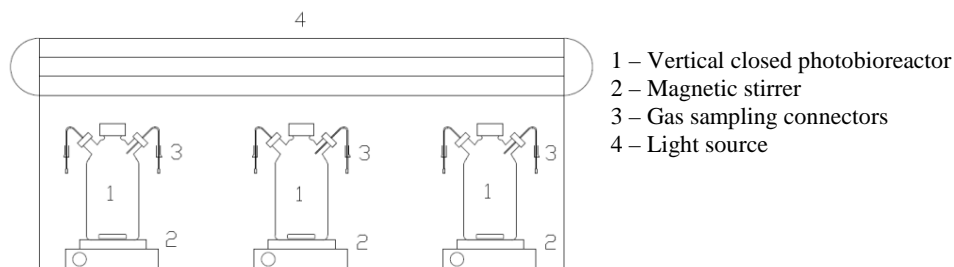


Fig. 1. Scheme of the laboratory stand

A mixture of microalgae culture consisting of *Chlorella* sp. (90%) and *Scenedesmus* sp. (10%) was used in the experiment. The initial concentration of dry organic matter of algae was $0.500 \pm 0.01 \text{ g/dm}^3$. The algae cells were suspended in a synthetic medium prepared according to the composition shown in Table 2.

Table 2. Composition of the synthetic nutrient medium [Zieliński et al., 2011]

Reagent	Dose
NH_4Cl	76.1 mg/l
$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	46.2 mg/l
NaCl	10.1 mg/l
$\text{KCl}, \text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	4.7 mg/l
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	16.7 mg/l
NaHCO_3	243.3 mg/l
Na_2CO_3	162.2 mg/l
$(\text{FeCl}_3 \cdot 6\text{H}_2\text{O}, \text{ZnSO}_4)$	<0.2 mg/l
$(\text{MnSO}_4 \cdot \text{H}_2\text{O}, \text{CuSO}_4)$	<0.2 mg/l
$\text{CH}_4\text{N}_2\text{O}$	80 mg/l

The zero measurements of composition of the biogas added to the algae mixture were carried, directly after connecting the gas tank to the photobioreactor. The subsequent measurements were carried out every 1 hour during the first 6 hours, and then after 24, 48, 72, and 78 hours. The goal was to observe changes in carbon dioxide and methane concentrations with the passing time. Every variant of the study was carried out in triplicate.

The GFM 416 portable gas analyser from Gas Data was used for the examination of the qualitative composition of the biogas. The following biogas components were analysed: CH_4 , CO_2 , O_2 , and H_2S . During the experiment, the

contents of ammonia nitrogen and orthophosphates (V) were monitored continuously using LCK Hach Lange cuvette tests. The dry organic matter (d.o.m.) content was analysed by gravimetric method.

The statistical analysis of the acquired results was made based on the STATISTICA bundle. Verification of the hypothesis concerning the decomposition of each tested variable was determined based on the W Shapiro-Wilk test. A one-factor analysis of variations (ANOVA) was conducted to determine the significance of differences between the variables. The Levene test determined the uniformity of the variations in groups. A RIR Tukey test was used to determine the differences between the analysed variables. The tests adopted the statistical significance of $p = 0.05$.

2. Results

In Variant 1, after 72 hours in the photobioreactors, the CO_2 concentration of the biogas was reduced to $10 \pm 3.5\%$ (Fig. 2). After this time, the CO_2 assimilation process stopped. The observed effect was 81% CO_2 removal efficiency from the biogas. In this part of the experiment, the final concentration of microalgae biomass was 278 ± 7.0 mg d.o.m./dm³ and biomass growth rate stood close to 76 ± 2.0 mg d.o.m./dm³·d (Fig. 5). The use of nutrients in the culture medium was 7.1 mg/dm³ in the case of N-NH₄ and 2 mg/dm³ in respect to P-PO₄ (Figs. 6 and 7). In the variant where the biogas was initially desulfurized before being introduced into the culture medium, more effective use of CO_2 for in growing biomass of microalgae was observed. The final concentration of the gas component of fermentation was approximately $4 \pm 0.3\%$, which was due to the absorption of CO_2 with an average efficiency of 91.7% (Fig. 3). During the experiment, 0.515 ± 0.08 g of CO_2 was removed from the biogas. This part of the experiment demonstrated significantly ($p = 0.05$) higher intensities of the biomass growth of microalgae. At the end of the experimental cycle, the concentration of microalgae in bioreactor was 310 ± 5.0 mg d.o.m./dm³; whereas, the biomass growth rate stood at an average level of 86.67 mg d.o.m./dm³·d (Fig. 5). The final concentration of N-NH₄ in the culture medium was 10.8 ± 0.3 mg/dm³, while the P-PO₄ was 2.8 ± 0.1 mg/dm³.

In the control test, where pure CO_2 was dosed into the system, we noted its complete removal from the gas phase. This had a direct impact on the resulting concentrations of algae biomass at the end of the experiment, amounting to close to 329 ± 5.0 mg d.o.m./dm³. In this case, the final content of the N-NH₄ was 10.1 ± 0.3 mg/dm³, while orthophosphate was 2.6 ± 0.1 mg/dm³ (Figs. 6 and 7). Variant 2 was characterized by an equally high demand for biogenic compounds.

In all variants of the experiment, a commensurate increase in oxygen relative to the removed CO_2 was observed. In Variant 1, the amount of oxygen

after 6 hours was 10%. After another 2 days, the amount of oxygen rose 40%. In Variant 2, after 6 hours, there was a decrease of 12% CO₂. At the same time, in the reactor, the oxygen content rose to 12%. In the control test, the final amount of O₂ was 100%, which indicated that a given amount of CO₂ was completely metabolized and converted into pure oxygen (Fig. 4).

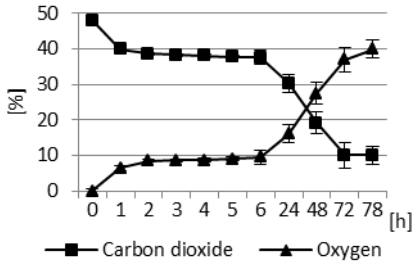


Fig. 2. Changes in the content of CO₂ and O₂ in Variant 2

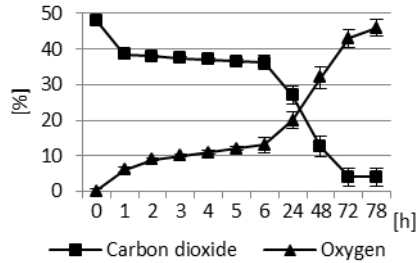


Fig. 3. Changes in the content of CO₂ and O₂ in Variant 2

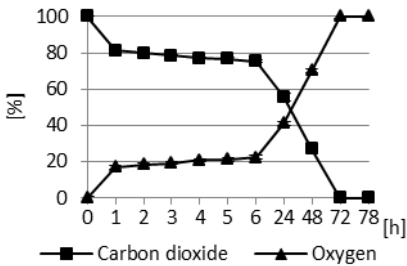


Fig. 4. Changes in the content of CO₂ and O₂ in the control test

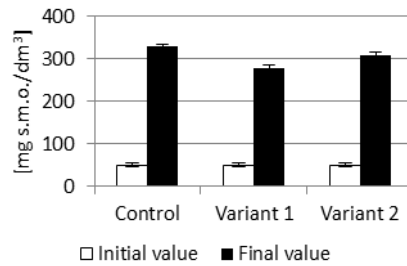


Fig. 5. The content of microalgae biomass in the culture medium

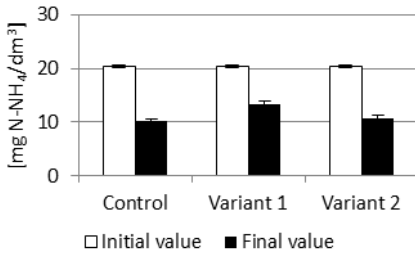


Fig. 6. The concentrations of N-NH₄ in the culture medium

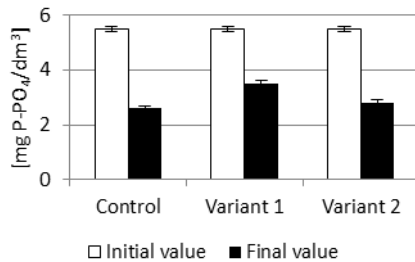


Fig. 7. The content of microalgae biomass in the culture medium

3. Discussion

Conde et al. [1993] and Mandeno et al. [2005] obtained a degree of carbon dioxide removal at levels of 74 – 95% and 87%, respectively. Tests performed in the present research confirmed CO₂ removal of more than 80% in all variants. Basu et al. [2013] used the *Scenedesmus obliquus* strain in the process of the purification of flue gas from carbon dioxide. Their experiment proved that the CO₂ concentration decreased from 13.8% to 0.5%, yielding an effectiveness of 96.38%. Zhao and Su [2014] carried out research aimed at the investigation of the tolerance of the algae cells to an increased concentration of carbon dioxide. The study consisted of the cultivation of a series of algae species in the presence of various CO₂ concentrations. The authors showed that *Chlorella* sp. was the most resistant algae strain, achieving a maximum rate of cell growth at a level of 0.9 g d.m./dm³·d. The control sample also showed a high growth rate of 90 mg d.o.m./dm³·d. Zhano and Su [2014] also proved that dosing desulfurized biogas with a flow rate of 0.1 vvm led to an efficiency of carbon dioxide capture at a level of 75%. When the flow rate was increased to 0.3 vvm, the efficiency dropped to approx. 60%.

The possibility of utilising algae for CO₂ removal from biogas is also confirmed by Meier et al. [2014]. In their studies, they used *Nannochloropsis gaditana* algae. *In the process of the biogas purification from CO₂, they obtained a total efficiency at a level of 96%; the algae removed approx. 84%, and the remaining 12% was dissolved in water.* Yue and Chen [2005] culturing freshwater microalgae of the genus *Chlorella*, which grew at elevated CO₂ concentrations, observed approximately 200% higher growth rate than that observed in the air. Even at 25% conversion of carbon dioxide in the reactor, Packer [2009] obtained 4 g d.o.m. / dm³·d dry weight of the algae, although this was grown in an open pond. In the present research, variants of biogas dosage yielded similar amounts of biogas-desulfurized biomass, but these were lower than in the reactor with carbon dioxide.

Chien-Ya et al. [2012] show that an adverse effect of hydrogen sulphide on algae biomass growth, which is confirmed by the present research. The authors described an experiment utilising a mutated *Chlorella* sp. strain for the capture of carbon dioxide from biogas, and they proved that concentrations of hydrogen sulphide exceeding 100 ppm adversely affect the growth of the algae biomass. After 7 days of the experiment, the researchers obtained 2.25 g d.m./dm³ from the initial level of 1.25 g d.m./dm³, with a hydrogen sulphide concentration of 100 ppm. In the case of the H₂S concentration equal to 150 ppm, dry matter increased only by 0.25 g d.m./dm³ in 7 days.

The positive results of laboratory tests made it possible to use carbon dioxide from flue gas. In order to increase *Chlorella* sp. Biomass, Chien-Ya K. et al. [2014] decided to use flue gas from the industrial sector. To this end, they introduced combustion gas with various dilutions, containing 2–14% CO₂, to an algae mixture. They achieved a maximum increase in the dry matter of the algae cells in the test for which combustion gas with the highest concentrations was used. After seven days of the experiment, they obtained a 2.855 g/dm³ increase in the dry matter content.

Published data indicates that algae can assimilate approx. 90% of carbon dioxide originating from various industrial installations [Takahashi, Murata, 2008; Brown, 1996]. Tang et al. [2011] indicate that the species *Scenedesmus obliquus* and *Chlorella pyrenoidosa* show a rapid increase in biomass in cultures kept up to 30% concentration of carbon dioxide. On the other hand, Chiu et al. [2009] report that a 5% concentration of carbon dioxide is harmful to species *Nannochloropsis oculata*. Lihong and Weigong [2005], while searching for an algae strain that is highly tolerant to the presence of carbon dioxide, chose *Chlorella* sp. They investigated the increase potential of the algae biomass by aerating the algae mixture with air of various CO₂ concentrations. The studies proved that the increase in the dry matter of cells might reach 200% in relation to the test with atmospheric air.

Conclusion

The results confirm the possibility of using carbon dioxide contained in biogas to intensify the production of microalgae biomass. Research has shown that the use of desulfurized biogas allows for higher technological effects related to biosequestration of carbon dioxide contained in a biogas, as well as the efficiency of microalgae biomass growth. The technological efficiency of biogas-powered systems was significantly lower compared to the variant in which the pure carbon dioxide was tested. However, given the economic aspect and the environmental advantages, the use of CO₂ from biogas technology is more promising. The use of biogas in the process of the intensification of farming microalgae allowed for efficient biomass growth and enrichment of the fermentation gas; however, it directly influenced the increase of oxygen in the biogas, which is undesirable, because it can produce a highly combustible mixture.

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Możliwość wykorzystania ditlenku węgla pochodzącego z biogazu w procesie produkcji biomasy mikroglonów

Słowa kluczowe

mikroalgi, ditlenek węgla, biogaz, biosekwestracja.

Streszczenie

Trwały rozwój cywilizacji wymaga wprowadzenia nowych technologii opartych na ekologicznych metodach produkcji energii. Zastosowanie biogazu pochodzącego z procesu fermentacji metanowej jest jednym z najbardziej obiecujących sposobów wytwarzania energii odnawialnej. Przeprowadzone badania miały na celu określenie możliwości wykorzystania biogazu pochodzącego z fermentacji metanowej ścieków mleczarskich do intensyfikacji produkcji biomasy mikroglonów. Testowaną kulturą była *Chlorella* sp. pochodząca z Kolekcji Kultur Glonów Bałtyckich. Badania prowadzone były w dwóch wariantach mających na celu określenie inhibicyjnego wpływu siarkowodoru na przyrost biomasy mikroglonów. Uzyskane wyniki potwierdziły możliwość efektywnego

wykorzystania ditlenku węgla zawartego w biogazie pofermentacyjnym do zwiększenia wydajności produkcji *Chlorelli* sp. Badania przeprowadzone w niniejszym badaniu potwierdziły usuwanie CO₂ w ilości ponad 80% we wszystkich wariantach (z surowym biogazem, z biogazem odsiarczonym oraz z czystym ditlenkiem węgla).

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