

## **Biogas-conditioning with microalgae**

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**Abstract:** To promote the expansion of feasible biogas production, an optimisation of the whole process chain is essential. In this context the optimisation of the biogas-conditioning process is of great importance. By improving this process, new fields of application, e.g. its usage as car fuel or natural gas substitute can be developed. Currently applied chemical/physical conditioning techniques are cost intensive and hinder a reasonable production for smaller biogas plants. At present a possible low-cost alternative by application of microalgae is being investigated at the University of Rostock. To determine their ability to reduce carbon dioxide from biogas, laboratory-scale photobioreactors with a culture volume of 0.45 l are deployed. In 2008 the microalgae *Chlorella sp.* was analysed in terms of conditioning biogas. As a result the biogas components CO<sub>2</sub> and H<sub>2</sub>S could be reduced up to 97.07% and 100%, respectively. Also an increase of microalgae cell count could be documented, which provides interesting alternatives for the production of algae ingredients.

**Key words:** Biogas, conditioning, microalgae, carbon dioxide, photobioreactor

### **INTRODUCTION**

In combination with increasing commodity prices in Germany biogas plants have been installed in great quantities. The produced biogas is used predominantly for conversion into heat and electricity and is also deployed as fuel or is fed into the natural gas system. However the more or less complex conditioning of the gas is required for energetic use. Since the methane content in the gas is approx. 55%, the proportions of carbon dioxide and hydrogen sulphide, especially, must be eliminated. Currently the hydrogen sulphide elimination is carried out either by using a desulphurisation filter or by addition of oxygen and ferrous ions, respectively, into the gas compartment. Although these procedures are comparatively inexpensive, the conditioning effect is suboptimal. Furthermore the carbon dioxide portion is unaffected. In larger plants the biogas is adapted to the quality of natural gas by applying cost-intensive conditioning procedures. In this case a reasonable production is only possible by producing high amounts of biogas.

Compared to the currently deployed biogas conditioning procedures the application of microalgae appears as a low-cost alternative. The results of previous studies showed that the proportion of carbon dioxide could be reduced (Anonymous, 2005; Conde et al., 1993; Tieze et al., 2006). Moreover the use of algae allows the production of marketable products such as proteins, pharmaceuticals, crop protection products, ameliorants and fish food (Griehl et al. 2007; Mar et al., 2007; Metting, 1996; Ördög et al., 2004; Pulz und Gross, 2004; Thomsickova and Kopecky, 2007).

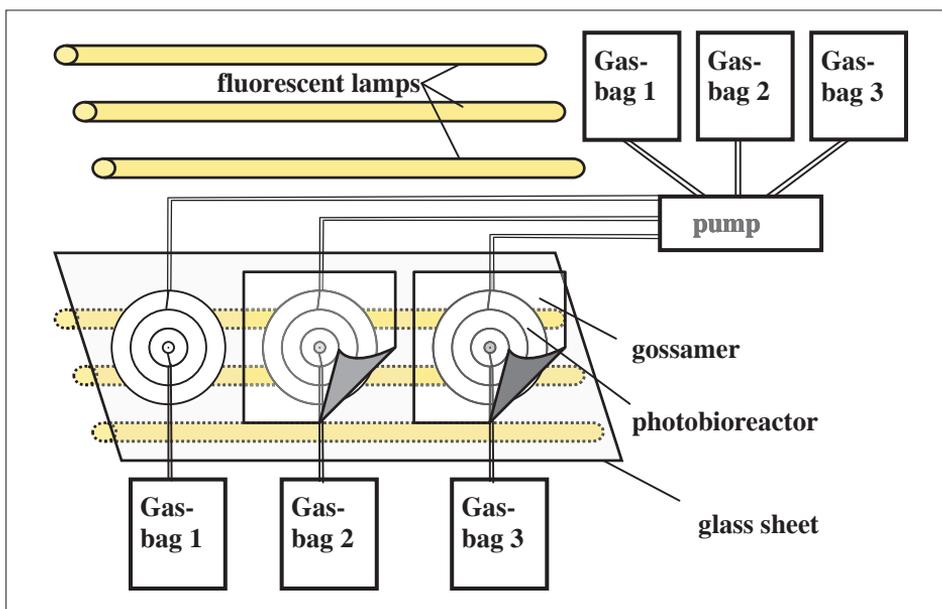
In this article the partial results of an experiment at the University of Rostock (Institute for Farm Animals Sciences and Technology/Institute of Biosciences) is described, in which biogas was treated by using *Chlorella vulgaris*. The aim of this investigation was to show the possibility of cultivating *Chlorella vulgaris* with biogas as a carbon source under three different light conditions.

### **State-of-the-art**

In the recent past studies of applying microalgae within the biogas process have been promoted in Germany. Analyses made by the Technical University of Dresden demonstrated the possibility of carbon dioxide reduction in biogas. The investigation of Schmack Biogas AG could prove these results. In pre-position of the investigation several microalgae were examined regarding their ability to convert carbon dioxide. Moreover the fermentative potential of microalgae substratum in the biogas process was of interest. According to this the development of a commercially applicable open pond reactor for culturing microalgae was attempted. Generated algae were successfully tested for conditioning biogas by this technique, however under central-European light conditions the efficiency of this culture technique was categorized as uneconomical (Schmack et al., 2009). In addition to gas conditioning the fermentative potential of *Spirulina sp.* was examined; a gas potential of 420 NI · kg<sup>-1</sup> ODM was obtained. Due to different gas volume under varying temperature and air pressure conditions, respectively, the gas potential is described as Norm litre (NI) at 0°C and 1013 hPa. The parameter ODM refers to the organic fraction of substratum dry mass.

## **MATERIAL AND METHODS**

In this investigation the strain *Chlorella vulgaris*, SAG 211-11b was tested. The culture media was Modified Bold's Basal Medium (MBBM) - modified by Starr and Zeikus (Starr & Zeikus, 1987). The media was filled up to 1000 ml and the pH (5.5) was adjusted. The media was then autoclaved and vitamins were added. In the presented experiment biogas was conducted through an algae suspension-containing photobioreactor. Thereby the biogas had a composition of CH<sub>4</sub> (58%), CO<sub>2</sub> (42%) and H<sub>2</sub>S (438 ppm). Previous to the cultivation the gas composition was analysed by a Gas Analyzer (Model GA 45+). During cultivation the biogas was conducted via Viton<sup>®</sup>-hoses from gas-prove gas bags to the photobioreactor by using the hose pump ISMATEC (model IP-ISM 942); the conditioned gas emission was recaptured in gas bags. Subsequent to the conditioning a further gas analysis was made.



**Fig. 1.** Schematic structure of the cultivation device.

In this single experiment each photobioreactor was aerated with biogas of identical composition. The difference in light intensity is shown in Fig. 1. The light adjustment at the surface of the photobioreactors was realised by using light meter LICOR (model LI-250). The measured light intensities were ca. 35, 60 und 100  $\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ . For achieving different light climates the photobioreactors were covered with gossamer of different thickness. The photobioreactors consisted of gas-proof, spiral-wound culture hoses. A PVC-plug with a hose connector was located at the upper end of the culture. The plugs were sealed with gas-proof compound. Sampling-junctions, secured by hose clips, were located at the lower end of the culture hose. These junctions, equipped with one-way syringes, were used for taking algae suspension probes (1 ml) daily. Against the background of dependent microalgal growth from pH and lowering solubility of carbon dioxide in water (McCutcheon et al., 1993), respectively, the pH-value was measured daily at a temperature of 25°C by using pH-meter Calimatic (model 765).

To ensure stable culture conditions the experiments were carried out at 21°C in a culture chamber at the Institute for Biosciences at the University of Rostock during 2008.

## RESULTS AND DISCUSSION

By comparing the gaseous compounds methane, carbon dioxide, oxygen and hydrogen sulphide, a variation in composition of the gas mixture (biogas) could be documented (Table. 1). The table shows that the initial value of carbon dioxide (41%) could be lowered after gas-conditioning to a level of 2.3% at a light intensity of

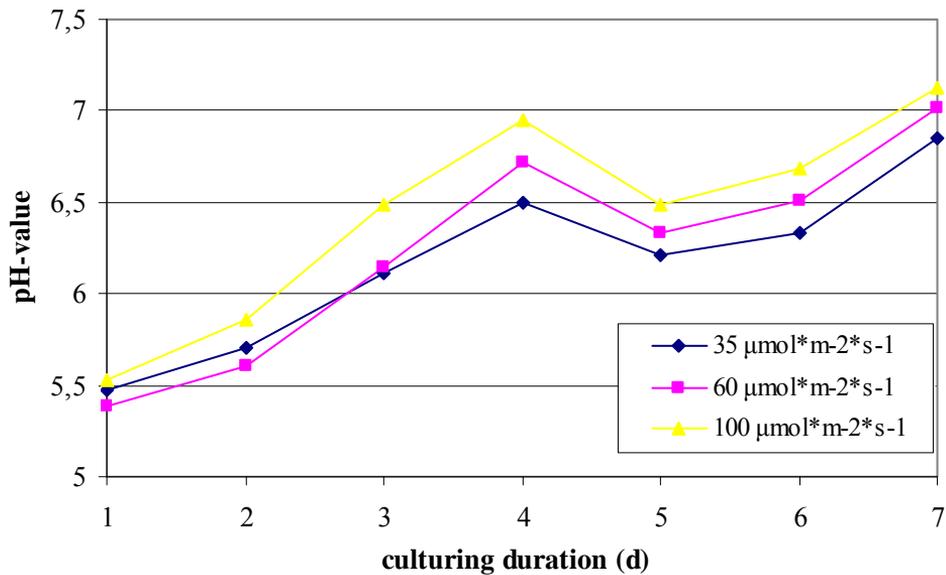
35  $\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ . After cultivation at light intensities of 60 and 100  $\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$  values of 1.2% and 2.5%, respectively, could be obtained.

**Table 1.** Gas composition before and after cultivation of *Chlorella vulgaris* (temp.: 21°C, air pressure: hPa 1014 mm).

Gas component		Proportion <b>before</b> cultivation	Proportion <b>after</b> cultivation at light intensity of:		
			53	60	100
			$\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$		
CO <sub>2</sub>	%	41.0	2.3	1.2	2.5
O <sub>2</sub>	%	1.0	21.5	23.4	18.2
H <sub>2</sub> S	(ppm)	438.0	0.0	0.0	0.0
CH <sub>4</sub>	(%)	57.5	52.2	50.1	53.3

After the cultivation of *Chlorella vulgaris* higher proportions of oxygen in the gas mixture were detected contrary to carbon dioxide. Compared with the initial value of 1% the proportions in the conditioned biogas increased to values of 21.5% (35  $\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ), 23.4% (60  $\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ) and 18.2% (60  $\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ). After cultivation, the amount of hydrogen sulphide (438 ppm) was completely removed at all light intensities. The content of methane declined from the initial value of 57.5% to 52.2% at 35  $\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ , 50.1% at 60  $\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$  and 53.30% at 100  $\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ .

To analyse the influence of different light intensities on growth of bacteria, parameters as average growth rate and, derived from this, the resulting daily duplication ratio were detected. However, due to differing measuring data referring to the coherency between photon flux and population density of the bacteria, no legalities could be stated. The relative reduction of carbon dioxide about 97.07 percentage points to an absolute level of 1.2 % exceeded literature results (Tieze et al., 2006). Compared to analyses of *Chlorella fusca* (Anonymus, 2005) and *Chlorella vulgaris* (Conde et al., 1993) higher CO<sub>2</sub>-reduction could be realised. The assimilation of carbon within photosynthesis is regarded as the explanation. Considering the decreasing content of methane, it has to be mentioned that the deployed microalgae strain was not axenic. Using un-axenic strains always results in a certain degree of “contamination” caused by ubiquitous present bacteria. Since an influence by growth and metabolism of these organisms could not be excluded, these organisms were quantified in addition to the microalgae. However the influences on the biogas conditioning could not be considered in detail within this investigation. Hence it is possible that the methane reduction was caused by methanotrophic bacteria. Another feasible reason for methane losses is methane oxidation based on the elevated oxygen proportions in the biogas after the cultivation of microalgae. As already mentioned in material and methods, the influence of organic carbon on the cultivation process ( $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$ ) has been examined by measuring the pH-value. A sample of algae suspension was taken daily from each photobioreactor for this purpose. The experiment was characterised by low pH-values at the beginning of the cultivation (Fig. 2).



**Fig. 2.** Characteristics of pH-value during cultivation of *Chlorella sp.* with biogas.

The graph illustrates the steady rise of the initial values (5.47 at  $35 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ , 5.38 at  $60 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$  and 5.53 at  $100 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ) up to 6.5 ( $35 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ), 6.72 ( $60 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ) and 6.95 ( $100 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ) on the fourth day of cultivation. On day five the values declined to a lower level (6.21 at  $35 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ , 6.33 at  $60 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$  and 6.49 at  $100 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ). Within the last two days of cultivation an increase up to pH 6.85 ( $35 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ), 7.02 ( $60 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ) and 7.13 ( $100 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ) was determined. Within cultivation at  $35 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$  measurements showed the lowest average pH-values. Highest average values were identified at  $100 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ .

The documented alteration of pH-value proceeds in intervals, which does not affect the carbon uptake by microalgae (Graham & Wilcox, 2000; Tieze et al., 2006). Compared to previous studies the average pH-values of the present study are situated in the lower range of the given intervals. In literature ranges of 6.8–8.5 (Tieze et al., 2006), 6.65–8.24 (Anonymus, 2005) and 6.61–8.09 (Doucha et al., 2005) are reported. All of the reported literature data is based on the experiences with two-phase-reactors, which consist of separated cultivation and gassing phase. In order to minimize process costs in this experiment the feasibility of a single phase reactor set-up was tested.

The steady pH rise during cultivation can be considered as a result of the algae growth, which is combined with a higher decomposition of nitrogen. Regarding the high proportions of carbon dioxide in the biogas (41%), no negative effect on the pH could be identified. Against the background of carbon dioxide reduction and parallel enrichment of oxygen it can be assumed that carbon dioxide was converted into algae biomass. This assumption was confirmed by the analyses of the C/N ratio and total organic carbon (TOC) of the media. In reference to the application of different light intensities the comparison of the pH-graphs shows a correlation between light intensity and height of pH-value. In this context at an intensity of  $100 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$  the highest, and at an intensity of  $35 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$  the lowest values were established.

## CONCLUSIONS

In this investigation a distinct positive synergistic effect between simultaneous biogas-conditioning and algae biomass production could be determined. Due to the small number of replications a statistical analysis could not be realised so far. However compared to literature data and considering the growth and conditioning results in three different light conditions, the cultivating of *Chlorella vulgaris* with biogas as carbon source is regarded as a feasible biogas-conditioning method. Thus, in principle, the presented biological process states an alternative to the biogas conditioning processes used until now.

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