

# Revival of the Biological Sunlight-to-Biogas Energy Conversion System

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**ABSTRACT:** In the quest for renewable resources, algae are increasingly receiving attention. Their high growth rate, high CO<sub>2</sub> fixation and their lack of requirement for fertile soil surface represent several advantages as compared to conventional (energy) crops. Through their ability to store large amounts of oils, they qualify as a source for biodiesel. Algal biomass, however, can also be used as such, namely as a substrate for anaerobic digestion. In the present research, we investigated the use of algae for energy generation in a stand-alone, closed-loop system. The system encompasses an algal growth unit for biomass production, an anaerobic digestion unit to convert the biomass to biogas and a microbial fuel cell to polish the effluent of the digester. Nutrients set free during digestion can accordingly be returned to the algal growth unit for a sustained algal growth. Hence, a system is presented that continuously transforms solar energy into energy-rich biogas and electricity. Algal productivities of 24–30 ton VS ha<sup>-1</sup> year<sup>-1</sup> were reached, while 0.5 N m<sup>3</sup> biogas could be produced kg<sup>-1</sup> algal VS. The system described resulted in a power plant with a potential capacity of about 9 kW ha<sup>-1</sup> of solar algal panel, with prospects of 23 kW ha<sup>-1</sup>.

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**KEYWORDS:** bioenergy; anaerobic digestion; microalgae; microbial fuel cell

## Introduction

At present, it is becoming increasingly clear that society is in need for alternative energy sources. To date, 80% of the world's energy use still originates from combusting fossil fuels (Goldemberg and Johansson, 2004). Yet the reserves

are limited, and their burning substantially increases greenhouse gas (GHG) concentrations. Substitute energy sources should be renewable and carbon-neutral to even carbon-negative. In this respect, bioenergy (energy production from biomass) can be seen as one of the key options. This is acknowledged by policy makers, which foresee biomass to have a share of 75% in the renewable energy sources in Europe by 2010 (European Commission, 1997, White paper for a community strategy and action plan: energy for the future: renewable sources of energy). Of the many bioenergy related processes being developed, those processes involving microorganisms are especially promising, as they have the potential to produce renewable energy on a large scale, without disrupting strongly the environment or human activities (Rittmann, 2008).

Large opportunities lie within the conversion of solar energy in photosynthetic microorganisms, and consequently the interest for microalgae is growing worldwide. Their high growth rates allow high CO<sub>2</sub> fixation rates (up to 6.24 kg m<sup>-3</sup> day<sup>-1</sup>) (Cheng et al., 2006). The potential productivity of algae, up to 50 ton dry weight (DW) per ha per year in North-West Europe (Wijffels, 2008), is a factor 10 higher than the productivity of conventional agricultural crops such as barley and sugar beet, being 5–11 ton DW ha<sup>-1</sup> year<sup>-1</sup> (Murphy and Power, 2009). Microalgae produce energetic compounds, which can be applied as biofuels. In a process called biophotolysis, green algae can generate the energy carrier H<sub>2</sub> from water (Skjanes et al., 2007). Furthermore, the high intracellular production of lipids turns them in a potential source for the production of biodiesel (Chisti, 2008a). Microalgal biomass itself also has the potential to be converted into biofuel. The conversion of biomass proceeds through thermochemical or biological methods (Skjanes et al., 2007).

Anaerobic digestion (AD) is a biological process which converts organic material into energy-rich biogas, containing CH<sub>4</sub> and CO<sub>2</sub>. The AD technology is now well established in terms of performance and is technically and economically feasible. Worldwide, AD reactors are treating

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various kinds of waste at full scale (Pham et al., 2006). The natural anaerobic digestion of microalgae has been demonstrated to attain a 40–80% conversion at 20°C in 200 days (Foree and McCarty, 1970). Application of a concentrated algal biomass mixture as a feeding for anaerobic digesters resulted in a lower performance than that with raw sewage sludge as substrate, yet values of 0.5 m<sup>3</sup> biogas kg<sup>-1</sup> algal organic dry matter (VS) supplied could be obtained (62.5% CH<sub>4</sub>) (Golueke et al., 1957). High amounts of ammonium (around 1,500 mg L<sup>-1</sup>) and residual fatty acids (1,500–2,100 mg L<sup>-1</sup>) were observed, and retention times of more than 7 days were required. Thermophilic conditions had a positive effect on the anaerobic process, achieving conversion efficiencies of 54%. A loading rate of 2.9 kg algal-VS m<sup>-3</sup> day<sup>-1</sup> could be reached. The anaerobic digestion of *Spirulina maxima* resulted in a biogas yield of 0.3–0.37 m<sup>3</sup> biogas kg<sup>-1</sup> VS, with 70% methane and conversion efficiencies up to 48% (Samson and Leduy, 1982, 1983a,b, 1986). Maximum yields were obtained with a retention time of 30 days and an algal concentration of 20 kg VS m<sup>-3</sup>. In contrast to the study of Golueke et al. (1957), a mesophilic temperature (35°C) was found most preferable for the degradation of the algal biomass (Samson and Leduy, 1986). Biogas productivity could be increased by mixing the proteinaceous algal biomass with carbon-rich wastes such as sewage sludge (Samson and Leduy, 1983b) or waste paper (Yen and Brune, 2007), thereby increasing the C/N ratio of the digester feeding. Mechanical and thermochemical pretreatments have been applied on algal biomass to increase the biodegradability of the algae. The resulting higher solubility of the biomass entailed a positive effect for the acid forming bacteria. The methanogenic bacteria, however, appeared to be only influenced by the chemical composition of the culture medium (Samson and Leduy, 1983a). Good results were obtained with a thermochemical pretreatment at 100°C for 8 h without NaOH, which could increase the efficiency of methane fermentation with 33%, up to 0.32 m<sup>3</sup> kg<sup>-1</sup> VS (Chen and Oswald, 1998).

Another element within the concept is the microbial fuel cell (MFC), treating discrete to complex wastewater, and generating electrical energy in the process. The technology is still in the development phase. In a microbial fuel cell a reduced (often organic) compound is being oxidized at an anode, a process in which bacteria deliver the electrons to the anodic electrode. The electrons pass an external load, generating electrical current, and are released at the cathode to reduce an oxidant such as oxygen (Logan et al., 2006; Rabaey et al., 2005). Photosynthetic microorganisms (or components thereof, Lam et al., 2006) have been used in (microbial) fuel cells: energy generation was based on the oxidation of in situ produced H<sub>2</sub> (Rosenbaum et al., 2005a,b) or mediated electron transfer to the anode (Chiao et al., 2006; Tanaka et al., 1985). Marine plankton has been applied as a substrate for the anode of an MFC, resulting in an 80% removal of the organic carbon applied after 2 months (Reimers et al., 2007). Also the cathode reaction

can benefit from compounds produced by photosynthetic microorganisms (oxygen). Illumination of a cathode bearing marine algae resulted in potential shift of +0.6 V (Berk and Canfield, 1964).

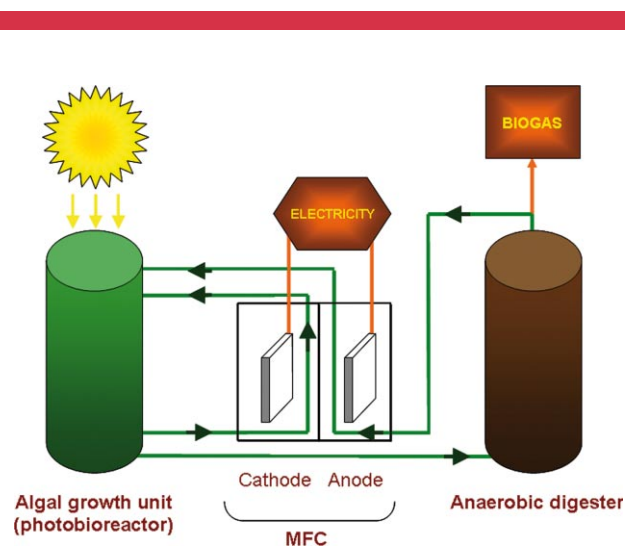
To develop an interesting bioenergy technology related to microalgae, it is advisable to integrate several processes within one technology hence maximizing efficiency and minimizing costs. Algae could for instance be cultured out of waste streams to remove and recuperate nutrients, after which the algal biomass can be digested (Richmond, 2004).

In the present manuscript a closed loop system is presented (see Fig. 1) for the biological conversion of solar energy to useful energy. Algal biomass is grown and used as feeding for an anaerobic digestion unit producing biogas. The remaining compounds from the breakdown of algal biomass, present in the AD effluent, are further oxidized at the anode of an MFC, while living algae are recirculated over the cathode to deliver the final electron acceptor (oxygen). During the entire process, the algal biomass is broken down to its constituents, which are subsequently used for the growth of fresh algal biomass, resulting in a closed loop system. A similar closed-loop concept was found to be proposed and tested by Golueke and Oswald (1959). The present socio-economical environment and current R&D development call for a reevaluation of the biological energy conversion system. In what follows, the possibilities of the algal growth–AD–MFC cycle are demonstrated.

## Materials and Methods

### Discontinuous Algal Growth–AD–MFC System

A closed loop reactor setup was built, consisting of an algal growth unit, an AD and an MFC, schematized in Figure 1 and S1. The system was first used in continuous mode, but



**Figure 1.** Schematic overview of the closed loop concept. [Color figure can be seen in the online version of this article, available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

later on operated discontinuously. Results presented here only refer to the operation in discontinuous mode.

The algal growth unit consisted of a cylinder with opaque sides and bottom, internal volume of 10 L and upper surface of 0.057 m<sup>2</sup>. The reactor was inoculated with a nondefined mixed culture of freshwater algae, obtained from hydroponic plant growth systems, supplemented with *Chlamydomonas reinhardtii* and *Pseudokirchneriella subcapitata*. The reactor was continuously aerated, and regularly supplied with NH<sub>4</sub>HCO<sub>3</sub>-N or KNO<sub>3</sub>-N, KH<sub>2</sub>PO<sub>4</sub>-P (in the order of 75 mg N and 7.5 mg P per feeding) and trace elements (Smith et al., 1993). During the course of the experiments, CO<sub>2</sub> fertilization was started by introducing fine bubbles of CO<sub>2</sub> in the algal suspension (Air Liquide, 100%). On average every two and a half (maximum six) days, 2 L of algal suspension (corresponding with a fourth of the internal volume, taking evaporation into account) was taken from the algal growth unit and was centrifuged to concentrate it to 200 mL, which was accordingly fed to the AD system. The algal growth unit was refilled with the supernatant (spent medium) with added nutrients or with tap water with added nutrients as indicated, together with the MFC effluent (see below) and with an extra volume of water to compensate for evaporation. Algal productivity is presented for the period from April 15, 2008 till July 14, 2008.

The algal biomass fed to the anaerobic system was thermally pretreated at 70°C for 60 h on average, in a system physically connected to the actual AD unit, to increase the digestibility of the microalgal biomass (Chen and Oswald, 1998). Subsequently, the algal suspension entered the AD unit. The latter was used in continuous mode before and was additionally inoculated with a total of 115 mL mesophilic sludge before and at the beginning of the presented dataset from the discontinuously fed system. Mesophilic operation with a short thermal pretreatment and the possibility for adequate heat recovery through heat exchangers was preferred to thermophilic operation, as this consumes less energy, and as thermophilic treatment was not univocally proven better in case of microalgae digestion (Samson and Leduy, 1986). The actual AD unit consisted of four sequential and interconnected reactors, of which three had an internal volume of 1.2 L, while the last one was filled with Kaldness rings for sludge retention (porosity = 0.75) and had a liquid volume of 8.2 L. The entire AD unit basically resembled a septic tank with internal baffles, followed by an upflow anaerobic filter (see also Fig. S1 for a more detailed scheme). Gas was collected through a water displacement system, allowing quantification and qualitative analysis of the gas produced. Measurements regarding the AD system refer to the period of March 7, 2008 till May 29, 2008; the period after partial mixing refers to the end of June 2008.

The effluent of the anaerobic digester was used to replace the recirculation liquid of the anode of an MFC, while the latter liquid was fed to the algal growth unit on each feeding day. The MFC (built according to Rabaey et al., 2005) had an

anode compartment filled with graphite granules (5 mm diameter, Le Carbone) and a void volume of 320 mL. The cathode compartment contained a graphite mat cathode (12.5 cm × 5 cm × 0.5 cm, Alfa Aesar) inoculated with a performant oxygen reducing cathodic culture (De Schampelaire et al., 2008) and had a volume of 320 mL. A suspension of living algae was recirculated over the cathode (1.92 L h<sup>-1</sup>) to introduce the electron acceptor oxygen. This suspension was, for practical reasons, cultivated in a separate cylindrical algal growth unit with a volume of 2 L and an upper surface of 0.0154 m<sup>2</sup>. A fixed external resistance of 75 or 100 Ω was connected between anode and cathode and cell potential was recorded every 15 min. Cathode redox potential was determined through the potential difference with an Ag/AgCl reference electrode. MFC related (electro)chemical data refer to the period of March 7, 2008 till May 29, 2008, except for the data recorded without aeration of the cathodic algal growth unit, which refer to a period from June 30, 2008 till August 4, 2008.

The anaerobic digestion unit and microbial fuel cell were placed in a closet heated to c. 40°C. Algal growth units were placed in a greenhouse with extra lighting (2 times 400 W, HQI), under a 16 h light – 8 h dark regime and with a temperature around 28°C (with fluctuations between 20 and 40°C).

## Batch Tests

Batch anaerobic digestion tests were performed in a thermostatic room of 34°C and in a thermostatic hot water bath of 41°C placed in that room. Schott bottles of 500 or 250 mL were filled with 500 respectively 100 mL mesophilic sludge, with and without addition of 40 respectively 30 mL concentrated algal suspension. Gas was collected through a water displacement system inside the 34°C room. Thermal pretreatment of algae involved a heating to 80°C during 2.5 h. All test were performed in triplicate, except for the control at 34°C, which was performed in duplicate. Further operational details can be found in Table I.

## Sample Analysis

Liquid samples were taken between each step in the system and analyzed according to Greenberg et al. (1992). The *n* reported in the results section refers to the number of samples analyzed through time. Algal productivity was determined through chemical oxygen demand (COD) analysis (potassium dichromate method) and recalculated to volatile algal organic matter (VS). VS measurements were made through drying and incineration. Volatile fatty acids were, after extraction in diethyl ether, analyzed on a flame ionization detector gas chromatograph (GC 8000 Carlo Erba Instruments). Ammonium was determined colorimetrically according to Nessler (Uvikon spectrophotometer 932). Anions were analyzed using ion chromatography (Dionex AS9HC

**Table 1.** Results obtained from batch digestion experiments at 34 and 41°C after respectively 14, 25, and 45 days.

Operating temperature (°C)	Time run (days)	Feeding (mg VS)	Loading (g VS L <sup>-1</sup> AD sludge)	Biogas production (mL)	Biogas		Specific biogas production (N m <sup>3</sup> kg <sup>-1</sup> VS)	Specific biogas production (N m <sup>3</sup> kg <sup>-1</sup> COD)
					production in control,	without algae (mL)		
34	14	304 ± 28	0.6	540 ± 5	418 ± 6	0.35 ± 0.04	0.32 ± 0.04	
	25			759 ± 12	608 ± 7	0.44 ± 0.06	0.40 ± 0.05	
	45			1149 ± 9	945 ± 15	0.60 ± 0.08	0.54 ± 0.07	
41	14	135 ± 1	1.4	263 ± 32	210 ± 31	0.35 ± 0.29	0.32 ± 0.27	
		143 ± 2 (pretreated)		255 ± 16		0.28 ± 0.22	0.25 ± 0.20	
	25	135 ± 1		298 ± 34	227 ± 46	0.47 ± 0.38	0.43 ± 0.34	
		143 ± 2 (pretreated)		290 ± 25		0.39 ± 0.33	0.36 ± 0.30	

column). Gas chromatography (GC-14B, Shimadzu) was used for biogas analysis. Microscopy was performed using a Zeiss microscope with 1,000× magnification.

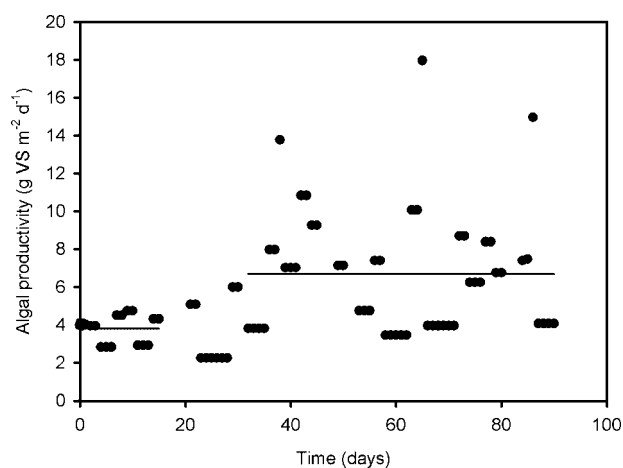
## Results

### Algal Growth Unit

The algal productivity, based on a harvest every 2.5 days on average, is depicted in Figure 2. The daily productivity (i.e., the harvest of algae divided by the time interval since the previous harvest) increased from 3.8 g algal volatile matter (VS) m<sup>-2</sup> day<sup>-1</sup> to 6.7 g VS m<sup>-2</sup> day<sup>-1</sup> upon CO<sub>2</sub> fertilization. Related to the illuminated surface and extrapolated to yearly productions per hectare, corresponding average productivities of respectively 14 and

24 ton VS ha<sup>-1</sup> year<sup>-1</sup> were obtained, with higher productivities around 30 ton VS ha<sup>-1</sup> year<sup>-1</sup> and a peak of 65 ton VS ha<sup>-1</sup> year<sup>-1</sup> in case of more frequent harvest. Concentrations of algal biomass in the harvested liquid increased from 256 to 498 mg VS L<sup>-1</sup> with a maximum of 703 mg VS L<sup>-1</sup>. The value of algal biomass as oxidizable substrate was evaluated by comparing the weight of volatile matter with the corresponding COD value. It was determined that the ratio of COD/VS is 1.1 ± 0.1 g COD g<sup>-1</sup> VS (*n* = 5).

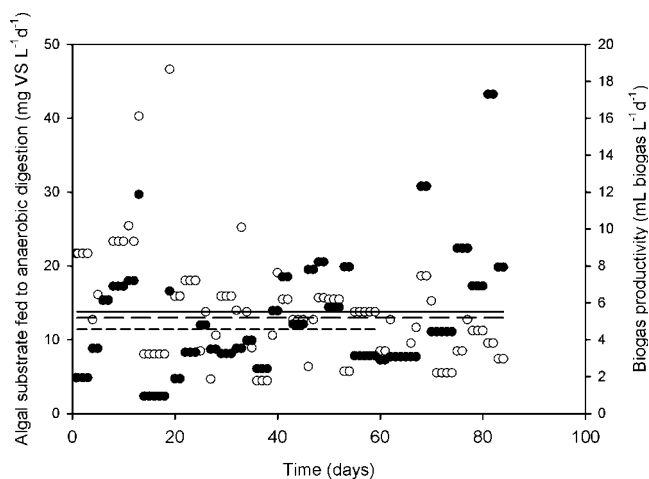
Microscopic analysis of algal suspensions at the end of the presented dataset revealed mixtures of green unicellular microalgae, which were dominated by two divergent species, the first one being a spherical microalga with a diameter of 4–6 μm, resembling *Chorella* species, and the second with a width of 5 μm and a length of 10–17 μm. *Pseudokirchneriella* and *Chlamydomonas* could only be detected at very low levels.



**Figure 2.** Algal productivity through time in g VS harvested per day, expressed per m<sup>2</sup>. The daily productivity was calculated by spreading each harvest equally over the time interval since the previous harvest. CO<sub>2</sub> fertilization was gradually introduced during day 21 till 30. The average values for the periods with and without CO<sub>2</sub> fertilization are indicated by horizontal lines. N-fertilisation changed from NH<sub>4</sub><sup>+</sup>-N to NO<sub>3</sub><sup>-</sup>-N on day 38. The system was replenished with spent medium, except from day 43 till 64 and from day 80 on, when it was replenished with tap water with nutrients.

### Anaerobic digestion

Every 2.5 days the semi-continuous anaerobic system was fed with an average of 442 mg COD or 402 mg VS of algal biomass, with absolute values varying between 123 and 1122 mg COD. Biogas production varied around 65 mL per day, representing a COD conversion rate around 84 mg COD day<sup>-1</sup>. Relating the biogas production to the amount of substrate—expressed in algal VS—added each day led to an average biogas production of 0.38 N m<sup>3</sup> biogas (averaged over the total 84 days, Fig. 3) to 0.49 N m<sup>3</sup> biogas (averaged over the first 59 days, not including higher loadings) per kg added algal VS. Methane concentrations varied between 40% and 65% CH<sub>4</sub>. Algal biomass conversion efficiencies were in the range of 49–64%. Short chain fatty acid concentrations in the effluent of the AD were 22 ± 10 mg L<sup>-1</sup>, with the value for COD being 187 ± 35 mg COD L<sup>-1</sup>. The pH of the AD influent was 8.0 ± 0.7, that of the AD effluent was 7.3 ± 0.2. The ammonium concentration in the influent of the AD system was 5.9 ± 6.4 mg NH<sub>4</sub><sup>+</sup>-N L<sup>-1</sup>, whereas the concentration in the effluent gradually increased over a period of 3 months from 14 to 99 mg NH<sub>4</sub><sup>+</sup>-N L<sup>-1</sup>. Later on, the AD unit was



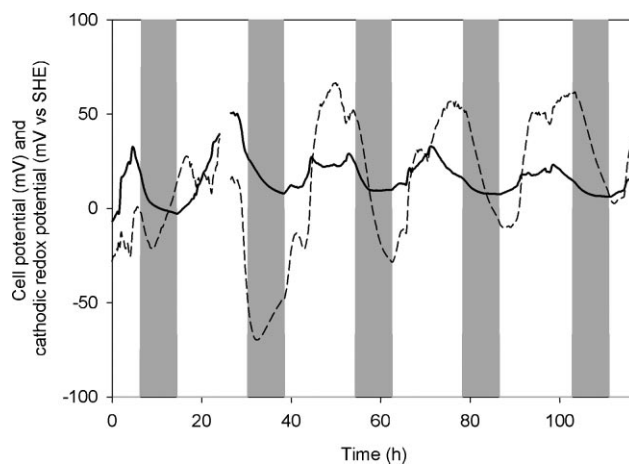
**Figure 3.** Biogas production in relation to substrate addition, (●) daily substrate addition in  $\text{mg VS L}^{-1} \text{ reactor day}^{-1}$ , (○) daily biogas production in  $\text{mL biogas L}^{-1} \text{ reactor day}^{-1}$ . The averages are indicated by horizontal lines (— biogas production, - - - substrate addition, including higher loadings, ···· substrate addition, not including higher loadings).

partially mixed, which resulted in higher effluent concentrations of up to  $299 \text{ mg NH}_4^+ \text{-N L}^{-1}$ . Oxidized nitrogen species were dosed tightly and obtained concentrations of  $1.8 \pm 2.1 \text{ mg NO}_3^- / \text{NO}_2^- \text{-N L}^{-1}$  in the influent and were negligible in the effluent. The phosphate level was  $5.0 \pm 5.6 \text{ mg PO}_4^{3-} \text{-P L}^{-1}$  in the influent and  $9.4 \pm 2.3 \text{ mg PO}_4^{3-} \text{-P L}^{-1}$  in the effluent, and  $17.4 \text{ mg PO}_4^{3-} \text{-P L}^{-1}$  after mixing.

Additionally, a series of batch anaerobic digestion tests was performed to evaluate the digestibility of the algal sludge. The results can be found in Table I.

### Microbial Fuel Cell

The current production by the MFC showed a highly fluctuating pattern in a 24 h-cycle, with a peak during daytime (around 3–4 pm) and minimum levels during night (around 3–4 am). Figure 4 shows a section of the data where the cathodic redox potential was recorded, demonstrating that redox potentials are even more influenced by light–dark patterns. Originally, the growth vessel (and hence recirculation vessel) of the cathodic algae was aerated to mix the liquid and to bring in  $\text{CO}_2$ . With a resistance of  $100 \Omega$ , an average current (averaged over night- and daytime, 1,380 h) of  $0.37 \text{ A m}^{-3} \text{ MFC}$  was then reached with an average power of  $12 \text{ mW m}^{-3} \text{ MFC}$  (average influent COD concentration  $187 \pm 35 \text{ mg L}^{-1}$ ). Changing the external resistance to a value of  $75 \Omega$  and omitting the aeration in the algal growth unit resulted in an average (averaged over 225 h) current of  $0.73 \text{ A m}^{-3} \text{ MFC}$  and an average power of  $32 \text{ mW m}^{-3} \text{ MFC}$  (average influent COD concentration  $261 \pm 27 \text{ mg L}^{-1}$ ). Maximum current and power outputs during daytime without cathode aeration, as determined by polarization



**Figure 4.** Cell potential (—) and cathodic redox potential (---) (vs. SHE). Periods of almost absolute darkness are indicated by grey vertical bars. There was no aeration of the cathode, the external resistance had a value of  $75 \Omega$ .

curves ( $1 \text{ mV s}^{-1}$  scan rate), were  $3 \text{ mA}$  and  $163 \mu\text{W}$  ( $4.7 \text{ A m}^{-3} \text{ MFC}$  and  $0.25 \text{ W m}^{-3} \text{ MFC}$ ).

Comparing influent and effluent concentrations for the anode of the MFC (with aeration in the algal growth unit) resulted in an average removal ( $n = 25$ ) of 37% COD from the influent, corresponding with a decrease of  $68 \pm 23 \text{ mg COD L}^{-1}$  and a coulombic efficiency (efficiency of electron transport) of 40%. The averaged removal efficiency of volatile fatty acids was 70%, corresponding with a decrease of  $16 \pm 9 \text{ mg L}^{-1}$  ( $n = 14$ ). These removals were furthermore characterized by an accompanying decrease in turbidity of 58% or  $11 \pm 7 \text{ NTU}$  ( $n = 12$ ). pH generally decreased from  $7.3 \pm 0.2$  to  $6.8 \pm 0.2$  ( $n = 29$ ).

Concentration of ammonium in the influent of the anode increased from 14 to  $99 \text{ mg NH}_4^+ \text{-N L}^{-1}$  through time, while the concentration of the effluent remained relatively stable at  $8.0 \pm 5.5 \text{ mg NH}_4^+ \text{-N L}^{-1}$ . After partial mixing of the AD contents, the concentrations of anode influent surpassed  $200 \text{ mg NH}_4^+ \text{-N L}^{-1}$ , whereas the concentration in anode effluent increased to  $29.5 \text{ mg NH}_4^+ \text{-N L}^{-1}$ . Levels of oxidized nitrogen species were negligible in the effluent of the AD unit as well as in the effluent of the MFC. Phosphorus had a value of  $9.4 \pm 2.3 \text{ mg PO}_4^{3-} \text{-P L}^{-1}$  in the influent of the anode and  $9.7 \pm 9.8 \text{ mg PO}_4^{3-} \text{-P L}^{-1}$  in the effluent of the anode ( $17 \pm 3$  and  $7 \pm 3 \text{ mg PO}_4^{3-} \text{-P L}^{-1}$  in influent and effluent of anode respectively after partial mixing of AD contents).

## Discussion

### Experimental Evaluation of the Concept

This work describes the concept of a closed loop system for conversion of solar energy into energy-rich biogas and electricity. A simulation of a closed cycle setup, involving an

algal growth unit, anaerobic digestion and microbial fuel cell was installed to evaluate the totality of this concept.

The algal growth unit was of the open pond type, which is a basin open to the air. It demonstrated the continued growth of a mixed and self-regulating culture of freshwater microalgal species, to which spent medium and AD effluent was regularly returned. Fertilization with CO<sub>2</sub> had a clear impact on algal productivity, almost doubling it. Values of 24–30 ton VS ha<sup>-1</sup> year<sup>-1</sup> were reached, which is comparable to productivities reported in literature (Carlsson et al., 2007). The data demonstrated an inverse relation between productivity and harvesting interval. This suggests that the productivity is rather limited by a maximum biomass concentration, and that a more frequent or higher volumetric harvest would result in a higher overall productivity. Indeed, biomass concentrations only reached maxima of 703 mg VSL<sup>-1</sup> in this system.

The results from the anaerobic digestion unit suggested that up to 0.49 N m<sup>3</sup> biogas (with up to 65% CH<sub>4</sub>) could be produced per kg algal VS, which is consistent with earlier findings (Golueke et al., 1957). The system was operated in plug flow, with low total volumetric loading rates (order of 10 mg L<sup>-1</sup> reactor day<sup>-1</sup>), influent concentrations in the order of 2 g COD L<sup>-1</sup>, and with a virtually indefinite residence time. These conditions are not appropriate for continuous, large scale operation of an AD system, but allowed an extensive conversion for research purposes, which was reflected in the estimated algal biomass conversion of up to 64%. Similar conditions and results were obtained in the batch experiments, where biogas productions of up to 0.6 N m<sup>3</sup> kg<sup>-1</sup> algal VS were obtained at 34°C after 45 days. Neither operation at 41°C nor thermal pretreatment did result in clear improvements regarding biogas production.

The entire conceptual system was originally operated in continuous mode, but the anaerobic digestion unit failed to produce any methane (results not shown). This might be due to: too low COD concentrations (around 300–500 mg COD L<sup>-1</sup>) and too high nitrate concentrations (15–30 mg NO<sub>3</sub><sup>-</sup> NL<sup>-1</sup> or higher) in the AD influent, and a too high water circulation, causing flushing of dissolved methane. Re-inoculation with active sludge and operation with higher biomass and lower NO<sub>3</sub><sup>-</sup>/NO<sub>2</sub><sup>-</sup> concentrations in the influent did result in a fair operation of the AD system. It hence appears likely that a concentrating step is required in the system setup.

As the total residence time in the AD system was longer than the time period presented here, the measurements of the AD effluent reflect the breakdown of algal matter accumulated during the preceding operation in continuous mode. This effluent demonstrated increasing concentrations of the essential nutrients N and P, present as NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup>. The N:P ratio evolved towards values of 10 to 17, which fits well within the range of N:P ratios of microalgal species (7.1–43.3 with a median of 17.7, Klausmeier et al., 2004). Two hundred milliliter AD effluent with the final N and P concentrations could support an algal growth of 1.2 g, which

is about equal to the highest biomass amount added during a feeding of 200 mL, representing a good nutrient balance between the two liquid streams. This suggests that a closed loop can be established. In the present setup, the supplementation of extra nutrients was still required due to residence times, sampling and an MFC with separate algal growth unit. Depending on the extent of microalgae breakdown, additional nutrition might be required in fully operational, large scale systems.

A microbial fuel cell was installed to polish the effluent of the anaerobic digester by anodically oxidizing reduced compounds. The polishing capacities were demonstrated by a decrease of the COD with 37%, fatty acids with 68%, and turbidity with 58%. As cell growth at an anode is low, the available nutrients in the anode influent will mainly be passed on to the algal growth unit. Indeed, with a COD removal of 68 mg L<sup>-1</sup> and a maximum anodic growth yield of 0.54 g biomass-C formed per g substrate-C used (Freguia et al., 2007), a maximum of 1.4 mg N L<sup>-1</sup> and 0.14 mg P L<sup>-1</sup> could be removed from the anodic liquid, which is a factor 100 lower than the concentrations in the anodic feeding. Nevertheless, substantial decreases in free nutrients could be noticed, which can be explained by the charge-balancing cation transport from anode to cathode compartment (Rozendal et al., 2006) and reversible adsorption or precipitation. Ammonium transport through the membrane does not represent a nutrient loss but a nourishment of the algae, since the contents of an algal growth unit—a second smaller system as in this experimental setup or the actual main unit—is recycled over the cathode for oxygen delivery.

As the volumetric loading rate of the MFC remained low, that is, about 18 g COD m<sup>-3</sup> MFC day<sup>-1</sup>, power production by the MFC remained low as well, with a maximum of 0.25 W m<sup>-3</sup> MFC. Maximum power densities in MFCs can reach values of 65 W m<sup>-3</sup> MFC (Clauwaert et al., 2007). However, the latter was obtained with a 100-fold higher volumetric loading. The present system reached average power outputs of 1.33 mW m<sup>-2</sup> illuminated footprint area, which is basically a factor 700 lower than the power which can be obtained from the AD part of the system (0.9 W m<sup>-2</sup>, see below). When COD-concentrations in the AD effluent will become higher, especially in case of a sub-optimal performance of the AD unit, the MFC will be able to further exploit its polishing properties, producing more power in the process. The anaerobic digester, however, will remain the main energy production unit. The MFC system also demonstrated that an algal culture can deliver the necessary electron acceptor for the cathode. Aeration of the cathodic recirculation liquid was not required to ensure good MFC performance. The day-night fluctuations in output from the MFC can be explained by temperature and light variations, controlling photosynthesis and hence the oxygen concentration and redox potential in the cathodic liquid.

The setup described allowed to initially evaluate the concept of the energy conversion system and demonstrated promising results for the key parts as well as their succession.

A thorough assessment of the sustainability, continuity and capacity of the closed loop system merits more attention and is subject of ongoing work performed at our laboratory.

### **Power Production by the Solar Energy Conversion System**

To evaluate the possible energy production by the closed loop system, reference must be made to the ultimate energy source. Solar irradiation within the world generally varies between a yearly 700 and 2,500 kWh per m<sup>2</sup>, with 1000 kWh m<sup>-2</sup> year<sup>-1</sup> to be obtained in a temperate region. For the photosynthetic conversion of this solar energy to biomass, a maximum theoretical efficiency of 9% is generally adopted (Wijffels, 2008). Based on this number and calorific values of microalgae of 20–25 kJ g<sup>-1</sup> DW (Illman et al., 2000; Kube, 2006; Renaud et al., 2002), an algal productivity of 130–160 ton DW ha<sup>-1</sup> year<sup>-1</sup> could be reached in a temperate climate. However, the highest reproducible (long term) productivities were only demonstrated at 50–60 ton DW ha<sup>-1</sup> year<sup>-1</sup> (Carlsson et al., 2007; Moheimani and Borowitzka, 2006). The main reason for this is that the maximum light conversion efficiency can only be reached at relatively low light intensity, typically 10% of full sunlight. At higher levels, light saturation occurs (Richmond, 2004).

When a productivity of 60 ton DW ha<sup>-1</sup> year<sup>-1</sup> would be reached, with an assumed calorific value of 24 kJ g<sup>-1</sup> DW, a complete transformation into the energy-rich biogas would yearly produce 400 MWh ha<sup>-1</sup>. This is again a theoretical maximum, which will be diminished through cell maintenance and growth, and substrate recalcitrance (Chen and Oswald, 1998). In practice, about 40–60% of algal volatile matter is transformed into biogas (Chen and Oswald, 1998; Oswald and Goluke, 1960; this study). With a biogas production of 0.5 m<sup>3</sup> biogas kg<sup>-1</sup> algal VS, methane concentration of 65%, and corresponding heat of combustion of 25 MJ per N m<sup>3</sup> biogas, about 200 MWh of gross energy production ha<sup>-1</sup> year<sup>-1</sup> is attainable, which represents a power plant with a capacity of 23 kW ha<sup>-1</sup>. The present conceptual study, reaching a productivity of 24 ton algal VS ha<sup>-1</sup> year<sup>-1</sup> represents a 9 kW power plant ha<sup>-1</sup>.

The potential gross energy conversion efficiency (vs. light energy) hence reaches a value of 2%. This is without taking into account energy required for the operation of the system and losses during combustion of biogas (although the heat can be recuperated to pasteurize the algae and heat the digester). Net energy conversion can be estimated to be of the order of 1%. As a reference, commercially available photovoltaic panels have light conversion efficiencies of 6–17% (Solar generation IV-2007, EPIA, 2007).

### **Anaerobic Digestion as a Valid Bioenergy Production Strategy**

In a general comparison of biofuels, biogas often turns out to be one of the most interesting biofuels. Firstly, this is due

to the required cultivation of specific crops for the production of biodiesel (e.g., rapeseed) and bioethanol (e.g., sugar beet) whereas biogas can be produced from waste, such as manure (Börjesson and Mattiasson, 2008). Secondly, all components of a biomass substrate can be anaerobically digested, unlike for instance biodiesel production, where only lipid components can be used. Accordingly, biogas production from biomass is more efficient, resulting in biofuel productions for transport corresponding to 18,500 km ha<sup>-1</sup> for biodiesel, 57,000 km ha<sup>-1</sup> for bioethanol and 71,200 km ha<sup>-1</sup> for biomethane (Vörstudie für einen nationalen Biomasseaktionsplan für Österreich, Austrian Energy Agency, 2006). Indeed, biogas can be upgraded and compressed to CNG (compressed natural gas) or liquefied to LNG (liquefied natural gas) to serve directly as a biofuel for transport. Finally, fuel separation demands more energy in case of the highly soluble bioethanol, as opposed to fatty acids (biodiesel) and particularly biogas, which spontaneously separate from the reactor slurry.

Oil accumulating algal species could be applied for biodiesel production with a subsequent digestion of the residual biomass. Based on a productivity of 82 ton ha<sup>-1</sup> year<sup>-1</sup> and an oil content of 20% of dry weight in the biomass, Chisti (2008b) attained an energy ratio of 2.8 (i.e., the renewable energy produced per unit of fossil energy input) and a total energy production of 1444 GJ ha<sup>-1</sup> year<sup>-1</sup>, with 57% of the energy resulting from the biogas production. Based on those data, the digestion of the complete algal biomass (assumed 50% conversion) would yield an energy ratio of 2.4. Recuperation of nutrients set free during digestion could increase the energy ratio's to 3.3 respectively 2.9. Both strategies are similar in yield, but in any case, biogas production is a must to make the system sufficiently economically viable. The one-step digestion has the advantage of a lower complexity and the production of a single type of energy carrier, which can be either combusted or employed as biofuel. In conclusion, anaerobic digestion of the complete microalgal biomass represents a promising alternative energy production strategy.

### **Perspectives and Opportunities**

The growth of algae has two major advantages over 'traditional' energy crops, such as rapeseed, or maize. Firstly, as already mentioned, higher growth rates and higher biomass productions can be obtained. Secondly, no valuable agricultural land is needed. Raceway ponds and photobioreactors (transparent tubes or plates) with small footprints could be used, meaning that brownfields and seemingly useless areas, such as roofs and walls of buildings, could hence be valorized. Contrary to photovoltaic cells, no scarce, expensive materials such as silicon are required. For the cultivation of the biomass, exhaust gases from nearby industry could be applied, as these contain essential nutrients in the form of CO<sub>2</sub> and NO<sub>x</sub> (Matsumoto et al., 1997). This strategy can increase the productivity and

decrease the production costs. The application of nutrient-containing wastewater might be an additional low cost option to make up for non-recuperable nutrients in the system. Energy required for the operation of the system can largely be generated through the intrinsic characteristics of the system. The solar panel enables the storage of solar heat, while the combustion of biogas could generate the extra heat required as a side stream.

As indicated, the concept of an energy production system based on microalgal biomass has already been introduced in the fifties (Golueke and Oswald, 1959), and has technoeconomically been assessed based on the application of high rate ponds (HRP) for algal growth (Oswald and Golueke, 1960). The HRP technology has been studied further, in combination with wastewater treatment (García et al., 2006), and is now applied worldwide.

As far as we know, no further reports on a closed loop biological conversion system have been published. However, in the light of the present growing need for renewable and carbon-neutral energy sources, such a biological concept merits renewed attention. The here presented setup demonstrated the possibilities of the concept and confirms the early results on the subject. Whereas the '59 study (Golueke and Oswald, 1959), which had an activated sludge unit inserted in the loop, was focused on the microalgal community and the overall performance of the system, the present study evaluated the performance of all key units, supported with chemical analyses. Furthermore, an MFC was applied for polishing the effluent of the digester, which can extract additional energy from (the breakdown compounds of) the algal biomass. Such an MFC can act as buffer in case of a malfunctioning AD system and can remove toxic and unwanted compounds (such as sulfides) from the digester effluent. By means of its electric output, it can furthermore act as a sensor indicating the suitability of the liquid for algal growth.

Possibilities to further improve the presented system involve the application of a closed photobioreactor (Richmond, 2004), which allows higher productivities, and higher algal biomass concentrations (up to  $17.5 \text{ g L}^{-1}$ , Hu and Richmond, 1996), possibly alleviating the need to thicken the algal suspension. Photobioreactors permit to create a solar algal panel, for instance on a roof. Although the investment and operating costs are higher for photobioreactors than raceway ponds, the harvesting costs are lower (due to the higher culture density), resulting in comparable biomass production costs. According to Chisti (2007), production costs can even be lower with photobioreactors than raceways, with a cost of respectively \$2.95 and \$3.80 per kg algal biomass in case of a yearly productivity of 100 ton. Our continuing efforts evaluate the use of a low-cost type of photobioreactor for the energy conversion system.

## Conclusions

With respect to renewable energy production, large opportunities lie within the conversion of solar energy in

photosynthetic microorganisms. In this research, a stand-alone energy production system has been proposed and a proof of concept has been offered. Microalgae were continuously cultivated, converted to biogas and electricity and the nutrients were returned for the growth of new microalgae. This resulted in a closed loop system, converting solar energy to useful energy through microalgae. Based on the numbers obtained in this research, a solar algal panel could result in a gross power production of  $9 \text{ kW ha}^{-1}$ , with prospects of  $23 \text{ kW ha}^{-1}$ . Hence, the presented combination of biomass production and efficient biological conversion constitutes a promising, green and carbon-negative strategy for renewable energy generation.

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