



AgEcon SEARCH
RESEARCH IN AGRICULTURAL & APPLIED ECONOMICS

The World's Largest Open Access Agricultural & Applied Economics Digital Library

This document is discoverable and free to researchers across the globe due to the work of AgEcon Search.

Help ensure our sustainability.

Give to AgEcon Search

AgEcon Search
<http://ageconsearch.umn.edu>
aesearch@umn.edu

*Papers downloaded from **AgEcon Search** may be used for non-commercial purposes and personal study only. No other use, including posting to another Internet site, is permitted without permission from the copyright owner (not AgEcon Search), or as allowed under the provisions of Fair Use, U.S. Copyright Act, Title 17 U.S.C.*

ALGAE USE FOR BIOHYDROGEN - AND BIOGAS PRODUCTION

LAKATOS, Gergely – PAP, Bernadett – NAGY, Péter Tamás – MARÓTI, Gergely

Abstract

Anaerobic digestion of microalgae has a real potential for feasible production of biogas. However, algae biomass production and the elimination of biogas production residual need considerable energy and nutrient utilization. By the application of algal-bacterial method hydrogen can be produced as an energy carrier, while the liquid phase of biogas sludge and the emitted carbon-dioxide can be recycled. This review focuses on the possible co-application and merging of biogas and biohydrogen production technologies for the further optimization of an environmentally friendly hybrid solution.

Introduction

Global energy consumption in 2013 was estimated at ~18TW-years (5.67×10^{20} J) and is predicted to rise by 44% to ~23TW-years (7.4×10^{20} J) by 2030. Concomitantly, 60–80% cuts in total CO₂ emissions relative to 1990 levels are thought to be required by 2050 to avoid the worst impacts of climate change (Stern and Treasury, 2006). Therefore, bridging the energy gap without increasing CO₂ emissions will require radical changes to the way energy is produced and consumed (Popp et al., 2016).

Beside the reduction of utilized energy yield the CO₂ emission can be significantly decreased by using of alternative energy sources, like sun-, wind-, water-, geothermal- or bioenergy. Bioenergy is based on the different utilization of biomass (Bai, 2015). Biomass is organic matter derived from living, or recently living organisms (Bai, 2013). Biomass can be used as a source of energy and it most often refers to plants or plant-based materials which are not used for food or feed, and are specifically called lignocellulosic biomass (Bai and Gabnai, 2014). Several biomass sources can be distinguished and classified by their utilization for biofuels.

The latest generation biofuels are based on algal biomass. Algal biomass has no competition with agricultural food and feed production (Demirbas, 2007). The photosynthetic microorganisms like microalgae require mainly light, carbon dioxide, and some nutrients (nitrogen, phosphorous, and potassium) for its growth, and to produce large amount of lipids and carbohydrates, which can be further processed into different biofuels and other valuable co-products (Brennan and Owende, 2010, Nigam and Singh, 2011). The short harvesting cycle of algae is the key advantage for its importance, which is better than other conventional crops having harvesting cycle of once or twice in a year (Chisti, 2007, Schenk et al., 2008). There are several advantages of algal biomass for biofuels production: ability to grow throughout the year, therefore, algal oil productivity is higher in comparison to the

conventional oil seed crops; higher tolerance to high carbon dioxide content; the consumption rate of water is very less i algae cultivation; no requirement of herbicides or pesticides in algal cultivation; the growth potential of algal species is very high in comparison to others; different sources of wastewater containing nutrients like nitrogen and phosphorus can be utilized for algal cultivation apart from providing any additional nutrient; and the ability to grow under harsh conditions like saline, brackish water, coastal seawater, which does not affect any conventional agriculture (Dismukes et al., 2008, Dragone et al., 2010, Spolaore et al., 2006). The algae can be converted into various types of renewable biofuels including bioethanol, biodiesel, biogas and photobiologically produced biohydrogen.

Products from algal biomass

From the aspect of the produced biogas yield, the utilization of algal biomass as a unique or supplementary substrate beside other substrates like corn silage is particularly feasible (Wirth et al., 2015). However, the only utilization of algae biomass for dark fermentation and biogas production in biogas fermenters is far the less cost-effective solution. The prices of the algal biomass are mainly influenced by the cultivation technology (Slade and Bauen, 2013). The algal biomass production has many different methods. Algae can be grown easily in simple open ponds or more precisely and developed way in photobioreactors (Singh and Sharma, 2012). But in both cases the prime cost can be significantly reduced by the production of other bio-products. There are many low-volumes, high-value chemicals, like carotenoids, long-chain poly-saturated fatty acids, phycobilins, proteins and vitamins which can be extracted from algae cells (Skjånes et al., 2013). There are also high-volume, low-value chemicals like bio-fuels (methane, ethanol, biodiesel and biohydrogen), which produced as a unique product are not cost effective (Wijffels et al., 2013). But with the serial utilization of the same algae biomass for the production of these different bio-fuels, the prime costs can be appreciably reduced. From these products, the biohydrogen has an exceptional advantage, the digestion of the algal cells for biohydrogen production is possible, but not necessary. Remarkable amount of hydrogen can be accumulated in closed systems using different hydrogen production methods reserving the intact state of the algal cells which can be further utilized for generation or extraction of other chemicals.

Hydrogen production by green microalgae

The benefit of the application of microalgae containing FeFe-hydrogenases for hydrogen production is the high H₂ production efficiency at ambient temperature and pressure in light conditions. However, the wild-type hydrogenases can only work under micro-aerobic or anaerobic environment. The accumulated oxygen, which is produced under photosynthesis rapidly and irreversibly inactivates the active center of the FeFe-hydrogenases. To overcome this phenomenon different solutions must be applied.

Three different approaches are studied in the field of light driven hydrogen production, which can supply algal biomass in proper quality and amount for fermentation in biogas fermenters. The best studied solution is the area of nutrient-depletions (Gonzalez-Ballester et al., 2015, Oey et al., 2015). This works with the skipping out of sulfur (Melis et al., 2000, Volgusheva et al., 2013), phosphate (Batyrova et al., 2015, Batyrova et al., 2012, Sialve et al., 2009), nitrogen (Li et al., 2015, Philipps et al., 2012) or magnesium (Volgusheva et al., 2015) ingredients from the medium. The nutrient depletions cause nutrient stresses which enable the temporal separation of the oxygen and hydrogen evolution. The nutrient stresses accompany with the decline of cell proliferation, photosynthetic activity and carbon fixation.

Considerable drawback of the nutrient depletion methods is that algae biomass must be grown aerobically before the application of nutrient depletion to obtain the proper amount of biomass for hydrogen production.

In some algal species adapted to light and anaerobiosis, H₂ photo-production is enhanced by the presence of acetate in nutrient-repleted media (Bamberger et al., 1982, Klein and Betz, 1978). In low light conditions, the presence of the acetate enhances the establishment of anaerobiosis and the growing of biomass, together (Wang et al., 2011). This way, the parallel production of hydrogen and the harvesting of remarkable yield of biomass are achievable in one step, while the methods based on nutrient-depletions consist of two steps (Jurado-Oller et al., 2015, Lakatos et al., 2014). First the cell cultures must be grown up, later the media of the cultures must be changed to achieve the nutrient starvation and hydrogen production, which is a time, energy and money consuming step (Melis et al., 2000). The problem of the weak hydrogen production efficiency of the nutrient-repleted cultures can be overcome by the addition of bacterial partner(s) to hydrogen producer algae(s) (Lakatos et al., 2014, Wirth et al., 2015). This way the net mitochondrial respiration of the algal and bacterial cells are elevated severely, which allows the efficient application of stronger light regimes during hydrogen production. Utilization of stronger illumination causes more intensive oxygen production and more active water splitting reaction in PSII, which results more electrons for hydrogen production. The excess oxygen is consumed by the bacterial partner, which enables remarkably rapid oxygen consumption and the establishment of anaerobiosis in 2-12 hours with the early start of hydrogen evolution (Lakatos et al., 2014, Wirth et al., 2015). Hydrogen accumulation rates can be further elevated by the reduction of the hydrogen uptake intensity using hydrogenase deficient mutant bacterial strains. Beside the advantages of rapid oxygen consumption and early start of hydrogen production, algae biomass can be grown in bacterial partner containing and nutrient-repleted media and further used as a substrate for anaerobic digestion and biogas production (Wirth et al., 2015).

Biogas production by algal biomass anaerobic digestion

The important properties of microalgal biomass to be used in anaerobic digestion include high lipids and/or carbohydrates content and lack of recalcitrant lignin (Posten and Schaub, 2009). The lipid and carbohydrate substances reach up to 50% of the biomass dry weight in some strains (Becker, 1994, Singh and Gu, 2010). The biogas potential depended strongly on the species and on the cell disruption method used. The CH₄ content of the gas evolved from the microalgae can be 7–13% higher than that from maize silage (54% vs. 61-67%), while the biogas productions are significantly lower in the case of algae strains comparing to maize silage (653 ± 37.7 ml g VS⁻¹ vs. $287 \pm 10.1 - 587 \pm 8.8$ ml g VS⁻¹) (Mussgnug et al., 2010). A closed-loop system to convert algal biomass to biogas and electricity has been tested (De Schampelaire and Verstraete, 2009). In this case the CH₄ concentration in the gas made from the algae-bacteria biomass substrate is approximately 58-61% (De Schampelaire and Verstraete, 2009, Mussgnug et al., 2010, Ward et al., 2014). The biogas CH₄ content from maize silage alone is 50-52% (Amon and Roth, 2015). Co-fermentation of algae-bacteria biomass with maize silage, in 1:1 ratio on the basis of organic dry matter, yields 54-57% CH₄ content, a medium value between maize silage and algae-bacteria biomass (Wirth et al., 2015).

The ratio of the volatile organic acids (VOAs) and total alkaline capacity (TAC) is an appropriate measure of the functional stability of the anaerobic digestion process (McGhee, 1968, Nordmann, 1977). A VOAs/TAC ratio below 0.1 means that the reactor needs feeding, whereas at a ratio ≥ 0.5 the biomass input is excessive and the process is out of balance. The

constant value of VOAs/TAC ratio is a reliable indicator of the stable fermentation process. During the digestion of algae biomass the VOAs/TAC ratio can stay between the threshold limits without any intervention.

From the decomposition of nitrogen containing compounds ammonia (NH_3) is formed, which is present in the aqueous medium in the form of ammonium ion (NH_4^+) (Alexander, 1985). Values above $3,000 \text{ mg NH}_4^+ \text{ L}^{-1}$ may have a negative effect on the methanogenic community (Chen et al., 2008, Nielsen and Angelidaki, 2008). In the case of using the algae-bacteria mixture the NH_4^+ content tended to increase, which would cause the inhibition of biogas production in long term. By the addition of corn silage, the rate of the NH_4^+ yield elevation can be reduced, which allows a long term continuous functioning.

The ideal C/N ratio for anaerobic digestion is 20-30 (Parkin and Owen, 1986), because the microbes in the anaerobic reactor can utilize carbon 20-30 times faster than nitrogen. The risks of carbon starvation increases if the C/N ratio is lower than 20, the methanogens are inhibited by the high NH_3 accumulation making the anaerobic digestion process vulnerable. On the other end of the spectrum, if the C/N ratio exceeds 30 the concentration of volatile fatty acids escalates leading to process inhibition. The C/N ratios of the algal biomass are usually 5-8, which are not enough for the long term stable process. With the addition of proper amount of corn silage to algae biomass this difficulty can be resolved and the long term continuous work of the biogas reactor can be maintained.

Conclusions

For direct energetic utilization microalgae can produce bioH_2 , biodiesel or other valuable products. Instead of considering the microalgal biomass left over from these processes as “waste” this organic material should be utilized as a useful substrate for biogas generation and this concept should be incorporated into the various bio-refinery applications. The presence of the mutualistic bacterial components dramatically alters the usefulness of microalgae for bioH_2 production. In a closed system the bacteria consume the oxygen evolved by the algae and create sufficiently anaerobic environment for H_2 evolution to commence. With the help of the bacterial partners, algae thus manage to capture light energy by photosynthetic water splitting and evolve H_2 at the same time without further manipulation of the system, such as sulfur deprivation (Ghirardi et al., 2000, Melis et al., 2000).

Anaerobic digestion and biogas evolution from the non-sterile microalgae-bacteria yield a gas enriched in CH_4 relative to the commonly used maize silage. Addition of maize silage to the algae-bacteria mixed biomass increases the C/N ratio considerably and improved the balanced digestibility of the microbial biomass. In the biogas technology at least half of the maize silage input can easily be replaced with inexpensive algae-bacteria natural biomass grown under non-sophisticated and non-sterile conditions.

Acknowledgements

Thanks to PIAC_13-1-2013-0145 project for financial assistance.

References

ALEXANDER, M. 1985. Biodegradation of organic chemicals. *Environmental science & technology*, 19, 106-111.

- AMON, T. & ROTH, U. 2015. *Gasausbeute in landwirtschaftlichen Biogasanlagen*, KTBL.
- BAMBERGER, E. S., KING, D., ERBES, D. L. & GIBBS, M. 1982. H₂ and CO₂ evolution by anaerobically adapted *Chlamydomonas reinhardtii* F-60. *Plant physiology*, 69, 1268-1273.
- BAI, A. 2013. Sertés-hígtrágyára alapozott kapcsolt energia- és takarmány-előállítás. *Journal of Central European Green Innovation* 1, 11-20.
- BAI, A., GABNAI, Z. 2014. Energianyeréssel kombinált innovatív szennyvízkezelési eljárások. *LVI. Georgikon Napok. Nemzetközi Tudományos Konferencia*, 2-3, 43-44.
- BAI, A. 2015. Helyi közlekedés és hulladékgazdálkodás. *Magyar Energetika*, 22, 21-25.
- BATYROVA, K., GAVRISHEVA, A., IVANOVA, E., LIU, J. & TSYGANKOV, A. 2015. Sustainable hydrogen photoproduction by phosphorus-deprived marine green microalgae *Chlorella* sp. *International journal of molecular sciences*, 16, 2705-2716.
- BATYROVA, K. A., TSYGANKOV, A. A. & KOSOUROV, S. N. 2012. Sustained hydrogen photoproduction by phosphorus-deprived *Chlamydomonas reinhardtii* cultures. *International Journal of Hydrogen Energy*, 37, 8834-8839.
- BECKER, E. W. 1994. *Microalgae: biotechnology and microbiology*, Cambridge University Press.
- BRENNAN, L. & OWENDE, P. 2010. 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.
- CHEN, Y., CHENG, J. J. & CREAMER, K. S. 2008. Inhibition of anaerobic digestion process: a review. *Bioresource technology*, 99, 4044-4064.
- CHISTI, Y. 2007. Biodiesel from microalgae. *Biotechnology advances*, 25, 294-306.
- DE SCHAMPHELAIRE, L. & VERSTRAETE, W. 2009. Revival of the biological sunlight-to-biogas energy conversion system. *Biotechnology and Bioengineering*, 103, 296-304.
- DEMIRBAS, A. 2007. Progress and recent trends in biofuels. *Progress in energy and combustion science*, 33, 1-18.
- DISMUKES, G. C., CARRIERI, D., BENNETTE, N., ANANYEV, G. M. & POSEWITZ, M. C. 2008. Aquatic phototrophs: efficient alternatives to land-based crops for biofuels. *Current opinion in biotechnology*, 19, 235-240.
- DRAGONE, G., FERNANDES, B. D., VICENTE, A. A. & TEIXEIRA, J. A. 2010. Third generation biofuels from microalgae.
- GHIRARDI, M. L., ZHANG, L., LEE, J. W., FLYNN, T., SEIBERT, M., GREENBAUM, E. & MELIS, A. 2000. Microalgae: a green source of renewable H₂. *Trends in biotechnology*, 18, 506-511.
- GONZALEZ-BALLESTER, D., JURADO-OLLER, J. L. & FERNANDEZ, E. 2015. Relevance of nutrient media composition for hydrogen production in *Chlamydomonas*. *Photosynthesis research*, 125, 395-406.
- JURADO-OLLER, J. L., DUBINI, A., GALVÁN, A., FERNÁNDEZ, E. & GONZÁLEZ-BALLESTER, D. 2015. Low oxygen levels contribute to improve photohydrogen production in mixotrophic non-stressed *Chlamydomonas* cultures. *Biotechnology for biofuels*, 8, 1.
- KLEIN, U. & BETZ, A. 1978. Fermentative metabolism of hydrogen-evolving *Chlamydomonas moewusii*. *Plant physiology*, 61, 953-956.
- LAKATOS, G., DEÁK, Z., VASS, I., RÉTFALVI, T., ROZGONYI, S., RÁKHELY, G., ÖRDÖG, V., KONDOROSI, É. & MARÓTI, G. 2014. Bacterial symbionts enhance photo-fermentative hydrogen evolution of *Chlamydomonas* algae. *Green Chemistry*, 16, 4716-4727.

- LI, L., ZHANG, L. & LIU, J. 2015. The enhancement of hydrogen photoproduction in marine *Chlorella pyrenoidosa* under nitrogen deprivation. *International Journal of Hydrogen Energy*, 40, 14784-14789.
- MCGHEE, T. 1968. A method for approximation of the volatile acid concentrations in anaerobic digesters. *Water Sewage Works*, 115, e166.
- MELIS, A., ZHANG, L., FORESTIER, M., GHIRARDI, M. L. & SEIBERT, M. 2000. Sustained photobiological hydrogen gas production upon reversible inactivation of oxygen evolution in the green alga *Chlamydomonas reinhardtii*. *Plant physiology*, 122, 127-136.
- MUSSGNUG, J. H., KLASSEN, V., SCHLÜTER, A. & KRUSE, O. 2010. Microalgae as substrates for fermentative biogas production in a combined biorefinery concept. *Journal of biotechnology*, 150, 51-56.
- NIELSEN, H. B. & ANGELIDAKI, I. 2008. Strategies for optimizing recovery of the biogas process following ammonia inhibition. *Bioresource technology*, 99, 7995-8001.
- NIGAM, P. S. & SINGH, A. 2011. Production of liquid biofuels from renewable resources. *Progress in energy and combustion science*, 37, 52-68.
- NORDMANN, W. 1977. Die Überwachung der Schlammfäulung. *KA-Informationen für das Betriebspersonal, Beilage zur Korrespondenz Abwasser*, 3, 77.
- OEY, M., SAWYER, A. L., ROSS, I. L. & HANKAMER, B. 2015. Challenges and opportunities for hydrogen production from microalgae. *Plant Biotechnology Journal*.
- PARKIN, G. F. & OWEN, W. F. 1986. Fundamentals of anaerobic digestion of wastewater sludges. *Journal of Environmental Engineering*, 112, 867-920.
- PHILIPPS, G., HAPPE, T. & HEMSCHMEIER, A. 2012. Nitrogen deprivation results in photosynthetic hydrogen production in *Chlamydomonas reinhardtii*. *Planta*, 235, 729-745.
- POPP, J., HARANGI-RÁKOS, M., GABNAI, Z., BALOGH, P., ANTAL, G., BAI, A. 2016. Biofuels and their co-products as livestock feed: global economic and environmental implications. *Molecules*, 21, 285-310.
- POSTEN, C. & SCHAUB, G. 2009. Microalgae and terrestrial biomass as source for fuels—a process view. *Journal of biotechnology*, 142, 64-69.
- SCHENK, P. M., THOMAS-HALL, S. R., STEPHENS, E., MARX, U. C., MUSSGNUG, J. H., POSTEN, C., KRUSE, O. & HANKAMER, B. 2008. Second generation biofuels: high-efficiency microalgae for biodiesel production. *Bioenergy research*, 1, 20-43.
- SIALVE, B., BERNET, N. & BERNARD, O. 2009. Anaerobic digestion of microalgae as a necessary step to make microalgal biodiesel sustainable. *Biotechnology advances*, 27, 409-416.
- SINGH, J. & GU, S. 2010. Commercialization potential of microalgae for biofuels production. *Renewable and sustainable energy reviews*, 14, 2596-2610.
- SINGH, R. & SHARMA, S. 2012. Development of suitable photobioreactor for algae production—A review. *Renewable and sustainable energy reviews*, 16, 2347-2353.
- SKJÅNES, K., REBOURS, C. & LINDBLAD, P. 2013. Potential for green microalgae to produce hydrogen, pharmaceuticals and other high value products in a combined process. *Critical reviews in biotechnology*, 33, 172-215.
- SLADE, R. & BAUEN, A. 2013. Micro-algae cultivation for biofuels: cost, energy balance, environmental impacts and future prospects. *Biomass and Bioenergy*, 53, 29-38.
- SPOLAORE, P., JOANNIS-CASSAN, C., DURAN, E. & ISAMBERT, A. 2006. Commercial applications of microalgae. *Journal of bioscience and bioengineering*, 101, 87-96.
- STERN, N. H. & TREASURY, H. M. S. 2006. *Stern Review: The economics of climate change*, HM treasury London.

- VOLGUSHEVA, A., KUKARSKIKH, G., KRENDELEVA, T., RUBIN, A. & MAMEDOV, F. 2015. Hydrogen photoproduction in green algae *Chlamydomonas reinhardtii* under magnesium deprivation. *RSC Advances*, 5, 5633-5637.
- VOLGUSHEVA, A., STYRING, S. & MAMEDOV, F. 2013. Increased photosystem II stability promotes H₂ production in sulfur-deprived *Chlamydomonas reinhardtii*. *Proceedings of the National Academy of Sciences*, 110, 7223-7228.
- WANG, H., FAN, X., ZHANG, Y., YANG, D. & GUO, R. 2011. Sustained photo-hydrogen production by *Chlorella pyrenoidosa* without sulfur depletion. *Biotechnology letters*, 33, 1345-1350.
- WARD, A., LEWIS, D. & GREEN, F. 2014. Anaerobic digestion of algae biomass: a review. *Algal Research*, 5, 204-214.
- WIJFFELS, R. H., KRUSE, O. & HELLINGWERF, K. J. 2013. Potential of industrial biotechnology with cyanobacteria and eukaryotic microalgae. *Current opinion in biotechnology*, 24, 405-413.
- WIRTH, R., LAKATOS, G., MARÓTI, G., BAGI, Z., MINÁROVICS, J., NAGY, K., KONDOROSI, É., RÁKHELY, G. & KOVÁCS, K. L. 2015. Exploitation of algal-bacterial associations in a two-stage biohydrogen and biogas generation process. *Biotechnology for biofuels*, 8, 1.

Authors:

Gergely Lakatos

Institute of Biochemistry, Biological Research Center, Hungarian Academy of Sciences, H-6726 Szeged, Temesvári krt. 62., Hungary
lakatos.gergely@brc.mta.hu

Bernadett Pap

Seqomics Biotechnology Ltd., H-6782 Mórahalom, Vállalkozók útja 7., Hungary
bernadett.pap@gmail.com

Péter Tamás Nagy

Educational and research Laboratory, Károly Róbert College, H-3200, Gyöngyös, Mátrai str. 36., Hungary
nagypt@karolyrobert.hu

Gergely Maróti

Institute of Biochemistry, Biological Research Center, Hungarian Academy of Sciences, H-6726 Szeged, Temesvári krt. 62., Hungary
maroti.gergely@brc.mta.hu